



*J. Serb. Chem. Soc.* 87 (9) 1049–1062 (2022)  
JSCS–5577

## Extraordinary regularities of zinc dendrites' growth under appropriate electrolysis conditions

DIMITAR D. GRAMATIKOV<sup>1,2</sup> and SVETOMIR A. HADŽI JORDANOV<sup>1\*</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Skopje 1000, Republic of North Macedonia and <sup>2</sup>Faculty of Economy, Ss. Cyril and Methodius University, Skopje 1000, Republic of North Macedonia

(Received 22 January, revised 17 March, accepted 26 March 2022)

**Abstract:** A case study is given of dendritic growth during zinc electrolysis in conditions that promote it. Subject of the main interest was how the electrolysis parameters affect the duration of dendrites life. The selected set of parameters did provide a surprisingly regular dendrite's life, *i.e.*, period from start of the electrolysis until dendrites detachment from the cathode. Dendrite's growth did proceed with lowering of the zinc current efficiency, and the end of life was manifested by intensive hydrogen evolution due to corrosion of detached zinc deposit in the acid electrolyte. Current efficiency was successfully followed by the bubble counting technique, invented especially for kinetic studies of gas including reactions. The acquired results on dendrites' life duration were so exact that it was easy to unify all five mono-variable dependencies into one five-variable expression. The calculated values of life duration did differ from the measured ones by only  $\pm 3\%$ ! This is a proof that the developed expression accurately presents the real nature of dendritic growth under the applied conditions, *i.e.*, 0.5 to 2 M zinc (II) ions, 0.41 to 3.06 M H<sub>2</sub>SO<sub>4</sub>, 10 to 2500 mg dm<sup>-3</sup> copper (II) ions, 0.14 to 14 g dm<sup>-3</sup> hexamethylenetetramine, and 4.25 to 103 mA dm<sup>-2</sup> current density. The eventual broader region of Zn dendrites' strict regular growth is not excluded.

**Keywords:** current efficiency vs. electrolysis conditions; bubble counting procedure; calculation of dendrites' life duration.

### INTRODUCTION

Formation of dendrites is undesirable in hydrometallurgy because it interferes with the normal electrolysis course, *i.e.*, it lowers the current efficiency and product's quality, as well as the smooth plant operation.<sup>1–4</sup> Over the years the industrial processes did master regimes that minimize or completely eliminate dendrites' growth by strict control of electrolysis parameters such as level of impurities, cur-

\* Corresponding author. E-mail: shj@tmf.ukim.edu.mk  
<https://doi.org/10.2298/JSC220122029G>



rent density, hydrodynamic conditions, *etc.*<sup>5,6</sup> According to the studies published over the past period<sup>7-9</sup> this problem seems to be solved. Today this issue is part of regular academic studies courses. Nevertheless, the interest for dendritic deposit's morphology still exists and attracts at least academic interest.<sup>10,11</sup>

In our electrochemical research we did develop an original experimental procedure for measuring the rate of gas evolution reactions, by transforming the gas into stream of bubbles of constant size, and subsequent counting the bubbles, as described in more details elsewhere.<sup>12,13</sup> In the present case study we were concerned with the regularities of dendrites' growth in conditions far from the electro-winning ones. We find that the bubbles counting technique was quite convenient for the purpose.

#### EXPERIMENTAL

The zinc electrolysis reaction  $\text{ZnSO}_4 + \text{H}_2\text{O} \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4$  was performed in a standard electrochemical cell, but modified for use of the bubbles counting technique. The scheme is shown in Fig. 1.

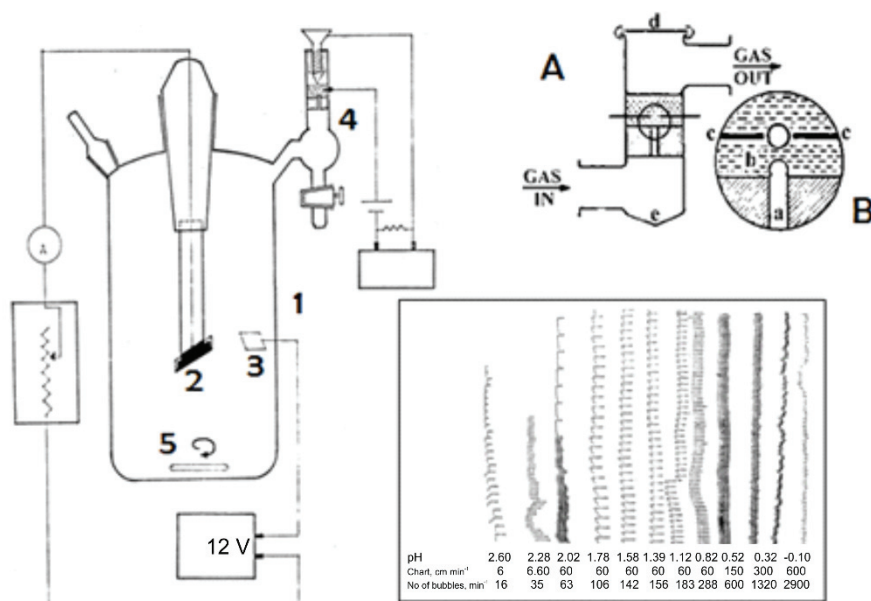


Fig. 1. Left: glass cell and the other measuring devices: 1) cell body, 2) zinc cathode, 3) Pt-anode, 4) bubble counting unit, 5) magnetic stirrer. Upper right: bubble counting details: A) complete unit, B) capillary, bubbles and microelectrodes; Bottom right: bubble counting time-voltage recordings for  $\text{H}_2$  developed by dissolving Zn in  $\text{H}_2\text{SO}_4$  solutions.

The glass cell's main body (1) is equipped with an inlet for the working electrode (2), built-in Pt-anode, (3), bubble counting unit (4) and magnetic stirrer (5). The working electrode was a zinc rod placed into a Teflon holder in a way to enhance bubbles' removal. Only for the bubbles' size calibration purposes a platinum working electrode instead of a zinc one was

placed at position 2, and acid solution without  $\text{ZnSO}_4$  was used in order to perform water electrolysis and generate gas mixture of  $\text{H}_2:\text{O}_2$  in 2:1 volume ratio. Solution magnetic steering enhanced reactants supply to the cathode, and removal of  $\text{H}_2$  bubbles. The gas outlet extends in a glass body closed with a capillary on top. The capillary's tip is immersed in a "water + surfactant reservoir" so that the escaping gas is transformed into a stream of tiny bubbles. The optimal measuring performance was achieved with bubble sizes below  $0.01 \text{ cm}^3$  each. By installing two Pt-microelectrodes were installed on the bubbles' escape way, so that each bubble produces an impulse for counting in the electric circuit (see Fig. 1, upper right).

The electrolysis parameters' values were varied as follows:

- Zinc ions concentration was preferentially 2 M, but 0.5 and 1 M were used as well.
- $\text{H}_2\text{SO}_4$  concentration was preferentially 2.04 M, but 0.41, 1.02 and 3.06 M were used as well.

- Copper(II) ions concentration was  $250 \text{ mg dm}^{-3}$  but 10, 50 and  $2500 \text{ mg dm}^{-3}$  were used as well. Cu was chosen among tested Sb (III), Ni (II), Cu (II), Co (II), Fe (III) and Fe(II) due to its moderate rate of dendrites growth promotion.<sup>11</sup>

- Hexamethylenetetramine's (HMT) concentration was  $5 \text{ g dm}^{-3}$ , but 0.14, 1.0, 2.5 and  $14.0 \text{ g dm}^{-3}$  were used as well. HMT was chosen based on its previous performance testing.<sup>14</sup>

- Current density was  $13 \text{ mA dm}^{-2}$  but 4.25 and  $103 \text{ mA dm}^{-2}$  were applied as well.

- Merck p.a. grade chemicals and distilled water were used for preparing the solutions.

Electrolyte volume in the cell was 0.15 L.

The electrolysis was performed at constant current strength\* and temperature of  $22 \pm 2 \text{ }^\circ\text{C}$ . The bubbling rate was measured in fixed time periods, typically 10 min. The measured rate values were used to calculate the electrolysis current efficiency. Calibration of the bubbles size was done for water splitting reaction from sulfuric acid solution without zinc sulfate, and using a Pt-cathode, when only hydrogen and oxygen gases are produced in a volume ratio of 2:1. When the zinc electrolysis runs under the same current strength, and zinc current efficiency is 100 %, only oxygen gas is evolved, and only one third of the previous volume of gases is generated. The relation between the gas quantity and the current quantity, as given by the electrochemical equivalent  $q$  (e.g.  $q_{(\text{O}_2)} = 0.298 \text{ g A}^{-1} \text{ h}^{-1}$ ) enables simple conversion of current quantity into gas mass, and in turn into gas volume. If water splitting gives rise to  $N$  bubbles/minute, and zinc electrodeposition under the same conditions gives  $n$  bubbles/minute, then the hydrogen current efficiency ( $CE_{\text{H}}$ ) was calculated by:

$$CE_{\text{H}} = 100(3n - N)/2N \quad (1)$$

The zinc deposition current efficiency ( $CE_{\text{Zn}}$ ) was calculated as the difference:

$$CE_{\text{Zn}} = 100 - CE_{\text{H}} \quad (2)$$

## RESULTS AND DISCUSSION

### *Presentation of the studied phenomena*

Three completely different types of plots zinc current efficiency ( $CE_{\text{Zn}}$ ) vs. time were registered in this study, as shown in Fig. 2.

Processes that take place over these sets of conditions are as follows: In the simplest case of pure solution (only  $\text{ZnSO}_4$  and  $\text{H}_2\text{SO}_4$ ), zinc current efficiency is

---

\* Galvanostatic conditions are troublesome to maintain when dendrites' growth continually increases the electrode surface area. So, naming this current regime as galvanostatic is correct only for the initial stage of electrolysis.

high, and almost constant over time, the hydrogen evolution being correspondingly low, *e.g.*, up to 5 %.

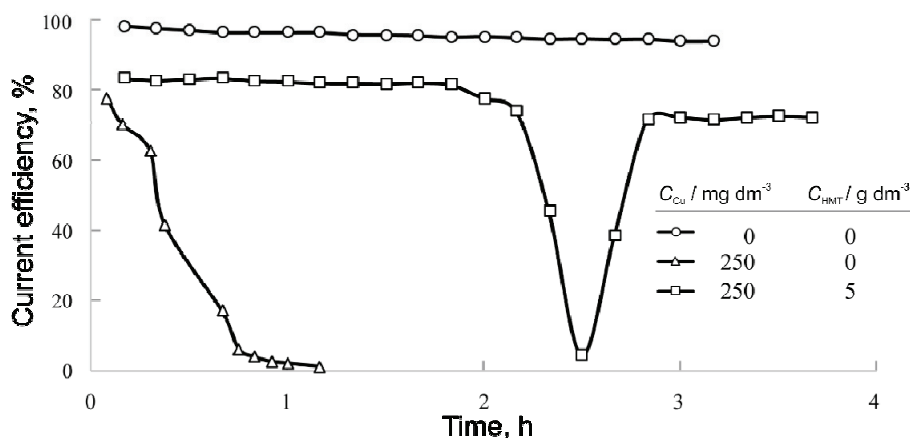


Fig. 2.  $CE_{Zn}$  from 2M  $ZnSO_4 + 2M H_2SO_4$  at  $4.25 \text{ mA dm}^{-2}$  from pure electrolyte, electrolyte with added  $250 \text{ mg dm}^{-3}$  copper(II)ions, and electrolyte with added  $250 \text{ mg dm}^{-3}$  copper(II)ions and  $5 \text{ g dm}^{-3}$  HMT.

The addition of Cu (II) ions to the previous electrolyte causes a higher initial hydrogen evolution ( $\sim 20 \%$ ), followed by a steep increase up to 100 % in one hour. After that, it is hard to recognize any deposition of Zn or Cu.

The addition of both Cu (II) ions and HMT\* causes the hydrogen evolution to prolong its period of 20 % evolution efficiency for many hours before the copper impurities in the cathode deposit become capable to increase the  $H_2$  efficiency dramatically. Visual observation shows that Zn dendrites grow fast after the induction period. Intensive electrolyte stirring imposes permanent mechanical pushing of the deposited 3D structure. When the dendrites reach such a critical size that they can no longer withstand the pressure, they are pushed out from the electrode. The floating Zn grains or the dendrite's parts corrode freely in the acid electrolyte and produce hydrogen in quantities that sometimes exceed even the ones at 100 % hydrogen current efficiency.

Electrolysis continues further after the dendrites' detachment, so that zinc and copper are deposited on top of the newly released cathode surface. In fact, these metals' deposition never stops, but the evolution of a large amount of hydrogen gas leads to such a false conclusion. The total (Zn + Cu) current efficiency reaches a constant value again, but lower than the one prior to the drop of the dendrites. The regularity in reaction sequences, *i.e.*, deposition, dendrite's incubation, growth,

\* According to Popov *et al.*,<sup>3</sup> organic additives may decrease the exchange current density of the deposition process by forming complexes with depositing ions or by maintaining the deposition overpotential below the critical values for dendritic growth initiations.

drop and corrosion, repeats in many turns as shown in Fig. 3, where an example is given with 3 cycles of growth, each with duration of almost 100 min.

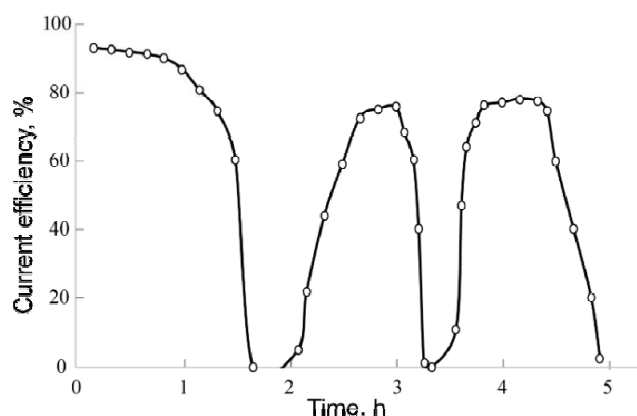


Fig. 3.  $CE_{Zn}$  during 3 sequences of deposition, formation and break of dendrites from  $2 \text{ M ZnSO}_4 + 1 \text{ M H}_2\text{SO}_4 + 250 \text{ mg dm}^{-3} \text{ Cu (II)} + 5 \text{ g dm}^{-3} \text{ HMT}$  at  $13 \text{ mA dm}^{-2}$ .

#### *Effect of the electrolysis parameters on $CE_{Zn}$*

In further stages, the effect of the electrolysis parameters was comprehensively studied. Beforehand valuable information was found elsewhere.<sup>5-8</sup>

*The effect of copper (II) ions concentrations\* on  $CE_{Zn}$ .* This effect was examined by adding 10, 50, 250 and  $2500 \text{ mg dm}^{-3} \text{ Cu (II)}$  to an electrolyte that contains  $2 \text{ M ZnSO}_4 + 2 \text{ M H}_2\text{SO}_4$  and  $5 \text{ g dm}^{-3} \text{ HMT}$  at  $13 \text{ mA dm}^{-2}$  (Fig. 4). The results are given in Table I as well.

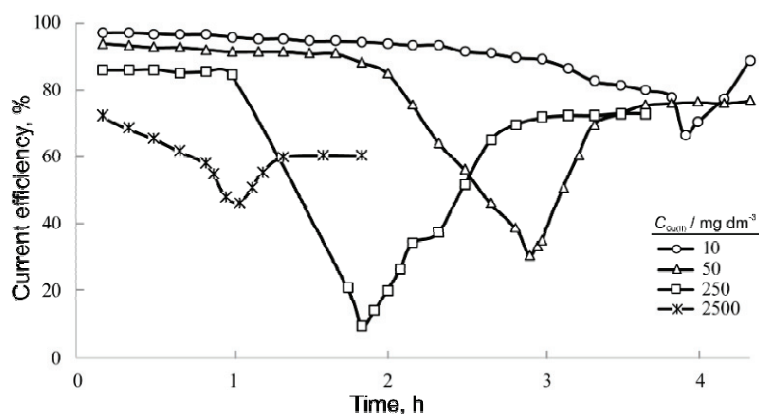


Fig. 4.  $CE_{Zn}$  from  $2 \text{ M ZnSO}_4 + 2 \text{ M H}_2\text{SO}_4 + 5 \text{ g dm}^{-3} \text{ HMT}$  at  $13 \text{ mA dm}^{-2}$ : 10, 50, 250 and  $2500 \text{ mg dm}^{-3} \text{ Cu (II)}$ , respectively.

\*The values of concentration of involved species (Zn (II) ions and sulfuric acid) used in this study are so high, that only their activities are relevant, but they are hard to determine.

TABLE I. Effect of copper (II) ions concentration on  $CE_{Zn}$ 

$C_{Cu(II)} / \text{mg dm}^{-3}$	$CE_{Zn}$ at $t \rightarrow 0$ , %	Time of maximal $H_2$ evolution, h <sup>a</sup>
10	97	3.92
50	93	2.95
250	84	1.87
2500	72	1.00

<sup>a</sup>The time of maximum  $H_2$  evolution, *i.e.*, the minimum of the plots in Fig. 4, is a sum of periods of: dendrite's growth/induction + dendrite's growth + dendrite's detachment + dissolution up to the maximum gas evolution.

It is concluded that Cu (II)-ion concentration decreases the value of  $CE_{Zn}$  at  $t \rightarrow 0$ , as expected by the copper's property to enhance hydrogen evolution. With  $2500 \text{ mg dm}^{-3}$  Cu (II) ions, Zn current efficiency at  $t \rightarrow 0$  falls to only 72 %. Increasing the Cu (II) ions concentration from 10 to  $2500 \text{ g dm}^{-3}$  reduces the period until the dendrites detachment, from near 4 to 1 h. Compared with the rest 3 plots in Fig. 4, the plot for  $2500 \text{ mg dm}^{-3}$  Cu (II) ions either does not follow the same regularity, or an experimental error is present.

*The effect of the Zn (II) concentration on  $CE_{Zn}$ .* These experiments were performed by varying  $ZnSO_4$  concentration (0.5, 1 and 2 M) in solution of 0.41 M  $H_2SO_4$ ,  $5 \text{ g dm}^{-3}$  HMT and  $250 \text{ mg dm}^{-3}$  Cu (II) ions, at  $13 \text{ mA dm}^{-2}$ . The results presented in Fig. 5 and Table II show that the increase of the Zn ions concentration increases the initial value of CE Zn at  $t \rightarrow 0$ , and prolongs the period before the dendritic growth, up to the dendrites' detachment.

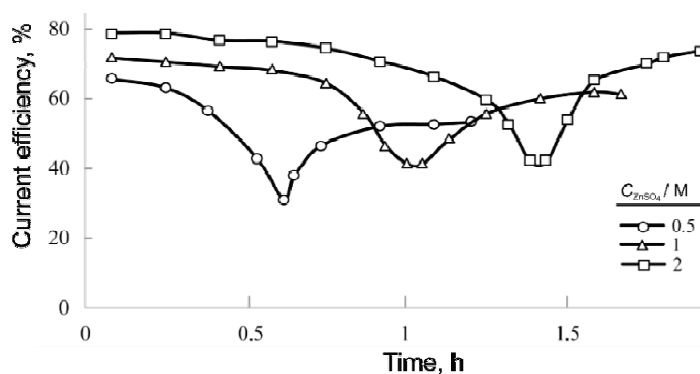


Fig. 5.  $CE_{Zn}$  from 0.41 M  $H_2SO_4$  +  $250 \text{ mg dm}^{-3}$  Cu (II) ions +  $5 \text{ g dm}^{-3}$  HMT at  $13 \text{ mA dm}^{-2}$  and 0.5, 1 and 2 M  $ZnSO_4$ , respectively.

TABLE II. Effect of Zn (II) concentration on  $CE_{Zn}$ 

$C_{ZnSO_4} / \text{M}$	$CE_{Zn}$ at $t \rightarrow 0$ , %	Time of max. $H_2$ evolution, h	$CE_{Zn}$ at dendrites detachment, %
0.5	65	0.60	30
1.0	71	1.03	39
2.0	78	1.40	47

The effect of  $H_2SO_4$  concentration on  $CE_{Zn}$ . This dependency was studied at 2 M  $ZnSO_4$ ,  $250\text{ mg dm}^{-3}$  Cu (II) ions,  $5\text{ g dm}^{-3}$  HMT and  $13\text{ mA dm}^{-2}$ , and the results are shown in Fig. 6 and Table III. They indicate that increase in the  $H_2SO_4$  concentration, enhances the hydrogen evolution, and consequently lowers the  $CE_{Zn}$ .

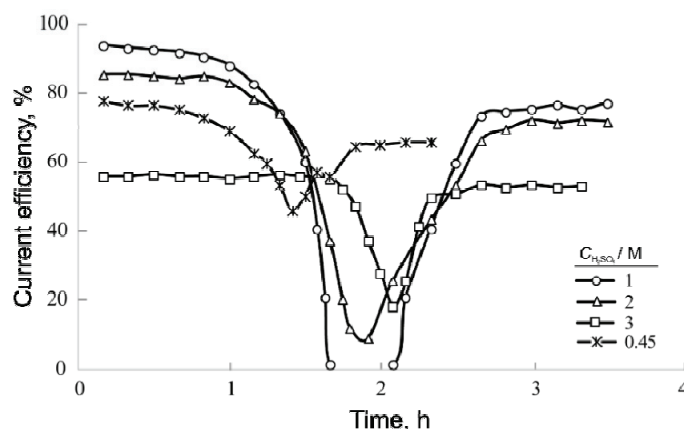


Fig. 6.  $CE_{Zn}$  from 2 M  $ZnSO_4$  +  $250\text{ mg dm}^{-3}$  Cu (II) ions +  $5\text{ g dm}^{-3}$  HMT at  $13\text{ mA dm}^{-2}$  in 1, 2, 3 and 0.45 M  $H_2SO_4$ , respectively.

TABLE III. Effect of the  $H_2SO_4$  concentration on  $CE_{Zn}$

$C_{H_2SO_4} / M$	$CE_{Zn}$ at $t \rightarrow 0 / \%$
1.0	93
2.0	85
3.0	56
0.45	(85)

The effect of current density on  $CE_{Zn}$ . The experiment was performed in 2 M  $ZnSO_4$ , 2 M  $H_2SO_4$ ,  $250\text{ mg dm}^{-3}$  Cu (II) ions,  $5\text{ g dm}^{-3}$  HMT, and the results are presented in Fig. 7 and Table IV.

The increase of current density correspondingly increases the  $CE_{Zn}$  at  $t \rightarrow 0$ , as well as after the dendrites' detachment and dissolution.

The effect of HMT concentration on  $CE_{Zn}$ . This experiment was performed in 2 M  $ZnSO_4$ , 2 M  $H_2SO_4$ ,  $250\text{ mg dm}^{-3}$  Cu(II) ions, at  $4.25\text{ mA dm}^{-2}$ . Results are shown in Fig. 8 and Table V.

The addition of HMT prolongs the induction period before the initiation of dendritic growth almost independently of the added amount, but lowers the  $CE_{Zn}$  at  $t \rightarrow 0$ , probably due to the formation of complexes with Zn (II) and/or Cu (II) ions. Immediately after the breakage of dendrites,  $CE_{Zn}$  increases with the concentration of added HMT.

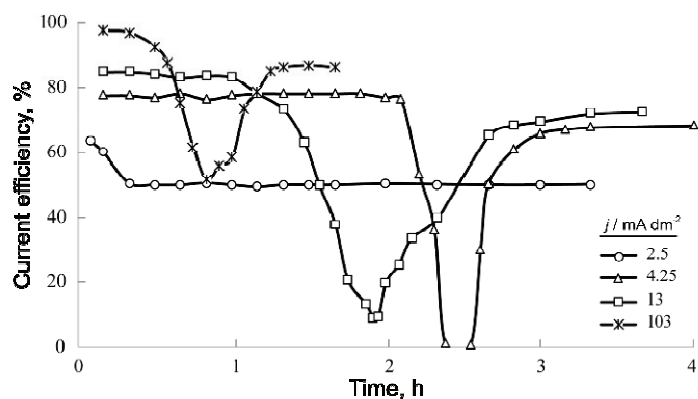


Fig. 7.  $CE_{Zn}$  from 2 M  $ZnSO_4$  + 2 M  $H_2SO_4$  + 250 mg  $dm^{-3}$   $Cu(II)$  ions + 5g  $dm^{-3}$  HMT at 2.5, 4.25, 13 and 103  $mA\ dm^{-2}$ , respectively.

TABLE IV. Effect of the current density on  $CE_{Zn}$

$j / mA\ dm^{-2}$	$CE_{Zn}$ at $t \rightarrow 0$ , %	Time of max. $H_2$ evolution, h	$CE_{Zn}$ after dendrites detachment, %
2.5	63	?	(50)
4.25	77	2.45	68
13	86	1.83	74
103	98	0.83	88

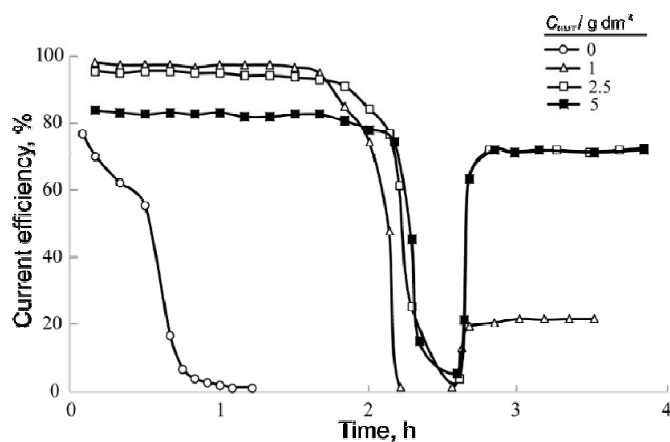


Fig. 8.  $CE_{Zn}$  from 2M  $ZnSO_4$  + 2M  $H_2SO_4$  + 250 mg  $dm^{-3}$   $Cu(II)$  at 4.25  $mA\ dm^{-2}$  with 0, 1, 2.5 and 5  $g\ dm^{-3}$  HMT, respectively.

TABLE V. Effect of HMT concentration on  $CE_{Zn}$

$C_{HMT} / g\ dm^{-3}$	$CE_{Zn}$ at $t \rightarrow 0$ , %	$CE_{Zn}$ after dendrites detachment, %
0	78	—
1.0	98	23
2.5	96	56
5.0	83	73



*The effect of HMT addition in extremely low or extremely high concentrations.* This experiment was done in the presence of 1 M ZnSO<sub>4</sub>, 1 M H<sub>2</sub>SO<sub>4</sub>, 318 mg dm<sup>-3</sup> Cu (II) ions, at 103 mA dm<sup>-2</sup> and the results are shown in Fig. 9.

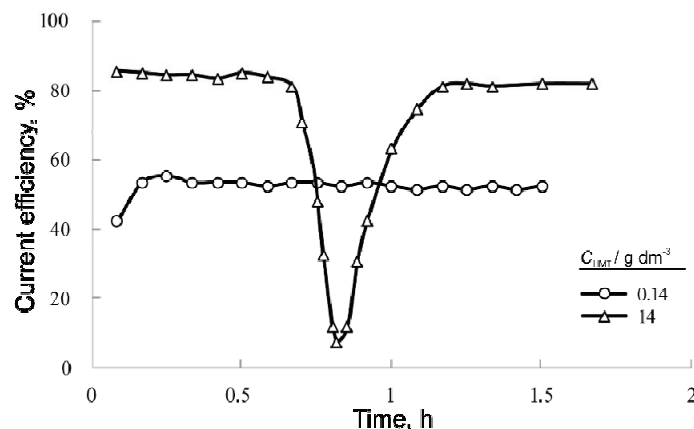


Fig. 9.  $CE_{Zn}$  from 1M ZnSO<sub>4</sub> + 1M H<sub>2</sub>SO<sub>4</sub> + 318 mg dm<sup>-3</sup> Cu (II) at 103 mA dm<sup>-2</sup>, with 0.14 and 14 g dm<sup>-3</sup> HMT, respectively.

With 0.14 g dm<sup>-3</sup> HMT the induction period before the initiation of dendritic growth lasts only 50 min, probably because there was not enough HMT to completely block the harmful action of Cu (II) ions added in concentration as high as 318 mg dm<sup>-2</sup>.

With a 100 times higher HMT concentration,  $CE_{Zn}$  varies only a bit around the 50 % all over the electrolysis duration. There is no dendritic growth, and thus no dendrite detachment. The electrode surface is probably covered with a thick layer of adsorbed HMT that prevents the dendrite precursor's protrusion during the whole 90-min deposition. Black zinc powder can be deposited as slurry, but it can also be easily removed.

#### *Resolution of resultant current efficiency curve to component curves*

In order to resolve the simultaneous zinc and copper deposition and hydrogen coevolution from 2 M ZnSO<sub>4</sub>, 2 M H<sub>2</sub>SO<sub>4</sub>, 250 mg dm<sup>-3</sup> Cu (II) ions, 5 g dm<sup>-3</sup> HMT, at 4.25 mA dm<sup>-2</sup>,  $CE_{Zn}$  was measured during a test where Cu (II) ions were deposited in limiting current conditions, making the resolution of the 3 processes feasible, as shown in Fig. 10.

#### *Derivation of integral equation for the duration of dendrites growth as influenced by the electrolysis parameters*

An example of further treatment of the acquired results is given in Fig. 11.

A plot of  $\log C_{Cu(II)}$  vs.  $t$  in Fig. 11 is linear and is expressed with:

$$t = -1.75 - 1.5 \log C_{Cu(II)} \quad (3)$$

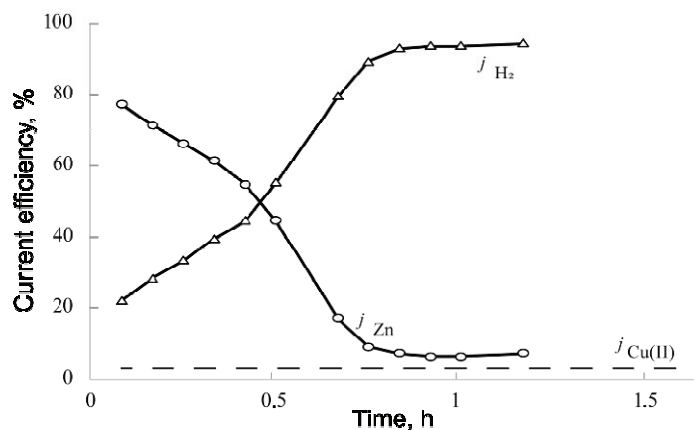


Fig. 10. Resolution of 3 electrode reactions that take place during zinc electrodeposition in presence of Cu(II) ions and HMT additives.

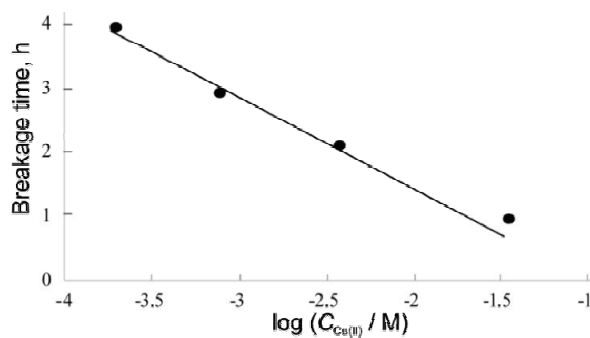


Fig. 11. Plot of  $\log(C_{\text{Cu(II)}} / \text{M})$  vs.  $t$  (see Table I).

A similar procedure was applied for the other 4 parameters and the resulting equations are given in Table VI, along with the values of parameters that were kept constant throughout the testing.

TABLE VI. The effect of the individual electrolysis parameters on the duration of dendrites life

One parameter equation	No.	$C_{\text{ZnSO}_4} / \text{M}$	$C_{\text{H}_2\text{SO}_4} / \text{M}$	$C_{\text{Cu(II)}} / \text{mM}$	$j / \text{mA dm}^{-2}$	$C_{\text{HMT}} / \text{mM}$
$t = 1 + 1.25 \log C_{\text{Zn(II)}}$	(I)	Variable	0.41	3.93	13	35.7
$t = 1.65 + 0.75 \log C_{\text{H}_2\text{SO}_4}$	(II)	2	Variable	3.93	13	35.7
$t = -1.75 - 1.5 \log C_{\text{Cu(II)}}$	(III)	2	2	Variable	13	35.7
$t = 3 - \log j$	(IV)	2	2	3.93	Variable	35.7
$t = 2.234 + 4.65 C_{\text{HMT}}$	(V)	2	2	3.93	4.25	Variable

Eqs. (I)–(IV) from Table VI are of logarithmic type and could be represented as a unique one, of general type, *i.e.*:

$$t = A + r \log C_{\text{Zn(II)}} + m \log C_{\text{H}_2\text{SO}_4} - n \log C_{\text{Cu(II)}} - p \log j \quad (4)$$

or:

$$t = A + \log \frac{C_{\text{Zn(II)}}^r C_{\text{H}_2\text{SO}_4}^m}{C_{\text{Cu(II)}}^n j^p} \quad (5)$$

Eqs. (I)–(IV) incorporated in Eq. (3):

$$t = -1.27 + \log \frac{C_{\text{Zn(II)}}^{1.25} C_{\text{H}_2\text{SO}_4}^{0.75}}{C_{\text{Cu(II)}}^{1.5} j} \quad (6)$$

or, if Eq. (V) from Table VI is included as well, the final form of Eq. (3) becomes:

$$t = -1.27 + 4.65 C_{\text{HMT}} + \log \frac{C_{\text{Zn(II)}}^{1.25} C_{\text{H}_2\text{SO}_4}^{0.75}}{C_{\text{Cu(II)}}^{1.5} j} \quad (7)$$

This expression condenses the effect of all the electrolysis parameters on the dendrites life duration. A comparison of measured *vs.* values calculated with the Eq. (7) is given in Table VII.

TABLE VII. Comparison of measured and calculated values of dendrites growth duration

No.	$C_{\text{ZnSO}_4}$ M	$C_{\text{H}_2\text{SO}_4}$ M	$C_{\text{Cu(II)}}$ mM	$j$ mA dm <sup>-2</sup>	$C_{\text{HMT}}$ mM	Dendrite's lifetime, h		Discrepancy %
						Measured	Calculated	
1.	2.0	2.04	0.786	13.00	35.70	2.93	2.95	0.68
2.	2.0	2.04	0.786	4.25	35.70	3.38	3.42	1.20
3.	2.0	2.04	0.393	13.00	35.70	1.64	1.67	1.82
4.	2.0	2.04	0.393	13.00	35.70	1.87	1.82	-2.70
5.	2.0	2.04	0.393	13.00	35.70	2.00	2.02	1.00
6.	2.0	2.04	0.157	13.00	35.70	3.94	3.97	0.76
7.	2.0	2.04	0.393	4.25	7.14	2.26	2.20	-2.70
8.	2.0	2.04	0.393	4.25	1.78	2.31	2.32	0.40
9.	2.0	0.41	0.393	13.00	35.70	1.36	1.35	-0.74
10.	1.0	0.41	0.393	13.00	35.70	1.00	0.97	-3.00
11.	0.5	0.41	0.393	13.00	35.70	0.59	0.60	1.70

Derivation of the equation that determines the duration of dendrites' life based on the values of all 5 relevant electrolysis parameters is a great achievement. The exactness of calculation falls within  $\pm 3\%$  of the measured span and this is as well a quality of this study.

The pointed highlights do result as a coincidence due to many factors:

– The quality of the applied measuring technique is the first one. Bubble counting is an exact, sensitive and reproducible method, as confirmed in its previous application.<sup>15,17</sup>

– Applied experimental conditions are beneficial as well, especially the intensive stirring that provides constant supply of reacting ions, reduces the diffusion layer thickness and removes the hydrogen bubbles, thus preventing the blockage of the cathode's surface. Maintaining a constant centrifugal force against the formed 3D dendrites is also a factor that contributes to the regularity of dendrites detachment.

– Proper choice of the span of applied concentrations and current density is also of help.

– Finally, the applied treatment of the experimental results that led to the derivation of the comprehensive equation is also a quality of this study.

This procedure may be beneficial in modeling the zinc electrolysis conditions and tailor the dendrite life duration and the product quality even in the presence of a higher level of impurities.

#### CONCLUSIONS

Regular zinc dendrites' growth during electrolysis from acid zinc solutions in presence of copper ions as an impurity and hexamethylenetetramine as surfactant is rare phenomenon that deserves attention.

The dendrite life  $t$  is expressed by the unified Eq. (6) with five electrolysis parameters, *i.e.*, the total duration is determined by the concentration of electrolyte's components and the current density.

The dendrite's life is prolonged by increasing the hexamethylenetetramine, zinc (II) ions, and sulfuric acid concentrations, the former one being of dominant influence. The opposite is observed with the increasing copper (II) ions' concentration and the current density  $j$ . It is hard to explain the effect of these parameters in more detail, but it should be stressed that all exponents in the above logarithmic equation are multiples of 0.25, *i.e.*,  $1.25 = 0.25 \times 5$ ;  $0.75 = 0.25 \times 3$ ;  $1.5 = 0.25 \times 6$  and  $1.0 = 0.25 \times 4$ . Such a coincidence may be an indicator in further research.

The most important merit of this case study is the identification of strong zinc dendrites' growth regularity and the definition of multi-parameter electrolysis conditions that govern such a growth. The practical benefit of such a discovery is hard to predict now. It may be a negligible one, but it may also lead to new achievements, not only in the recent field, but in some others, maybe more significant ones, as well.

Such a bold forecast is based on the fact that the experimental research very seldom ends in results that obey multifactorial behavior, as the five-factorial in the present study.

They may open a wide front for further study of dendrites growth in other systems. In doing so, present results will be of an important significance. Zinc wining electrolysis process is precisely mastered in defined conditions so that it

rends pure metal. With an imaginative modification of process conditions, the same process becomes a generator of vivid structures that live, grow, collapse and so, again and again in many turns.

The consecutive repetition of the dendrites' growth and drop cycles identified in this study deserves to be further studied and clarified. The intrinsic mechanism of dendrite's induction, growth and end of life is as well yet to be clarified,<sup>6,10,16</sup> in order to better understand the discovered phenomenon of dendrites' well-organized evolution during zinc electrolysis in appropriate conditions. The eventual broader region of Zn dendrites' growth's strict regularity is not excluded.

## ИЗВОД

## ИЗУЗЕТНЕ ПРАВИЛНОСТИ РАСТА ДЕНДРИТА ЦИНКА У ОДГОВАРАЈУЋИМ УСЛОВИМА ЕЛЕКТРОЛИЗЕ

DIMITAR D. GRAMATIKOV<sup>1,2</sup> и SVETOMIR A. HADŽI JORDANOV<sup>1</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Skopje 1000, Republic of North Macedonia u <sup>2</sup>Faculty of Economy, Ss. Cyril and Methodius University, Skopje 1000, Republic of North Macedonia

Приказана је студија случаја раста дендрита током електролизе цинка у условима који то промовишу. Предмет главног интересовања био је како параметри електролизе утичу на животни век дендрита. Одабрани скуп параметара је обезбедио изненађујуће правилан раст дендрита, односно период од почетка електролизе до одвајања дендрита од катоде. Раст дендрита се наставио са смањењем искоришћења струје по цинку, а крај животног века се манифестовао интензивним издвајањем водоника услед корозије одвојеног депозита цинка у киселом електролиту. Тренутно искоришћење струје је успешно праћено техником бројања издвојених мехурова гаса, која је посебно развијена за кинетичка проучавања реакције коју прати издвајање гаса. Добијени резултати о животној веку дендрита били су довољно прецизни како би се лако објединило свих пет моноваријабилних зависности у један израз са пет променљивих величина. Израчунате вредности за животни век дендрита су се разликовале од измерених за само  $\pm 3\%$ ! Тиме је показано да предложена једначина тачно описује стварну природу дендритичног раста у примењеним условима: 0,5 до 2 М јона цинка(II), 0,41 до 3,06 М  $\text{H}_2\text{SO}_4$ , 10 до 2500  $\text{mg dm}^{-3}$  јона бакра (II), 0,14 до 14  $\text{g dm}^{-3}$  хексаметилентетрамина и 4,25 до 103  $\text{mA dm}^{-2}$  густине струје. Није искључено да се правилни раст Zn дендрита одиграва и у ширим распонима наведених параметара.

(Примљено 22. јануара, ревидирано 17. марта, прихваћено 26. марта 2022)

## REFERENCES

1. V. A. Ettl, B. V. Tilak, in *Electrochemical Processing, Comprehensive Treatise of Electrochemistry*, Vol. 2, J. O'M. Bockris, B. E. Conway, E. Yeager, R. E. White, Eds., Plenum Press, New York, 1981, p. 78 (ISBN 978-1-4684-3787-4)
2. D. M. Dražić, S. Hadži Jordanov, Z. Nagy, *Croat. Chem. Acta* **45** (1973) 199 (<https://hrcak.srce.hr/197061>)
3. K. I. Popov, S. S. Djokić, B. N. Grgur, *Fundamental aspects of electrometallurgy*, Kluwer Academic Publishers, New York, 2002, pp. 72, 95 (ISBN 0-306-47269-4)

4. S. Zečević, S. Gojković, B. Nikolić, *Electrochemical Engineering*, Faculty of Technology and Metallurgy, Belgrade, 2001 (in Serbian)
5. M. M. Jakšić, *Surf. Technol.* **24** (1985) 193 ([https://doi.org/10.1016/0376-4583\(85\)90071-8](https://doi.org/10.1016/0376-4583(85)90071-8))
6. I. Ivanov, *Hydrometallurgy* **72** (2004) 73 ([http://dx.doi.org/10.1016/S0304-386X\(03\)00129-4](http://dx.doi.org/10.1016/S0304-386X(03)00129-4))
7. A. R. Despić, J. W. Diggle, J. O'M. Bockris, *J. Electrochem. Soc.* **115** (1968) 507 (<https://doi.org/10.1149/1.2411297>)
8. D. R. Hamilton, *Electrochim. Acta* **8** (1963) 731 ([https://doi.org/10.1016/0013-4686\(63\)85018-5](https://doi.org/10.1016/0013-4686(63)85018-5))
9. A. Milchev, *Russ. J. Electrochem.* **44** (2008) 619 (<https://doi.org/10.1134/S1023193508060025>)
10. E. A. Rosenberg, *MSc. Thesis*, NTNU, 2017 (<http://hdl.handle.net/11250/2615762>)
11. D. D. Gramatikov, *MSc Thesis*, Faculty of Technology and MetallurgySkopje, 1979, p. 92 (in Macedonian)
12. S. Hadži Jordanov, *PhD Thesis*, Faculty of Technology and Metallurgy, Belgrade, 1973 (in Serbian)
13. S. Hadži Jordanov, D. M. Dražić, *Chem. Instrum.* **6** (1975) 107
14. S. Hadži Jordanov, J. Naumovski, in *Proceedings of Conference Corrosion and Corrosion protection '82*, Central Council of STU in Bulgaria, Varna, Bulgaria, 1982, p. 32
15. S. Hadži Jordanov, in *Proceedings of 7<sup>th</sup> International congress on metallic corrosion*, Rio de Janeiro, Brazil, 1978, p. 365
16. A. C. Scott, R. M. Pitblado, G. W. Barton, in *APCOM 87: Proceedings of the Twentieth International Symposium on the Application of Computers and Mathematics in the Mineral Industries*, Vol. 2, South African Institute of Mining and Metallurgy in association with the Council for Mineral Technology, Johannesburg, South Africa, 1987, p. 51
17. S. Hadži Jordanov, P. Paunović, *Electrolysis, Theory and Technology*, Faculty of Technology and Metallurgy, Skopje, 2008 (in Macedonian).