

1 **The shape of the polarization curve and diagnostic criteria**
2 **for the metal electrodeposition process control**

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12
13 Abstract. The simulated shapes of the polarization curves were correlated with the type of metal
14 electrodeposition process control in a function of the exchange current density to the limiting
15 diffusion current density (j_0/j_L) ratios. Diagnostic criteria based on the j_0/j_L ratios were
16 established. For $j_0/j_L > 100$, the system is under the ohmic control. In the range $1 < j_0/j_L \leq 100$
17 there is the mixed ohmic-diffusion control. The pure diffusion control appears in the range $0.1 <$
18 $j_0/j_L \leq 1$. For $j_0/j_L \leq 0.1$, the system is activation controlled at the low overpotentials. The
19 proposed diagnostic criteria were verified by comparison of the simulated curves with
20 experimentally recorded ones and by morphological analysis of deposits obtained in the different
21 types of metal electrodeposition process control.

22 *Keywords:* lead; zinc; copper; simulation; morphology; scanning electron microscope (SEM).

23
24 **RUNNING TITLE:** Polarization curves and diagnostic criteria

25
26 INTRODUCTION

27
28 Morphology, as the most important characteristic of electrodeposited metal, mainly
29 depends on the kinetic parameters during the electrodeposition process and on the overpotential

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30 or current density applied.¹ Also, compositions of electroplating solutions, temperature of
31 electrolysis and the type of working electrode strongly affect the final morphology of
32 electrodeposited metal. The morphology of an electrodeposited metal depends also on the
33 deposition time until the deposit has attained its final form.

34 According to their general kinetic behaviour in aqueous solution, metals can be classified
35 into three classes.^{2,3} These classes are:

36 (a) *Class I, so-called normal metals*: Pb, Sn, Tl, Cd, Hg, Ag (simple electrolytes), Zn.

37 These metals have characteristic low melting points and high exchange current densities ($j_0 > 1 \text{ A}$
38 dm^{-2} ; j_0 is the exchange current density). Also, they show high overpotentials for hydrogen
39 discharge.

40 (b) *Class II, intermediate metals*: Cu, Au, Ag (complex electrolytes). These metals are
41 characterised by moderate melting points, medium exchange current densities (j_0 in the interval
42 from 10^{-2} to 1 A dm^{-2}) and lower hydrogen overpotentials.

43 (c) *Class III, inert metals*: Fe, Co, Ni, Mn, Cr, Pt. These metals have high melting points,
44 low exchange current densities and very low hydrogen overpotentials. For this class of metals, j_0
45 is between 10^{-2} and $10^{-12} \text{ A dm}^{-2}$.

46 Formation of the individual and regular grains at lower and dendrites at higher
47 overpotentials is characteristic of electrodeposition processes characterized by extremely large
48 exchange current densities.¹ The spongy deposits are formed at lower overpotentials and
49 dendrites at higher ones during electrodeposition of metals characterized by large exchange
50 current densities. Finally, compact deposits are obtained at lower overpotentials, while both
51 dendritic and spongy-dendritic deposits are formed at higher overpotentials during
52 electrodeposition of metals characterized by medium and low exchange current densities.

53 Obviously, morphology of metal electrodeposits is strictly correlated with the type of
54 control of the electrodeposition process. For example, the activation controlled electrodeposition
55 of copper produces large grains with relatively well defined crystal shapes. This happens at
56 overpotentials belonging to the region of the Tafel linearity.^{4,5} At overpotentials situated between
57 the end of the Tafel linearity and the beginning of the limiting diffusion current density plateau
58 (the mixed activation-diffusion control), morphological forms are created by the mass transfer
59 limitations and large grains are not formed.^{6,7} Dendrites are formed at overpotentials inside the
60 plateau of the limiting diffusion current density, and at the higher ones at which there is no a

61 hydrogen evolution or hydrogen evolution is not enough to affect hydrodynamic conditions in the
62 near-electrode layer.^{8,9} The above consideration is valid for all electrodeposition processes
63 characterized by medium and low values of the exchange current density, in the absence of the
64 noticeable hydrogen evolution reaction.⁹ In the presence of strong hydrogen evolution, the
65 honeycomb-like deposits are formed.⁹

66 On the other hand, electrodeposition of metals characterized by the high values of the
67 exchange current density occurs in the conditions of the ohmic, the mixed ohmic-diffusion and
68 only diffusion control of the electrodeposition.¹⁰⁻¹² Formation of spongy deposits at the lower and
69 dendrites at the higher overpotentials was explained by assumption about the diffusion-controlled
70 electrodeposition in the whole range of overpotentials.¹⁰ The linear dependence of the current
71 density on the overpotential is ascribed to the ohmic control,¹¹ and the regular grains are formed
72 by electrodeposition in this control. In this way, formation of regular particles at lower and
73 dendritic deposits at higher overpotentials in the mixed ohmic-diffusion control can be
74 explained.¹²

75 Simultaneously, the shape of the polarization curves strongly depends on the exchange
76 current density values. The limiting diffusion current density (j_L) values are other important
77 characteristic of electrodeposition systems, indicating on the strong dependence of the shape of
78 polarization curves on the j_0/j_L ratios. Since the continuous change of the exchange current
79 density to the limiting diffusion current density (j_0/j_L) ratios on the shape of the polarization
80 curves can be only obtained by the digital simulation, the software MathLab will be used to
81 examine the dependence of the shape of polarization curve on j_0/j_L ratios. This will enable to
82 establish diagnostic criteria relating the shape of polarization curves through j_0/j_L ratios with the
83 type of electrodeposition control. The proposed diagnostic criteria will be verified by comparison
84 with experimentally recorded polarization curves and by morphologies of deposits obtained in the
85 different types of electrodeposition control.

86

87

EXPERIMENTAL

88

89 Polarization curves for electrodeposition of lead, zinc and copper were recorded from the
90 following solutions:

91 (a) 0.050 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 ,

- 92 (b) 0.10 M Pb(NO₃)₂ in 2.0 M NaNO₃,
 93 (c) 0.20 M Pb(NO₃)₂ in 2.0 M NaNO₃,
 94 (d) 0.40 M Pb(NO₃)₂ in 2.0 M NaNO₃,
 95 (e) 0.45 M Pb(NO₃)₂ in 2.0 M NaNO₃,
 96 (f) 0.10 M ZnSO₄ in 2.0 M NaOH,
 97 (g) 0.10 M CuSO₄ in 0.50 M H₂SO₄.

98
 99 Experimental procedure for recording of the Pb polarization curves is given in Refs.^{13,14}

100 For the morphological analysis of deposits, lead, copper and zinc were electrodeposited
 101 potentiostatically at overpotentials of 10, 50 and 100 mV (Pb), 90, 210, 650 and 1000 mV (Cu)
 102 and 45 and 100 mV (Zn). The times of electrodeposition are indicated in Figure caption.

103 Double-distilled water and analytical grade chemicals were used for the preparation of
 104 solutions used for the electrodeposition of all metals. All experiments were performed in an open
 105 cell at room temperature on vertical cylindrical copper electrodes. The geometric surface area of
 106 copper electrodes was 0.25 cm². The reference and counter electrodes were of the same metals as
 107 deposited ones. The counter-electrodes were metallic foils with 0.80 dm² surface area and placed
 108 close to the cell walls. The reference electrodes were wires of the corresponding metals whose
 109 tips were positioned at a distance of about 0.2 cm from the surface of the working electrodes. The
 110 working electrodes were placed in the centre of a cell, in the same location for each experiment.

111 Morphologies of lead, copper and zinc deposits were examined using a scanning electron
 112 microscope – TESCAN Digital Microscopy.

113 Digital simulation was realized using the software MathLab.

114

115 RESULTS AND DISCUSSION

116

117 The polarization curve equation taking the concentration dependence of j_0 into account and
 118 the linear dependence of j_0 on the C_s/C_0 ratio is given by Eq. (1):¹¹

$$119 \quad j = \frac{j_0(f_c - f_a)}{1 + \frac{j_0}{j_L}(f_c - f_a)} \quad (1)$$

120 To enable a digital simulation of the polarization curve equation for the different j_0/j_L ratios,
 121 the Eq. (1) can be re-written in the form:

$$\frac{j}{j_L} = \frac{\frac{j_0}{j_L}(f_c - f_a)}{1 + \frac{j_0}{j_L}(f_c - f_a)} \quad (2)$$

being valid for all j_0/j_L ratios and overpotentials. Because of this, this form will be used in discussion of the effect of the j_0/j_L ratio on the shape of the polarization curves. Using the current density – overpotential relationship and the procedure for the determination of the ohmic potential drop, the polarization curves for electrodeposition processes can be successfully simulated.^{11,15}

In Eqs. (1) and (2), j is the current density, C_s and C_0 are the surface and bulk concentrations of depositing ion, and

$$f_c = 10^{\frac{\eta}{b_c}} \quad \text{and} \quad f_a = 10^{-\frac{\eta}{b_a}} \quad (3)$$

where b_a and b_c are the cathodic and anodic Tafel slopes and η is the overpotential. The Eqs. (1) and (2) are modified for use in electrodeposition of metals using the values of the cathodic current density and overpotential as positive. In Eqs. (1) and (2), the ohmic potential drop is not included in the overpotential values. Equations (1) and (2) are operative if IR error is eliminated by using the electronic devices that distinguish the superfast change in potential that occurs in this IR portion, when the current density is switched on and off from the slower change of the electrode potential itself, where the charging of the interfacial capacitor takes time.¹⁵ In this way, the polarization curves which do not include the ohmic potential drop can be simulated using Eq. (2).

In any other case the measured value of overpotential, η_m , include the ohmic potential drop and it is given by

$$\eta_m = \eta + j \frac{L}{\kappa} \quad (4)$$

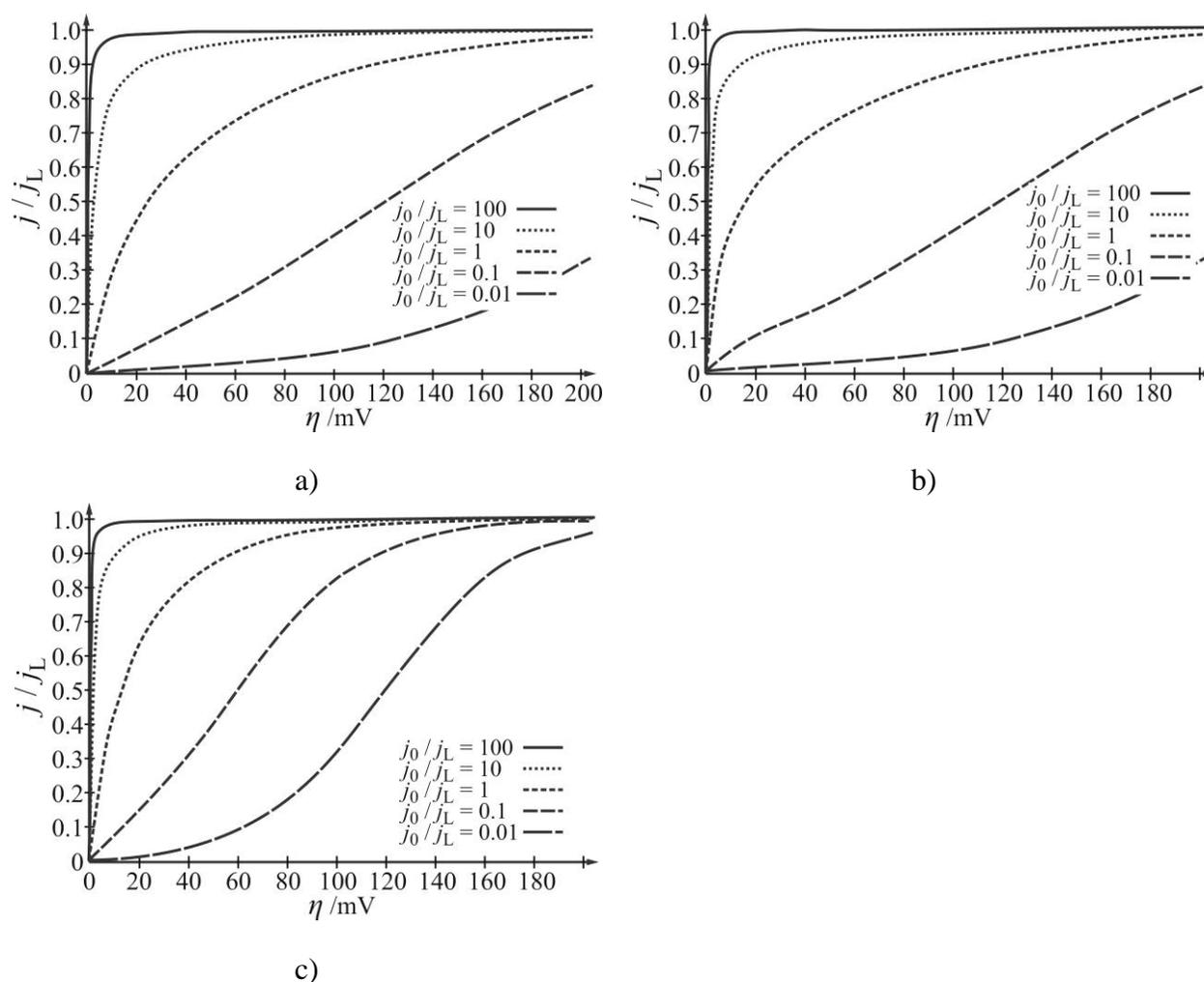
where L is the length of the electrolyte column between the tip of a liquid capillary and the electrode and κ is the specific conductivity of the electrolyte. Hence, the polarization curves which include ohmic potential drop can be simulated by using the Eqs. (2) and (4).

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147 *Simulation of polarization curves*

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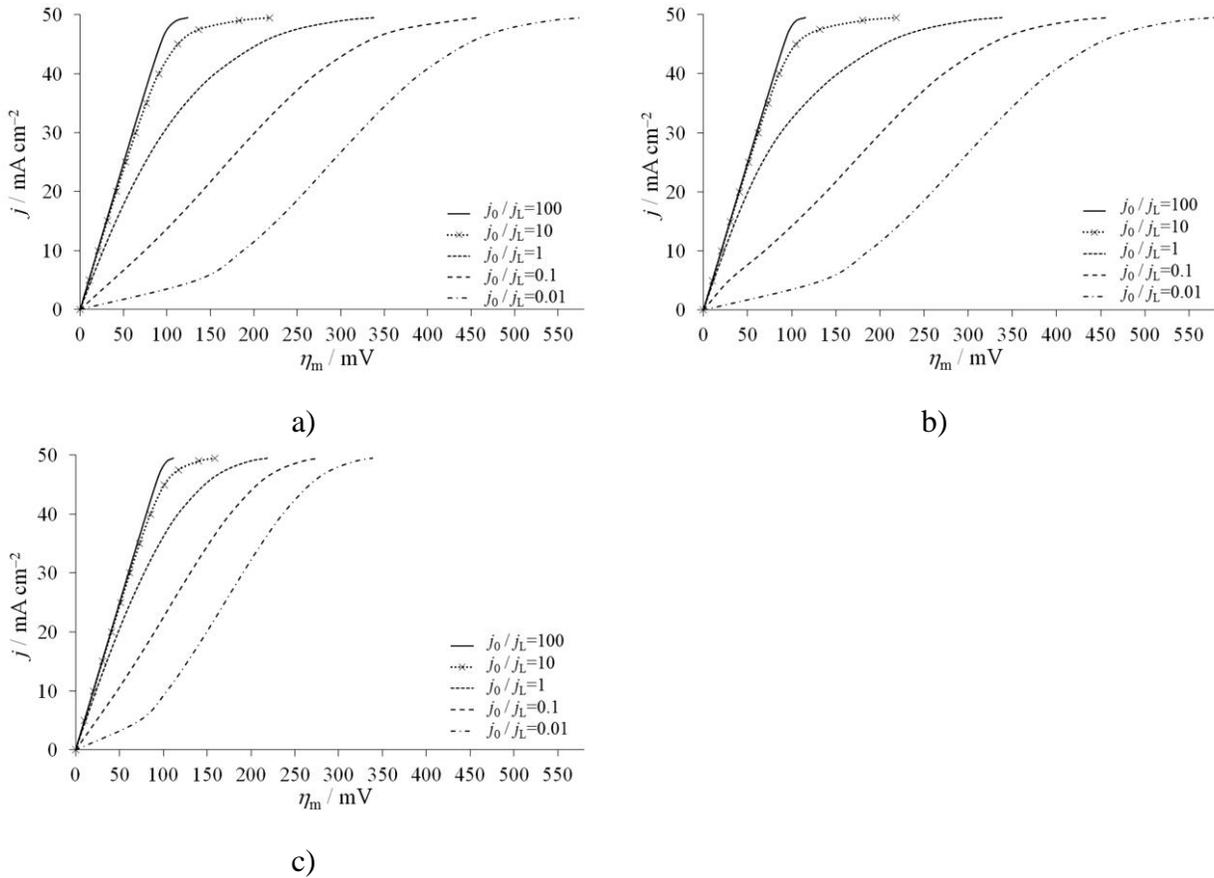
149 The polarization curves without included the ohmic potential drop for different j_0/j_L ratio
 150 values for both, one and two electron reactions, are shown in Fig.1. They are obtained by using
 151 the Eq. (2) for the different j_0/j_L ratios for a different η , b_a and b_c values in the dependence of the
 152 mechanism of electrodeposition reactions. From Fig. 1, it is a clear that these dependencies are
 153 similar to each others for the large values of the j_0/j_L ratio and at any low value of overpotential.
 154 Because of this, the polarization curves without included the ohmic potential drop are not suitable
 155 and, for that reason, will not be treated further.



156 Figure 1. Dependencies $j/j_L - \eta$ calculated using the Eqs. (2) and (3) for the different values of
 157 j_0/j_L ratio: a) $b_a = 120 \text{ mV dec}^{-1}$, $b_c = 120 \text{ mV dec}^{-1}$, b) $b_a = 40 \text{ mV dec}^{-1}$, $b_c = 120 \text{ mV}$
 158 dec^{-1} and c) $b_a = 60 \text{ mV dec}^{-1}$, $b_c = 60 \text{ mV dec}^{-1}$.

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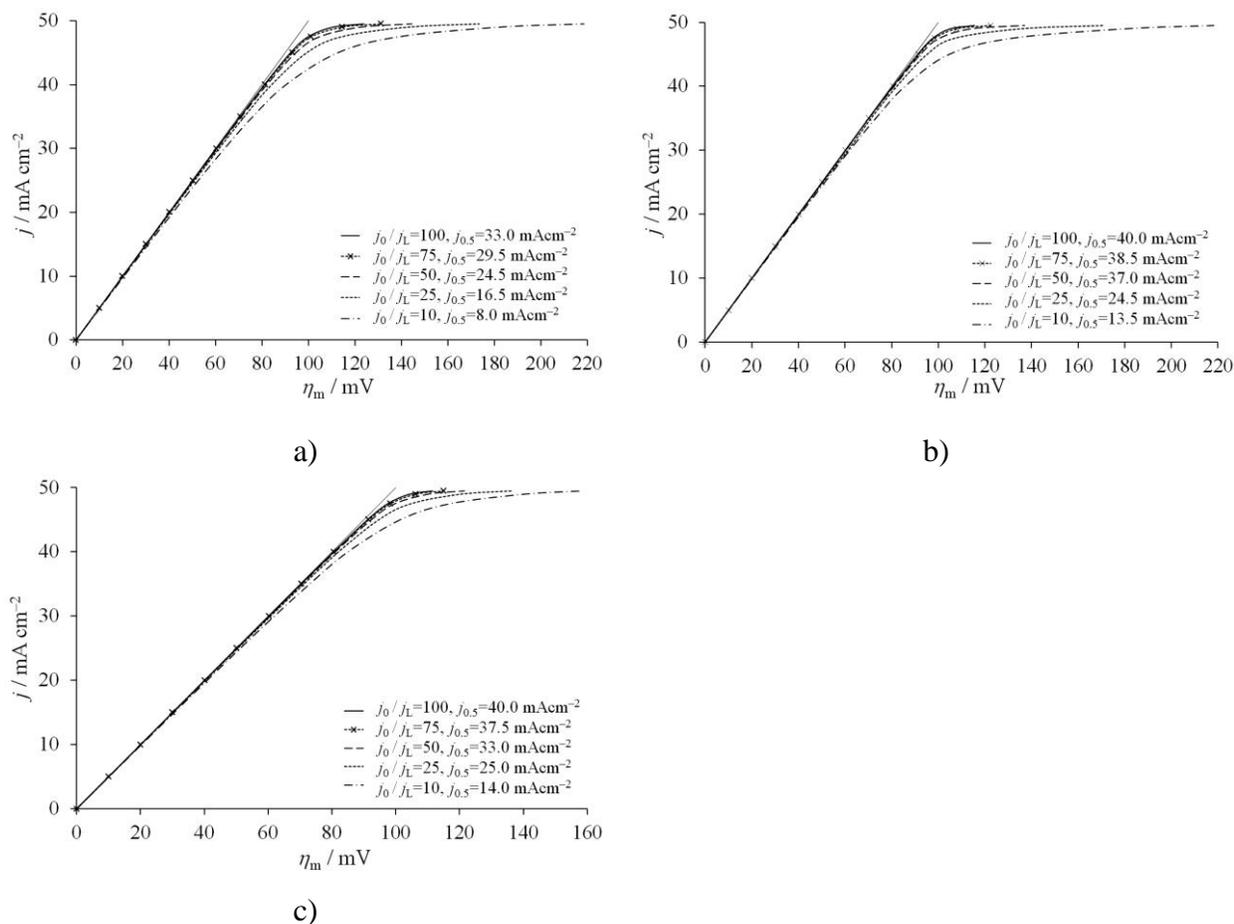
160 The simulated polarization curves with included the ohmic potential drop are shown in
 161 Fig. 2. They are obtained using the same data as those shown in Fig. 1 and for $j_L = 50 \text{ mA cm}^{-2}$, L
 162 $= 0.2 \text{ cm}$ and $\kappa = 0.1 \text{ S cm}^{-1}$. In all cases, for $j_0/j_L = 100$ there is linear dependence of the current
 163 density on overpotential up to $j = 45 \text{ mA cm}^{-2}$, or to $j/j_L \approx 0.9$. In these cases, the overpotential
 164 without included ohmic potential drop (see Fig. 1) is very low and the measured overpotential is
 165 practically equal to the ohmic potential drop between the working and the reference electrodes.
 166 Hence, for $j_0/j_L > 100$ there is the ohmic control of the electrodeposition process. It is obvious that
 167 the shape of the linear part of polarization curve does not depend on the mechanism of the
 168 electrode reaction.



169 Figure 2. Dependencies $j - \eta_m$ calculated using the Eqs. (2), (3) and (4) and the different values of
 170 j_0/j_L ratio for $j_L = 50 \text{ mA cm}^{-2}$, $L = 0.2 \text{ cm}$ and $\kappa = 0.1 \text{ S cm}^{-2}$: a), b) and c) as in
 171 captions in Fig. 1.

172
 173 The polarization curves consist of two parts in the mixed ohmic-diffusion controlled
 174 electrodeposition.¹² The first part corresponds the ohmic control (it is the linear part), and the

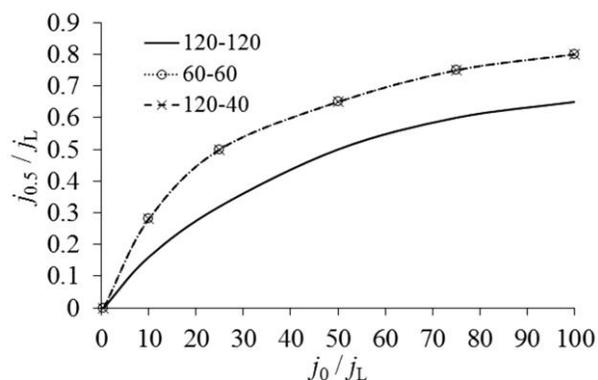
175 second one corresponds to the diffusion control (Fig. 3). The length of the ohmic part at the
 176 polarization curve decreases with decreasing the j_0/j_L ratio values. Assuming that the diffusion
 177 control of the electrodeposition process becomes visible at $\eta_m \geq 0.5$ mV, the values of $j_{0.5}/j_L$ at the
 178 end of the linear part of polarization curves are calculated and shown in the function of j_0/j_L ratio
 179 in Fig. 4 and given in Table 1. It can be seen from Fig. 4 and Table 1 that the linear part of the
 180 polarization curve vanishes at $j_0/j_L = 1$. Hence, there is the mixed ohmic – diffusion control in the
 181 interval of $1 < j_0/j_L \leq 100$.



182 Figure 3. Dependencies $j - \eta_m$ for $10 \leq j_0/j_L \leq 100$ calculated as those in Fig. 2.

183 At values of j_0/j_L ratio lower than 1, the complete diffusion control of the electrodeposition
 184 process arises at all overpotentials. The lower limit of the region of the complete diffusion control
 185 can be determined as follows: it is obvious that the convex shape of the polarization curve
 186 characterizes the diffusion control of deposition process and the concave one the activation
 187 control of deposition process. The j/j_L ratio as function of η is shown in Fig. 1 and the j as a
 188 function of η_m in Fig. 2. In both cases the convex shape of curves changes in the concave one at

189 approximately $j_0/j_L \sim 0.1$, meaning that the diffusion control changes in the activation one at the
 190 beginning of the polarization curve at low η and η_m . At larger overpotentials the diffusion control
 191 occurs. Hence, the diffusion control at all overpotentials appears at $0.1 < j_0/j_L \leq 1$, while the
 192 activation control appears at $j_0/j_L \leq 0.1$ at low overpotentials.



193
 194 Figure 4. Dependencies $j_{0.5}/j_L$ ratio on the j_0/j_L ratio. a), b) and c) as in captions in Fig. 1.

195
 196 TABLE I. Calculated value of $j_{0.5}$ as function of j_0/j_L ratio. a), b) and c) as in captions in Fig. 1

j_0/j_L	$j_{0.5} / \text{mA cm}^{-2}$		
	a	b	c
10	8.0	13.5	14.0
25	16.5	24.5	25.0
50	24.5	37.0	33.0
75	29.5	38.5	37.5
100	33.0	40.0	40.0

197
 198
 199 It can be seen from Figs. 1 and 2 that the same conclusion can be derived for the
 200 polarization curves with and without included ohmic overpotential drop. The simulated
 201 polarization curves with included ohmic drop are calculated using data for 1 M solution of
 202 typically fully dissociated electrolyte without supporting electrolyte.¹⁵ It is obvious that for less
 203 concentrated solutions with supporting electrolyte (mainly some acid or base) the ohmic potential
 204 drop can be neglected. Because of this fact η instead of η_m will be used, except for some special
 205 cases indicated.
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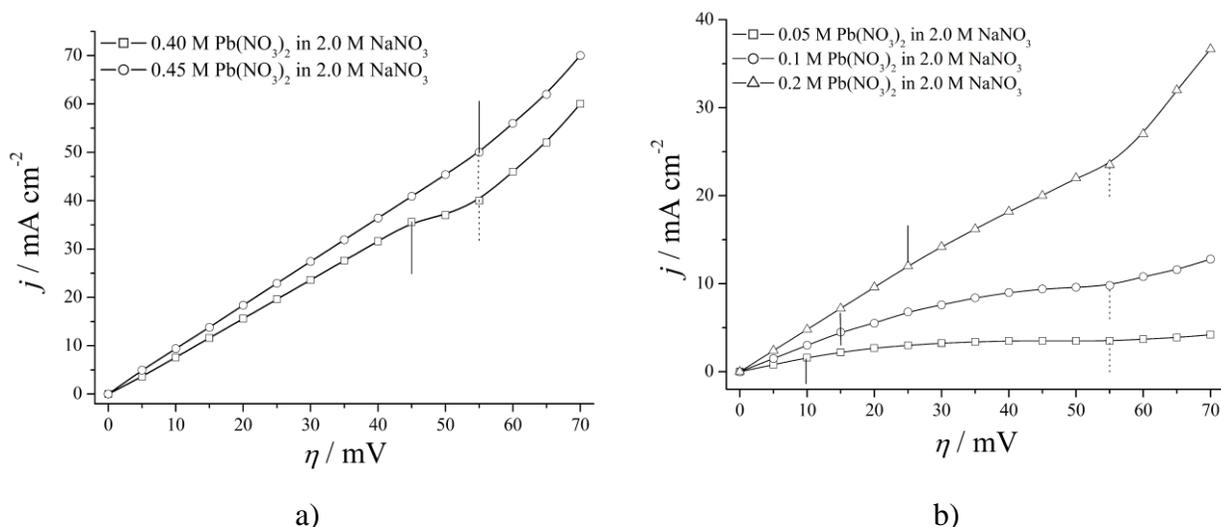
207 *Experimental verification of the simulated polarization curves with the included ohmic potential*
208 *drop*

209
210 The nearest experimental curves to the simulated curves for $j_0/j_L = 100$ (the full ohmic
211 control) and $1 < j_0/j_L \leq 100$ (the mixed ohmic - diffusion control) are recorded during lead
212 electrodeposition processes because electrodeposition of lead occurs in the conditions of the
213 mixed ohmic-diffusion or even full ohmic control.¹² Lead is characterized by the extremely high
214 exchange current density value ($j_0 \rightarrow \infty$; the fast electrochemical processes), and there is no a
215 precise and unique way for the determination of the exchange current density values. For that
216 reason, the comparison of simulated and experimentally recorded polarization curves can be
217 excellent auxiliary method for the approximate estimation of the exchange current density of
218 lead, as well as the other metals from the group of normal metals. The ratio of the ohmic to the
219 overall control of the electrodeposition increases with increasing concentration of Pb^{2+} so that the
220 electrodeposition process becomes a full ohmic controlled one at high concentrations of Pb^{2+} .¹²

221 The typical Pb polarization curves recorded from solutions of different Pb^{2+}
222 concentrations are shown in Fig. 5. The end of the ohmic control is denoted by vertical solid line,
223 while the inflection point is denoted by vertical dot line. The linear dependence of the current
224 density on the overpotential up to the inflection point corresponds to the full ohmic control, and
225 the current density at the inflection point corresponds to the limiting diffusion current density.¹²
226 As seen from Fig. 5a, the condition of the full ohmic control is fulfilled with concentrations of
227 Pb^{2+} ions of 0.45 M (the linear dependence of $j - \eta$ up to the inflection point) and furthermore
228 with 0.40 M because the linear dependence of $j - \eta$ is up to about $j/j_L \approx 0.9$.

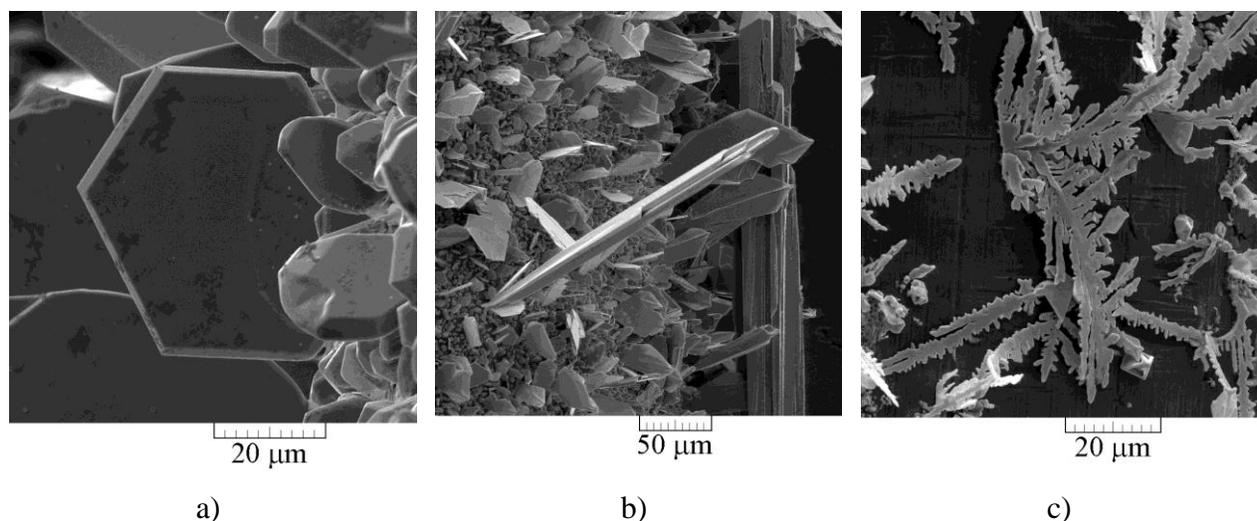
229 With decreasing concentration of Pb^{2+} ions (Fig. 5b), electrodeposition of Pb occurs in the
230 conditions of the mixed ohmic-diffusion control. After the inflection point, electrodeposition
231 system remains in the diffusion control and the fast increase in current density with further the
232 increase in overpotential is due to a strong increase of surface area of the electrode caused by
233 instantaneous formation and growth of dendrites. The ratios of j/j_L , where j corresponds to the
234 end of the linear dependence and j_L to the inflection point at the polarization curve were
235 approximate 0.51, 0.46 and 0.46 for 0.20, 0.10 and 0.050 M Pb^{2+} , respectively.

236
237



238 Figure 5. The polarization curves for lead electrodeposition from: a) 0.40 and 0.45 M and b)
 239 0.050, 0.10 and 0.20 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M NaNO_3 .

240 The typical surface morphologies of lead obtained from 0.10 M $\text{Pb}(\text{NO}_3)_2$ in 2.0 M
 241 NaNO_3 are shown in Fig. 6. The regular hexagonal particles are formed by electrodeposition in
 242 the ohmic control (Fig. 6a; $\eta = 10$ mV). The elongated irregular particles (precursors of
 243 dendrites) and dendrites of the different shape (needle-like and „tooth of saw“-like dendrites)
 244 were formed under the diffusion control before (Fig. 6b; $\eta = 50$ mV) and after (Fig. 6c; $\eta = 100$
 245 mV) the inflection point at the polarization curve. Following the classical Wranglen definition of
 246 a dendrite,^{16,17} the dendrites of Pb belong to 2D (two-dimensional) primary (P) type dendrites.
 247 The dendrites of lead were very similar to those obtained by silver electrodeposition processes
 248 from the nitrate electrolytes,¹⁸⁻²⁰ indicating on the strong dependence of the shape of dendrites on
 249 the affiliation to the determined group of metals.
 250



251 Figure 6. The typical surface morphologies of lead electrodeposited from 0.10 M $\text{Pb}(\text{NO}_3)_2$ in 2.0
 252 M NaNO_3 at overpotentials of: a) $\eta = 10$ mV (the ohmic control); time of the
 253 electrodeposition (t), $t = 25$ min, b) $\eta = 50$ mV (the diffusion control before the
 254 inflection point), $t = 210$ s, and c) $\eta = 100$ mV (the diffusion control after the inflection
 255 point), $t = 140$ s.

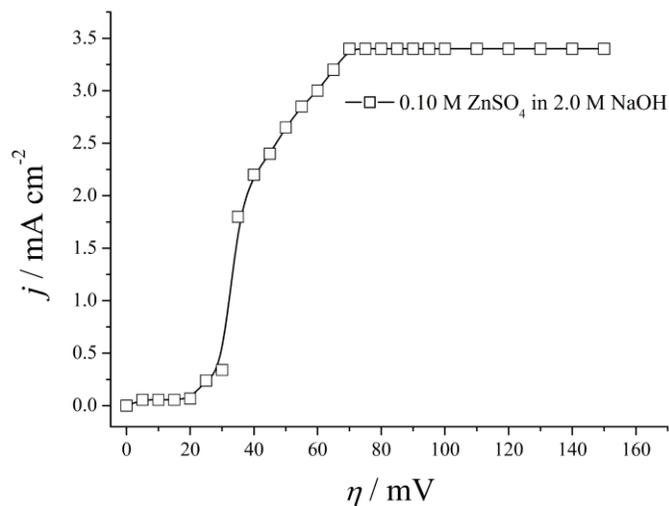
256 Zinc also belong to the group of normal metals characterized by $j_0 \rightarrow \infty$, but the shape of
 257 the polarization curve is completely different from those characteristic for Pb. The typical Zn
 258 polarization curve obtained from 0.10 M ZnSO_4 in 2.0 M NaOH is shown in Fig. 7a. As seen
 259 from Fig. 7a, there is no the ohmic controlled part at this polarization curve. After the initial part
 260 determined by the low nucleation rate, the shape of polarization curve takes the convex shape up
 261 to a reach of the plateau of the limiting diffusion current density. Comparing this shape of the
 262 polarization curve with the simulated ones, it is clear that Zn is „slower metal“ than Pb, with the
 263 ratio $j_0/j_L < 1$.

264 Morphology of electrodeposited Zn was also completely different from the one observed
 265 during electrodeposition of Pb. Unlike of regular grains formed by Pb electrodeposition, the
 266 spongy particles were formed at overpotentials belonging to the convex shape at the polarization
 267 curve (Fig. 7b; $\eta = 45$ mV). Simultaneously, dendrites were electrodeposited at the plateau of the
 268 limiting diffusion current density (Fig. 7c; $\eta = 100$ mV).

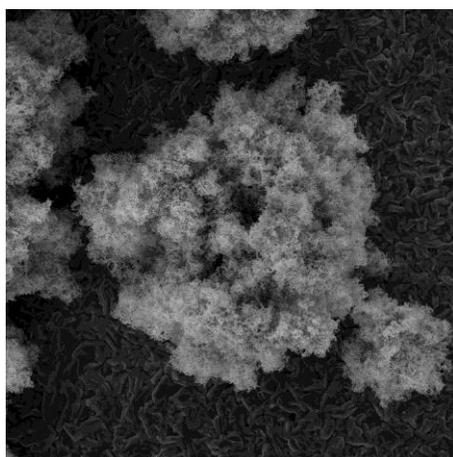
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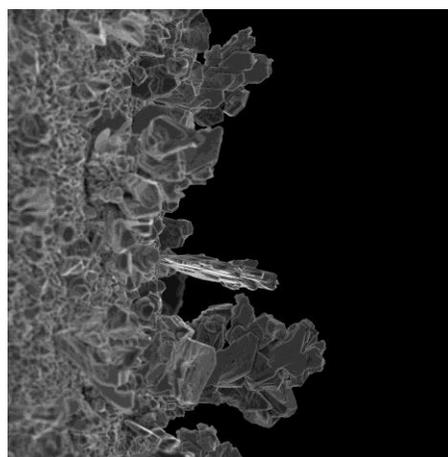
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a)



b)



c)

272 Figure 7. a) The polarization curve for Zn electrodeposition from 0.10 M ZnSO₄ in 2.0 M NaOH,
 273 and the typical surface morphologies obtained at overpotentials of: b) $\eta = 45$ mV (the
 274 zone of the fast increase in the current density with increasing overpotential), $t = 60$ min,
 275 and c) $\eta = 100$ mV (the plateau of the limiting diffusion current density), $t = 50$ min.

276 The further lowering the exchange current density leads to the further change of the shape
 277 of the polarization curve. As result of this, the initial part of the polarization curve transforms
 278 from the convex (the diffusion control) to concave (the activation control) one at approximately
 279 $j_0/j_L \leq 0.1$. The typical representative of this group of metals is copper. Namely, Cu belongs to the

280 group of the intermediate metals characterized by the medium exchange current density values.^{2,3}
281 The polarization curve obtained from solution containing 0.10 M CuSO₄ in 0.50 M H₂SO₄ is
282 shown in Fig. 8a. For this solution,¹ $j_0 = 0.11 \text{ mA cm}^{-2}$ and $j_L = 9.2 \text{ mA cm}^{-2}$ and hence $j_0/j_L =$
283 0.012. This polarization curve consists of four parts: a) activation, b) mixed activation-diffusion,
284 c) diffusion, and d) the zone of the fast increase of current density with overpotential.
285 Electrodeposition in each of these regions produces characteristic surface morphologies. The
286 large grains are obtained in the activation controlled electrodeposition (Fig. 8b). The carrot-like
287 (Fig. 8c) and globular forms (Fig. 8d) are formed in the mixed activation-diffusion control. The
288 3D (three-dimensional) pine-like dendrites formed inside the plateau of the limiting diffusion
289 current density are shown in Fig. 8e. The shape of pine-like Cu dendrites was very similar to Ag
290 dendrites obtained from the various types of complex electrolytes like those with the addition of
291 ammonia^{20,21}, tungstosilicate²² and citric²³ acids, or to Au dendrites.²⁴ In this way, the strong
292 correlation between the surface morphologies and the affiliation to the determined group of
293 metals is confirmed. Due to the lower overpotentials for hydrogen evolution reaction, the effect
294 of evolved hydrogen as parallel reaction to copper electrodeposition at the high overpotentials
295 become visible in the zone of the fast increase of the current density with increasing
296 overpotential. The honeycomb-like structures can be formed in this zone (Fig. 8f).

297 Finally, electrodeposition of metals from the group of inert metals occurs parallel with
298 hydrogen evolution reaction in the whole range of potentials and current densities. The corrected
299 polarization curves can be only obtained after IR drop correction,²⁵ making their analysis out of
300 scope of this investigation. Due to vigorous hydrogen evolution, the spongy-like and globular
301 particles, as well as degenerate dendrites are formed.²⁶⁻²⁸

302

303

CONCLUSIONS

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305 The polarization curves for the different the exchange current densities to the limiting
306 diffusion current densities (j_0/j_L) ratios were simulated. The correlation between the shape of
307 polarization curve and the type of metal electrodeposition process control was established on the
308 basis of these ratios. The four diagnostic criteria based on j_0/j_L ratios were established: (a) $j_0/j_L >$
309 100 - the ohmic control, (b) $1 < j_0/j_L \leq 100$ - the mixed ohmic-diffusion control, (c) $0.1 < j_0/j_L \leq 1$
310 - the diffusion control and (d) $j_0/j_L \leq 0.1$ - the activation control at the low overpotentials. The

311 verification of the proposed diagnostic criteria was successfully done by comparison with
312 experimentally obtained polarization curves and by the surface analysis of deposits obtained in
313 the different types of metal electrodeposition process control.

314

315 **Acknowledgement**

316

317 The work was supported by the Ministry of Education, Science and Technological Development
318 of the Republic of Serbia under the research project: “Electrochemical synthesis and
319 characterization of nanostructured functional materials for application in new technologies” (No.
320 172046).

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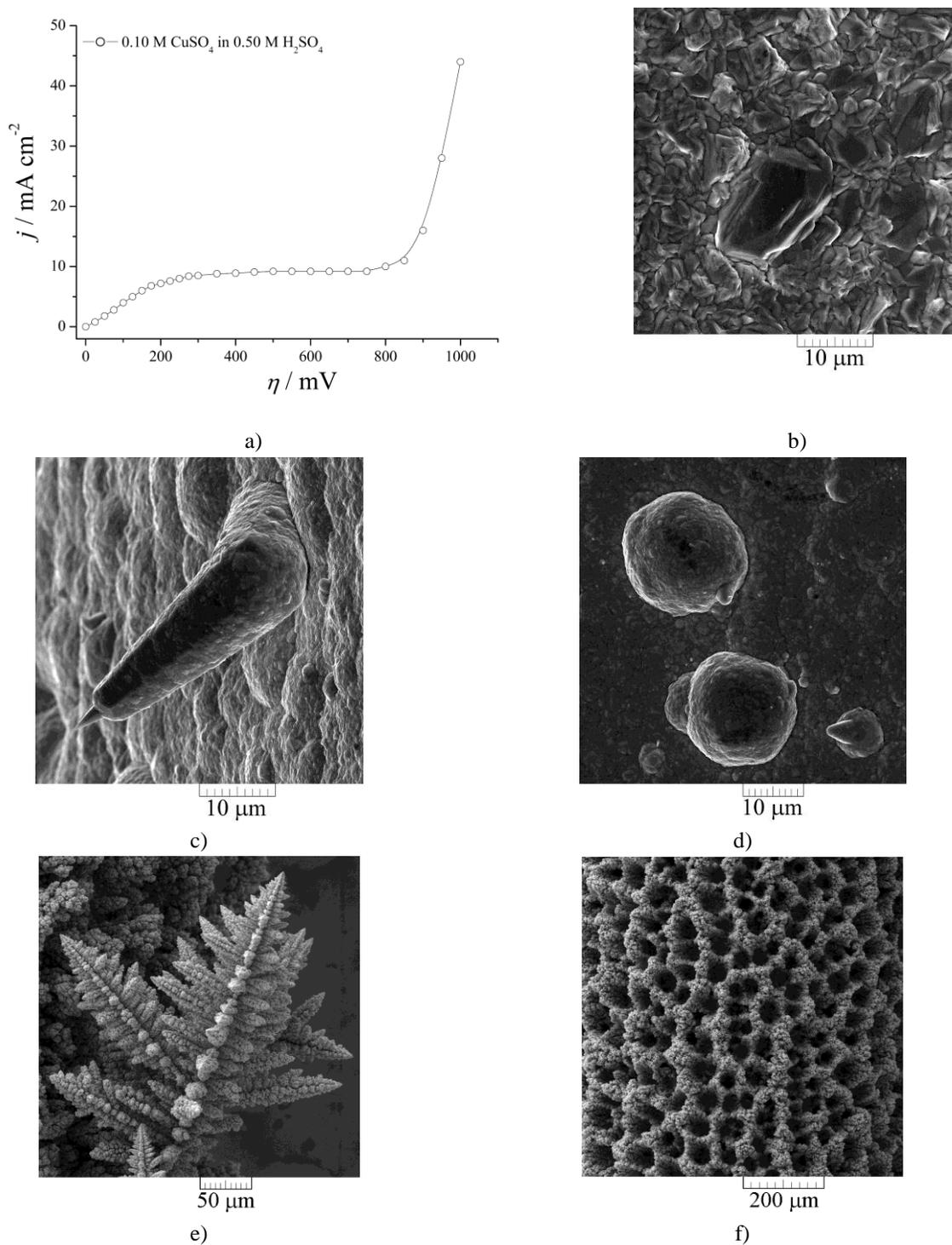
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336 Figure 8. a) The polarization curve for Cu electrodeposition from 0.10 M CuSO_4 in 0.50 M
 337 H_2SO_4 , and the typical surface morphologies obtained in the different types of control: b)
 338 activation, $\eta = 90 \text{ mV}$; $t = 120 \text{ min}$, c) and d) activation-diffusion, $\eta = 210 \text{ mV}$; $t = 45 \text{ min}$, e)
 339 diffusion, $\eta = 650 \text{ mV}$; $t = 52 \text{ min}$, and f) zone of the fast increase of current density with
 340 overpotential, $\eta = 1000 \text{ mV}$; $t = 120 \text{ s}$.

ИЗВОД

ОБЛИК ПОЛАРИЗАЦИОНЕ КРИВЕ И ДИЈАГНОСТИЧКИ КРИТЕРИЈУМИ ЗА
КОНТРОЛУ ПРОЦЕСА ЕЛЕКТРОХЕМИЈСКОГ ТАЛОЖЕЊА МЕТАЛАКОНСТАНТИН И. ПОПОВ^{1,2}, ПРЕДРАГ М. ЖИВКОВИЋ¹,
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Србија

Поларизационе криве добијене дигиталном симулацијом су биле корелисане са типом контроле процеса електрохемијског таложења метала у функцији односа густине струје измене и граничне дифузионе густине струје (j_0/j_L). На основу j_0/j_L удела утврђени су дијагностички критеријуми. За $j_0/j_L > 100$, систем је под омском контролом. У опсегу $1 < j_0/j_L \leq 100$ постоји мешовита омско-дифузиона контрола. Дифузиона контрола се јавља у опсегу $0.1 < j_0/j_L \leq 1$. За $j_0/j_L \leq 0.1$, систем је активационо контролисан на малим пренапетостима. Предложени дијагностички критеријуми су потврђени поређењем симулираних кривих са експериментално снимљеним кривама и анализом морфологија талога добијених у различитим типовима контроле процеса електрохемијског таложења метала.

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