



Estimation of the exchange current density and comparative analysis of morphology of electrochemically produced lead and zinc deposits

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Abstract: The processes of lead and zinc electrodeposition from the very dilute electrolytes were compared by the analysis of polarization characteristics and by the scanning electron microscopic (SEM) analysis of the morphology of the deposits obtained in the galvanostatic regime of electrolysis. The exchange current densities for lead and zinc were estimated by comparison of experimentally obtained polarization curves with the simulated ones obtained for the different the exchange current density to the limiting diffusion current density ratios. Using this way for the estimation of the exchange current density, it is shown that the exchange current density for Pb was more than 1300 times higher than the one for Zn. In this way, it is confirmed that the Pb electrodeposition processes are considerably faster than the Zn electrodeposition processes. The difference in the rate of electrochemical processes was confirmed by a comparison of morphologies of lead and zinc deposits obtained at current densities which corresponded to 0.25 and 0.50 values of the limiting diffusion current densities.

Keywords: electrodeposition; lead; zinc; exchange current density; scanning electron microscope (SEM).

INTRODUCTION

Metals like Pb, Sn, Zn, Cd, and Ag are classified into group of normal metals characterized by the large exchange current density, low melting point and high overpotentials for hydrogen discharge.^{1,2} The common characteristic of these metals is the absence of a precise and unique way for a determination of the

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exchange current density (j_0) as one of the main parameter characterizing electro-deposition processes. As result of this, the j_0 values which can be found in the literature are often contradictory, or furthermore, there is no data about j_0 value for some of them (Pb). On the other hand, diagnostic criteria based on a simulation of the polarization curve equation for a different j_0/j_L ratios (j_L – the limiting diffusion current density) were proposed recently for a determination of the type of electro-deposition process control.³ It is clear that comparison of the simulated shapes of the polarization curves obtained for a different j_0/j_L ratios with the experimentally obtained polarization curves can be excellent auxiliary criteria for estimation of the j_0 values, especially of the normal metals due to a lack reliable way for determination of their j_0 values. Since the polarization curves are simulated in a function of j_0/j_L ratios, then the superposition between the experimental and simulated curves inside the plateau of the limiting diffusion current density is only relevant for this method of the estimation of j_0 .⁴ The good agreement between the j_0 values estimated by this method⁴ and those found in the literature⁵ was observed in the case of Zn electro-deposition. Also, application of this unique procedure enables mutual comparison of the j_0 values of the different metals, because all electro-deposition systems are treated in the same way.

Electro-deposition processes of the normal metals are accompanied by formation of various morphological forms, such as granules, crystals of regular and irregular shapes, needle-like and spongy-like particles, dendrites, *etc.*^{6–23} During many years systematic investigations,^{24,25} differences in formation of the morphological forms of these metals were specified. It is concluded that Pb and Zn can be denoted as the limiting cases from the group of the normal metals. Namely, the processes of electro-deposition of Pb belong to very fast electrochemical processes with a significant contribution of the ohmic control.^{17,25} On the other hand, the processes of Zn electro-deposition contain certain similarities with those of Cu belonging to group of the intermediate metals characterized by the lower values of the exchange current density than the j_0 values of the normal metals.

In this study, Pb and Zn electro-deposition processes from the dilute electrolytes were compared with the aim to estimate the exchange current density values. The compositions of electrolytes were selected to approach the experimental shapes of polarization curves with the simulated ones. Morphologies of Pb and Zn deposits obtained in the galvanostatic regime of electrolysis at the same ratios of the current density of electro-deposition to the limiting diffusion current density (j/j_L) were also compared.

EXPERIMENTAL

Lead and zinc were electro-deposited from the following electrolytes:

- a) 0.010 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 and
- b) 0.010 M ZnSO_4 in 2.0 M NaOH .

For preparation of the electrolytes for electrodepositions of Pb and Zn were used doubly distilled water and analytical grade chemicals. All electrodepositions were performed at the room temperature in an open cell.

The polarization curves for Zn and Pb were recorded by potentiostatically at working electrodes of Zn (for Zn) and Pb (for Pb). The reference and counter electrodes were of either Zn or Pb. The procedure for recording of the polarization curves is described elsewhere.^{26,27}

For morphological analysis, Zn and Pb were electrodeposited galvanostatically at current densities (j) which corresponded to $0.25j_L$ and $0.50j_L$. These current densities were 0.15 and 0.30 mA cm⁻² (Zn), and 0.065 and 0.13 mA cm⁻² (Pb). For electrodeposition of the both metals, the working electrodes of polycrystalline copper wire, the surface area of 0.50 cm², were used. The length of Cu electrode was 2.0 cm, while its diameter was 0.080 cm. The counter electrodes were either of pure Zn (in the case of Zn electrodeposition) or of pure Pb (in the case of Pb electrodeposition). Lead was electrodeposited with quantities of the electricity of 19.5 mA s cm⁻², and 234 mA s cm⁻². Zn was electrodeposited with a quantity of the electricity of 1080 mA s cm⁻². The electrodeposition of Zn with the lower quantities of electricity did not affect the surface morphology. The times of electrodeposition for each sample are provided in Figure caption.

Morphologies of Pb and Zn deposits were characterized by the scanning electron microscope Tescan digital microscopy.

The polarization curves were simulated using the software MatLab.

RESULTS AND DISCUSSION

The polarization curves for electrodeposition of lead from 0.010 M Pb(NO₃)₂ in 2.0 M NaNO₃ and zinc from 0.010 M ZnSO₄ in 2.0 M NaOH are shown in Fig. 1a. The polarization curves normalized to the limiting diffusion current density values (j/j_L vs. η) are given in Fig. 1b. Then, comparison of the normalized polarization curves was made with the simulated curves with the aim to estimate the exchange current densities for Pb and Zn.

The shape of the polarization curve taking the concentration dependence of the exchange current density into account in the form given by Eq. (1) was used to obtain the simulated dependences of j/j_L vs. η :^{3,28,29}

$$\frac{j}{j_L} = \frac{\frac{j_0}{j_L}(f_c - f_a)}{1 + \frac{j_0}{j_L}(f_c - f_a)} \quad (1)$$

Equation (1) is valid for all both j/j_L ratios and overpotentials. In Eq. (1), j is the current density, j_0 is the exchange current density, j_L is the limiting diffusion current density and:

$$f_c = 10^{\frac{\eta}{b_c}} \quad \text{and} \quad f_a = 10^{-\frac{\eta}{b_a}}$$

where b_c and b_a are the cathodic and anodic Tafel slopes and η is the overpotential. The Eq. (1) is modified for use in electrodeposition of metals using the values of the cathodic current density and overpotential as positive.

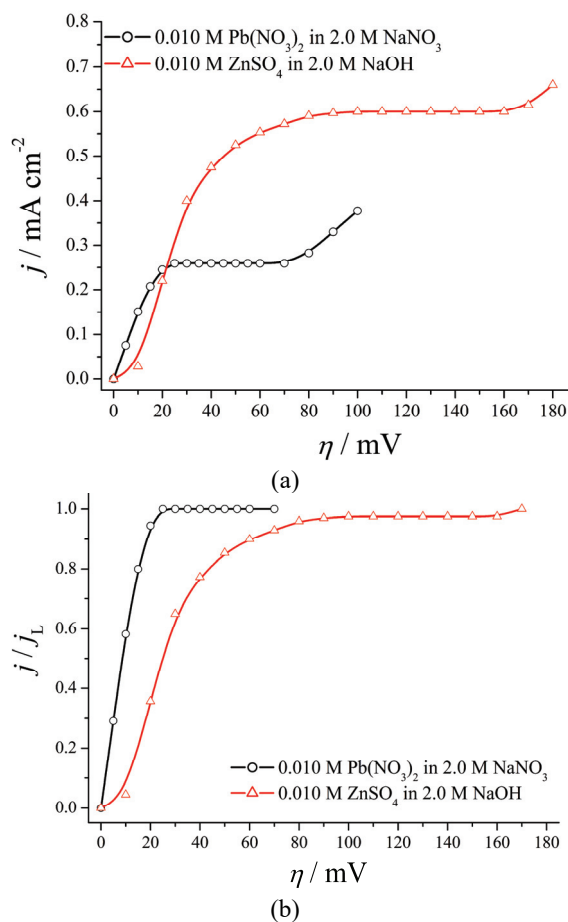
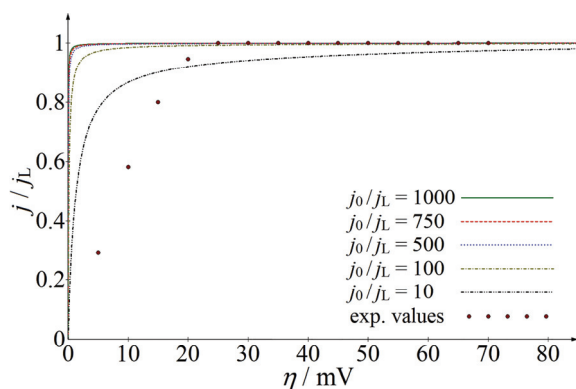


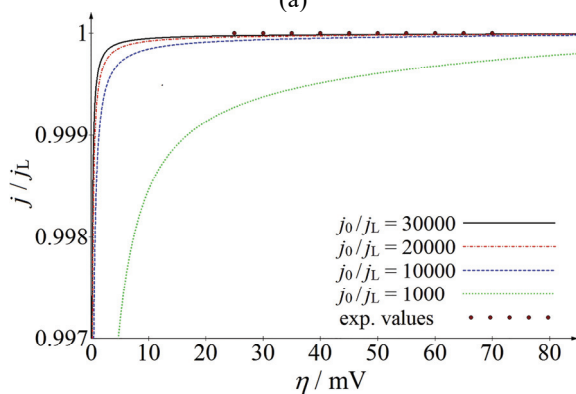
Fig. 1. a) The polarization curves for electrodepositions of Pb from 0.010 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 and Zn from 0.010 M ZnSO_4 in 2.0 M NaOH , and b) the normalized polarization curves to the limiting diffusion current density values (j/j_L vs. η) for the same electrolytes.

For electrodeposition of zinc from alkaline electrolytes, the values of the anodic and cathodic Tafel slopes are: $b_a = 40 \text{ mV dec}^{-1}$ and $b_c = 120 \text{ mV dec}^{-1}$.⁵ The same values of the anodic and cathodic slopes are valid for electrodeposition of lead if the one electron reaction step is supposed.¹⁷ The comparison of experimental and simulated dependencies j/j_L vs. η for Pb is shown in Fig. 2a. As already mentioned, since the simulated curves as a parameter consider j_0/j_L ratios then comparison with the experimental values in the region of the limiting diffusion current density is only relevant for this method. For more precise estimation of j_0 value, the dependencies of j/j_L in the range of 0.997 to 1 on η for the very high j_0/j_L ratios were analyzed and presented in Fig. 2b, from which can be

noticed that the best superposition between the experimental and simulated curves inside the plateau of the limiting diffusion current density is obtained for the j_0/j_L ratio of 30000. It is necessary to note that the good superposition between experimental and simulated polarization curves will also be achieved for the j_0/j_L ratios larger than 30000. Anyway, we define the j_0/j_L ratio of 30000 as the lowest value of the good superposition between experimental and simulated curves, and take it for the estimation of j_0 value for Pb. For the limiting diffusion current density for Pb of 0.26 mA cm^{-2} (Fig. 1a) and the j_0/j_L ratio of 30000, the estimated exchange current density for this Pb system is 7800 mA cm^{-2} or higher.



(a)



(b)

Fig. 2. Comparison of experimental and simulated dependencies of j/j_L vs. η for Pb ($b_a = 40 \text{ mV dec}^{-1}$ and $b_c = 120 \text{ mV dec}^{-1}$).

Comparison of the experimental and simulated dependencies j/j_L vs. η for Zn is shown in Fig. 3. In this case, the nearest superposition of the experimental and simulated dependencies for the values corresponding to the plateau of the limiting diffusion current density was achieved for $j_0/j_L \approx 10$. Taking the value of the limiting diffusion current density for Zn of 0.60 mA cm^{-2} (Fig. 1a), the exchange current density for Zn from this solution was estimated to be 6.0 mA cm^{-2} .

Hence, the estimated exchange current density for Pb was more than 1300 times higher than the one for Zn for the same concentration of depositing ions.

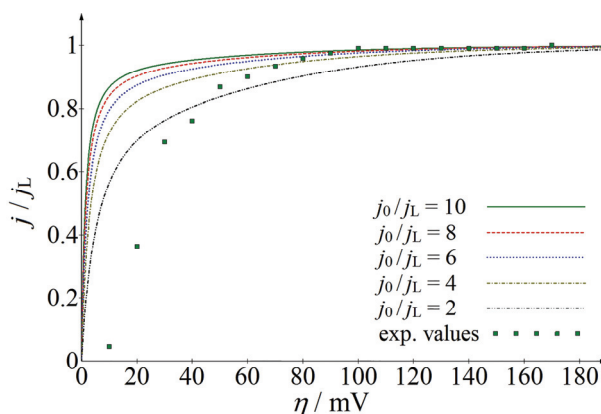


Fig. 3. Comparison of experimental and simulated dependencies of j/j_L vs. η for Zn ($b_a = 40 \text{ mV dec}^{-1}$ and $b_c = 120 \text{ mV dec}^{-1}$).

In this study, since the polarization curve equation taking the concentration dependence of the exchange current density was used in the process of simulation, the electrolytes with the same concentrations of Pb(II) and Zn(II) ions were analyzed. The second way for estimation and comparison of the exchange current density values would include comparison of the electrodeposition systems with approximately the same values of the limiting diffusion current density. In the case of Pb and Zn it was not possible because electrodeposition of lead occurs in the conditions of the mixed ohmic-diffusion control where the ratio of the ohmic control to the overall control of electrodeposition process increases with increasing concentration of Pb(II) ions.¹⁷ At the higher concentrations of Pb(II) ions, the electrodeposition process becomes full ohmic controlled one.^{17,30} For a concentration of Pb(II) ions of 0.010 M, the contribution of the ohmic control was almost negligible (Fig. 1a). This means that the increase of concentration of Pb(II) ions would cause the larger deviation of the experimental from simulated curves because the simulated polarization curves do not include the ohmic control.^{3,25} Also, the well-defined plateaus of the limiting diffusion current density are lost with the increase of concentration of Pb(II) ions.

Figure 4 shows Pb deposits obtained with a quantity of the electricity of $19.5 \text{ mA s cm}^{-2}$ at current densities of 0.065 mA cm^{-2} ($j = 0.25j_L$; Fig. 4a and b) and 0.13 mA cm^{-2} ($j = 0.50j_L$; Fig. 4c and d). The cobweb-like or the rose-like particles were formed at the current density which corresponded to $0.25j_L$ (Fig. 4a and b). This type of the particles is ascribed to the group of spongy-like ones.³¹ On the other hand, various regular particles, largely octahedrons and tetrahed-

rons, surrounded by small needle-like particles were formed at a current density of $0.50j_L$ (Fig. 4c and d).

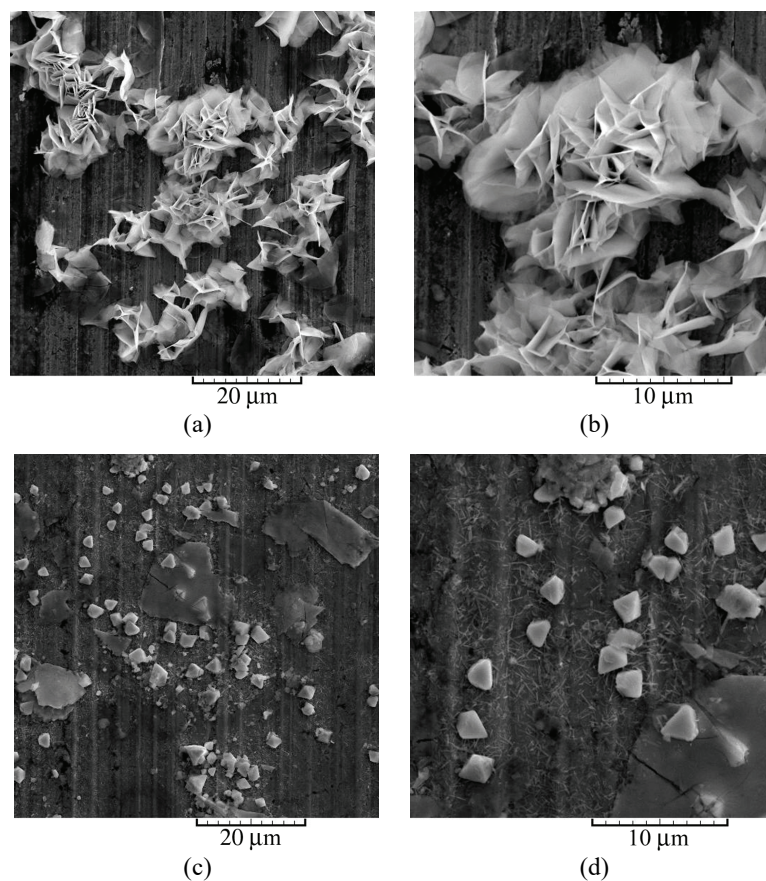


Fig. 4. Lead deposits obtained by electrodeposition from 0.010 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 with a quantity of the electricity of $19.5 \text{ mA s cm}^{-2}$ at current densities of: a) and b) 0.065 mA cm^{-2} ; the time of electrodeposition: $t = 300 \text{ s}$, and c) and d) 0.13 mA cm^{-2} ; $t = 150 \text{ s}$.

Pb deposits obtained at the same current densities, but with a quantity of the electricity of 234 mA s cm^{-2} are shown in Fig. 5. The mixture of particles of various shapes from crystals of irregular shape (Fig. 5a and b) to regular octahedrons and small needle-like particles (Fig. 5c) was formed at a current density of 0.065 mA cm^{-2} . It is necessary to note that octahedrons and the needle-like forms are formed in „shadow“ of the larger irregular particles. The similar situation was also observed at a current density of 0.13 mA cm^{-2} , as seen from Fig. 5d–f. The mixture of irregular crystals (Fig. 5d and e) and the needle-like particles of nano dimensions formed among them (Fig. 5f) were a characteristic of the electrodeposition process at a current density of 0.13 mA cm^{-2} .

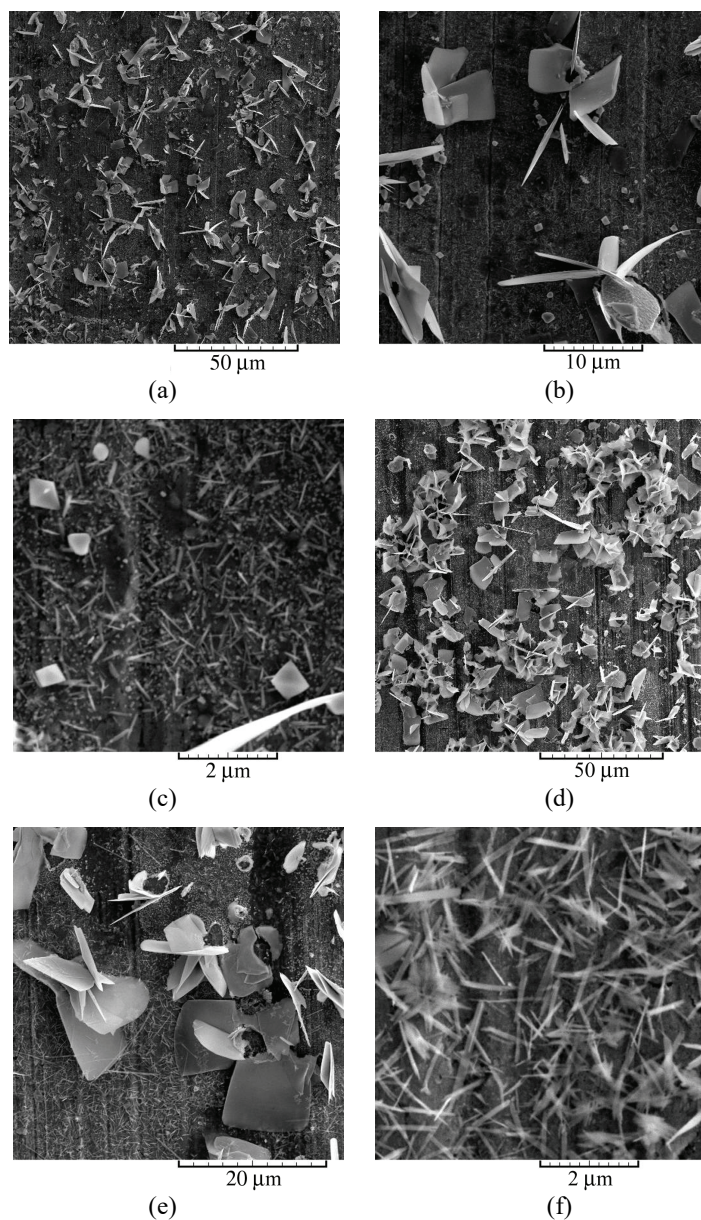


Fig. 5. Lead deposits obtained by electrodeposition from 0.010 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 with a quantity of the electricity of 234 mA s cm^{-2} at current densities of: a)–c) 0.065 mA cm^{-2} , $t = 3600 \text{ s}$, and d)–f) 0.13 mA cm^{-2} , $t = 1800 \text{ s}$.

Zinc deposits obtained with the same ratios to the limiting diffusion current density as those from Pb are shown in Fig. 6. At the first sight, strong difference with respect to Pb surface morphologies can be noticed. The relatively compact

deposit with clearly visible grains or crystals was formed at a current density of 0.15 mA cm^{-2} which corresponded to $0.25j_L$ (Fig. 6a and b). On the other hand, the spongy-like particles constructed from nano-filaments were formed at a current density of 0.30 mA cm^{-2} , *i.e.* at $0.50j_L$ (Fig. 6c–e).

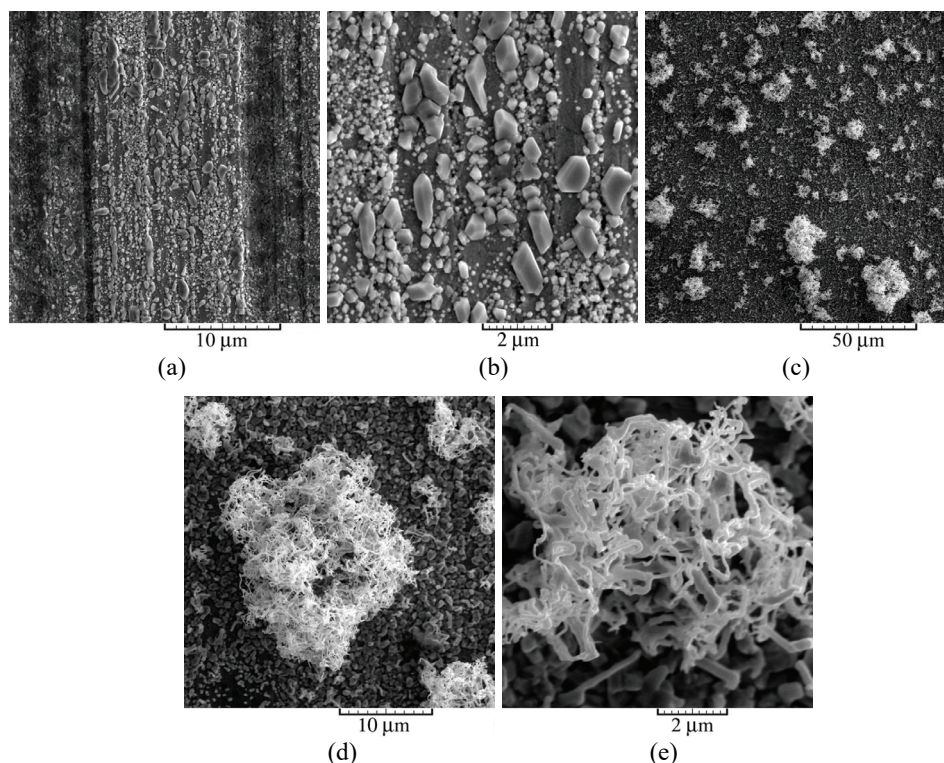


Fig. 6. Zinc deposits obtained by electrodeposition from 0.010 M ZnSO_4 in 2.0 M NaOH with a quantity of the electricity of $1080 \text{ mA s cm}^{-2}$ at current densities of: a) and b) 0.15 mA cm^{-2} , $t = 2 \text{ h}$ and c)–e) 0.30 mA cm^{-2} , $t = 1 \text{ h}$.

Comparison of Pb and Zn deposits obtained with the same ratios to the limiting diffusion current density confirms that the processes of Pb electrodeposition were considerably faster than those for Zn. Namely, unlike from the relatively compact deposit of Zn (Fig. 6a and b), the spongy-like particles with the smaller (Fig. 4a and b) and the irregular crystals with the larger quantity of electricity (Fig. 5a and b) were formed at the current density which corresponded to $0.25j_L$. This irregular Pb crystals, denoted as precursors of dendrites,^{17,21} clearly prove the higher degree of the diffusion control in the case of Pb than in the case of Zn for the same j/j_L ratio. The similar consideration can be also performed for the current density which corresponded to $0.50j_L$. The predominant formation of the irregular crystals (precursors of dendrites) by the Pb electro-

deposition in relation to the spongy-like particles constructed from nano filaments obtained by the Zn electrodeposition clearly confirms the fact that the Pb electrodeposition process is faster than the Zn electrodeposition process at j/j_L of 0.50.

Although the obtained values of the exchange current density for Pb and Zn represent relatively ones, this method enables successfully comparison of the rate of electrochemical processes of the normal metals, for which there is no a precise way of the determination of the exchange current density. The validity of proposed method is confirmed by morphological analysis of Pb and Zn deposits obtained at the same j/j_L ratios.

CONCLUSIONS

The exchange current densities for Pb and Zn were estimated using new method based on comparison of the experimental polarization curves in the form j/j_L with the simulated dependencies obtained for the different j_0/j_L ratios. The both metals belong to the group of *the normal metals* for which there is no precise and unique way for estimation of the exchange current density values. The estimated values of the exchange current density were larger than 7800 mA cm^{-2} for Pb and 6.0 mA cm^{-2} for Zn, indicating that the j_0 value for Pb was more than 1300 times higher than the one for Zn.

This difference in the exchange current densities was proved by the morphological analysis of Pb and Zn deposits obtained at current densities which corresponded to 0.25 and 0.50 values of the limiting diffusion current density. The spongy-like particles with the smaller and precursors of the dendrites (as the dominant morphological form) with the larger amount of electricity were primary formed by Pb electrodeposition at a current density of 0.25 value of the limiting diffusion current density for Pb. Simultaneously, the almost compact deposit with clearly visible grains was formed in the case of Zn at the same ratio to the limiting diffusion current density.

The fact that the processes of Pb electrodeposition are faster than those for Zn is also seen by the analysis of Pb and Zn morphologies obtained at the current densities which corresponded to 0.50 values of the limiting diffusion current densities. The precursors of dendrites are predominately formed by Pb electrodeposition, while the spongy-like particles were formed by Zn electrodeposition.

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ИЗВОД

ПРОЦЕНА ГУСТИНЕ СТРУЈЕ ИЗМЕНЕ И УПОРЕДНА АНАЛИЗА МОРФОЛОГИЈА
ЕЛЕКТРОХЕМИЈСКИ ИСТАЛОЖЕНИХ ТАЛОГА ОЛОВА И ЦИНКАНЕБОЈША Д. НИКОЛИЋ¹, ПРЕДРАГ М. ЖИВКОВИЋ², ГОРАН БРАНКОВИЋ³ И МИОМИР Г. ПАВЛОВИЋ¹¹ИХТМ – Центар за електрохемију, Универзитет у Београду, Његишева 12, Београд, ²Технолошко–металуришки факултет, Универзитет у Београду, Карнегијева 4, Београд и ³Институт за мултидисциплинарна истраживања, Универзитет у Београду, Кнеза Вишеслава 1а, Београд

Процеси електрохемијског таложења олова и цинка из веома разблажених електролита су били међусобно упоређени анализом поларизационих карактеристика и морфолошким анализом талога добијених у галваностатском режиму електролизе техником скенирајуће електронске микроскопије (СЕМ). Густине струје измене за олово и цинк су процењене поређењем експериментално добијених поларизационих кривих са симулираним кривама добијеним за различите односе густине струје измене и граничне дифузионе густине струје. Коришћењем овог начина за процену густине струје измене, показано је да густина струје измене за олово је била више од 1300 пута већа од оне за цинк. На овај начин, потврђено је да процеси електрохемијског таложења олова су приметно бржи од процеса електрохемијског таложења цинка. Разлика у брзини електрохемијских процеса је потврђена поређењем морфологија талога олова и цинка добијених на густинама струје које су одговарале 0,25 и 0,50 вредности граничних дифузионих густина струје.

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