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Comparative studies of the electroreduction of zinc ions from gluconate solutions

Badania porównawcze katodowej redukcji jonów cynkowych z roztworów glukonianowych

Abstract

This study considers the role of chloride and sulphate anions in the cathodic reduction of zinc ions from gluconate solutions (chloride, sulphate, chloride-sulphate). Cyclic potentiodynamic and potentiostatic polarization measurements, as well as chronoamperometric experiments, were performed. Electrochemical results were correlated with the speciation of the baths. The experiments revealed the inhibiting effect of sulphate ions on the cathodic process caused by the formation of stable neutral $ZnSO_4$ complex in the sulphate-gluconate bath. It resulted in zinc deposition under a limiting current, with the release of metal cation as a rate-determining step. The less stable $ZnGlu^+$ complex dominated both chloride-containing baths, thus the metal deposition ran under activation control. Independent of the solution composition, the nucleation of zinc occurred according to the instantaneous model.

Keywords: electrodeposition, voltammetry, chronoamperometry, polarization, nucleation

Streszczenie

W artykule przedstawiono rolę anionów chlorkowych i siarczanowych w katodowej redukcji jonów cynku z roztworów glukonianowych (chlorkowy, siarczanowy, chlorkowo-siarczanowy). Przeprowadzono pomiary cyklicznej polaryzacji potencjodynamicznej i potencjostatycznej oraz eksperymenty chronoamperometryczne. Wyniki elektrochemiczne skorelowano ze składem jonowym roztworów. Eksperymenty wykazały hamujący wpływ jonów siarczanowych na proces katodowy w kąpieli siarczanowo-glukonianowej spowodowany tworzeniem się stabilnego obojętnego kompleksu $ZnSO_4$. W rezultacie, w elektrolicie siarczanowym osadzanie cynku zachodziło w warunkach prądu granicznego, a etapem powolnym było uwalnianie jonu metalu z kompleksu. W obecności jonów chlorkowych dominujący kompleks stanowił mniej trwały $ZnGlu^+$, a redukcja jonów cynku zachodziła w warunkach kontroli aktywacyjnej. Niezależnie od składu roztworu stwierdzono natychmiastowe zarodkowanie cynku.

Słowa kluczowe: osadzanie katodowe, woltamperometria, chronoamperometria, polaryzacja, nukleacja

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1. Introduction

Zinc has many industrial applications, being the fourth most common technical metal after iron, aluminum, and copper [1]. It is estimated that every year, 50–60% of global production of metallic zinc is consumed to protect iron and steel against corrosion. The first acidic and alkaline cyanide baths for zinc electrodeposition were patented in the second half of 19th century, but they were rather hard to operate [2]. Today, due to restrictive environmental regulations, non-cyanide and low-cyanide baths have been investigated and implemented for industrial zinc plating [3, 4]. Moreover, chloride and sulphate acid, mild acidic and alkaline zincate baths have been intensively developed as "green" electrolytes.

Gluconate solutions belong to the latter group of plating baths. They contain sodium gluconate as a cheap and biologically safe additive. The compound is characterized by good buffering properties and can form soluble complexes with many metal cations in both acidic and alkaline electrolytes [5–8]. Despite the fact that a gluconate-based zinc plating solution was established fifty years ago [9], up to date only a few more papers on the zinc electrodeposition from sulphate-gluconate baths were published [10–15]. Therefore, the aim of this paper was to develop knowledge about zinc-gluconate electrolytes and electrochemical reduction of metal ions by showing the different behaviour of the system depending on the presence of chloride or sulphate anions. Such a simple modification to electrolyte composition further affects metal nucleation and deposit characteristics.

2. Experiment

Electrodeposition of zinc was carried out from three solutions containing 0.25 M Zn^{2+} (as $ZnCl_2$ or/and $ZnSO_4$; $ZnCl_2$:$ZnSO_4$ in 1:1 molar ratio), 0.25 M boric acid H_3BO_3 as a buffering component, and 0.25 M sodium gluconate $C_6H_{11}O_7Na$ as a complexing agent. For comparative purposes, 0.5 M zinc salt solutions (with no change to the other component concentrations) were used. The pH of all baths was 6.0.

Electrochemical measurements were carried out in a three-electrode cell using glassy carbon (GC) working electrode (0.196 cm^2), a platinum plate (2 cm^2) as a counter electrode and an Ag/AgCl electrode as a reference electrode (all potentials in the further text are referred to this electrode). Cyclic voltammetry was realized at a sweep rate of 10 mV/s with a forward scan towards more negative potentials. Potentiostatic polarization curves were calculated from the data of potentiostatic zinc deposition (60 min) performed in the same electrochemical cell, but with copper plates (0.44 cm^2) as the cathode substrates. Chronoamperometric measurements were performed on the GC electrode for 40 s at selected constant potentials. Before each experiment, the glassy carbon electrode with a mirror finish was chemically cleaned, while copper sheets were chemically polished in a mixture of concentrated acids (HNO_3:H_3PO_4:CH_3COOH with 1:3:1 volume ratio). All electrochemical experiments were performed at ambient temperature using an Autolab potentiostat / galvanostat (PGSTAT30) and non-agitated solutions with a volume of 20 cm^3.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetric (CV) measurements were realized on a glassy carbon electrode due to the wide "potential window", where the initial stages of the electrochemical processes are not interrupted by electrochemically favored hydrogen evolution. Figure 1 shows the curves registered in the gluconate electrolytes containing zinc salts of various anions (chloride or sulphate) or a mixture of them (chloride-sulphate). Electrodeposition of zinc started at potentials below -1.1 V developing cathodic peak C_{Zn} at about -1.24 V. It was followed by a decrease in the cathodic currents caused by mass transport limitations and the formation of another cathodic peak C_H at about -1.45 V corresponding to hydrogen evolution. During the reverse scan, single anodic peaks with maxima in the potential range from -0.8 V to -0.6 V were developed.
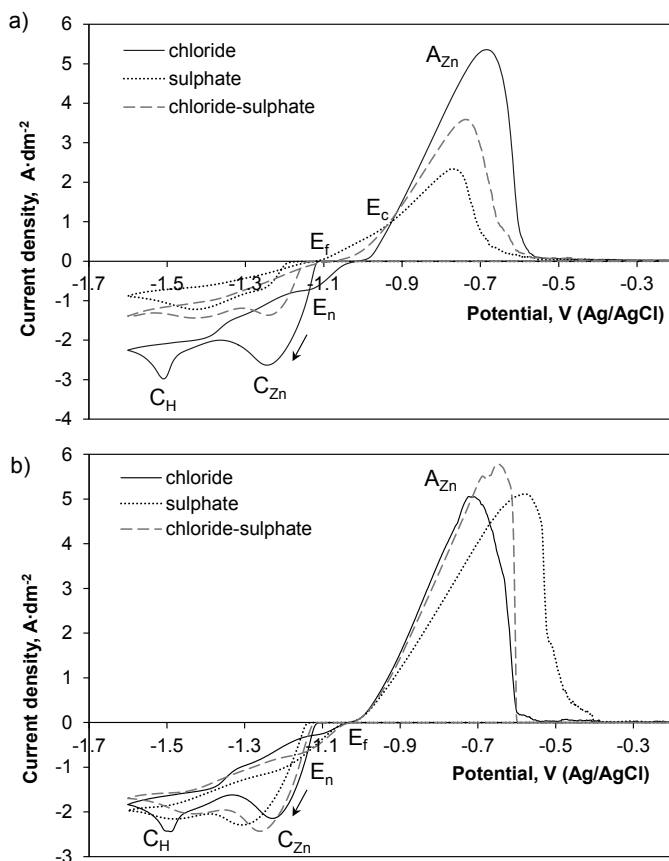

Fig. 1. CV curves registered in gluconate solutions: a) 0.25 M Zn(II); b) 0.5 M Zn(II)

The course of the CV curves was dependent on both the composition of the bath (the type of anions) and the concentration of zinc ions. Figure 2 shows the distribution of zinc species in the investigated solutions. It was calculated using Hyss software and complex stability constants adopted from the UPAC database [8]. Independent of total zinc content in the aqueous solutions, two complexes are dominant. These are positively charged zinc-gluconate complex $ZnGlu^+$ ($K = 50$) and neutral $ZnSO_4$ complex ($K = 199$). $ZnGlu^+$ is the main species in the chloride bath, while $ZnSO_4$ prevails in the sulphate bath. The type of the main complex in the chloride-sulphate bath is affected by the total concentration of zinc ions.
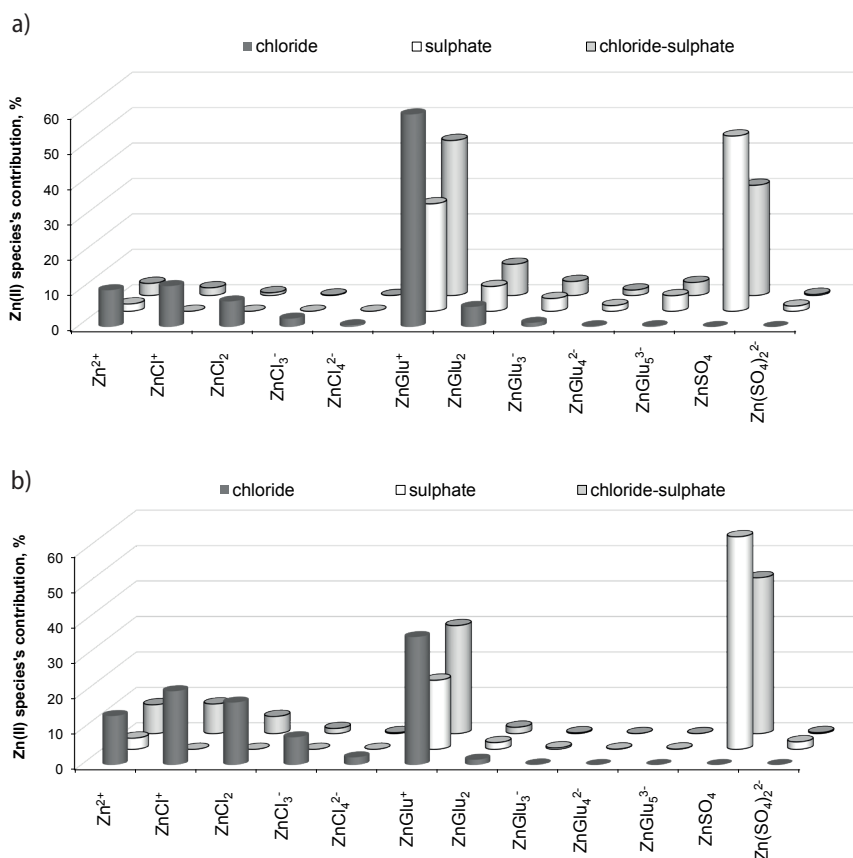

Fig. 2. Distribution of zinc species in gluconate solutions: a) 0.25 M Zn(II); b) 0.5 M Zn(II)

A comparison of the CV curves and the bath speciations shows the significant influence of the latter on the zinc deposition from more diluted solutions, while the course of the curves is practically the same for 0.5 M Zn(II). Moreover, the increase in the total zinc concentration enhanced the deposition of zinc from sulphate-containing baths, but not

from the chloride solution. Detailed analysis has shown that the main factor governing the electroreduction of zinc ions is the concentration of free Zn^{2+}. It was found that the concentrations of uncomplexed Zn^{2+} ions in 0.25 M solutions were $2.6 \cdot 10^{-2}$ M, $8.6 \cdot 10^{-3}$ M and $5.2 \cdot 10^{-3}$ M in the chloride, chloride-sulphate and sulphate solution, respectively. For higher total zinc concentrations, the amounts of free Zn^{2+} ions were almost at the same level, i.e. 10^{-2} M. This was very well correlated with the cathodic currents (Fig. 1). These increased in the order for the chloride, chloride-sulphate and sulphate baths with 0.25 M Zn(II), while no changes in the cathodic currents were observed for all 0.5 M Zn(II) solutions.

During the reverse scan, two or three characteristic crossovers between the branches for the negative and positive sweeps were observed. At more negative potentials, nucleation potentials E_n (i.e. crossover potential at the nucleation loop) were found. Nucleation potential is associated with an electrocatalytic point and is diagnostic for the nuclei formation on the electrode [16]. Second crossover potentials E_f appeared at higher values (approx. −1.0 V for 0.5 M Zn(II) or a little more negative for 0.25 M Zn(II)). These values were related to the formal potentials of the metal electrode. According to the simplified Nernst equation, where molar concentration instead of activity of species was substituted, the equilibrium potential of the zinc electrode can be written as follows:

$$E_{o,Zn/Zn^{2+}} = E^o_{Zn/Zn^{2+}} + \frac{2.3RT}{2F} \log c_{Zn^{2+}} \tag{1}$$

where:

$E_{o,Zn/Zn^{2+}}$ – standard potential of the Zn/Zn^{2+} electrode (−0.762 V vs. SHE),
 R – gas constant (8.31 J/mol·K),
 T – temperature (298 K),
 F – Faraday's constant (96,500 C/mol),
 $c_{Zn^{2+}}$ – concentration of free Zn^{2+} ions in the solution.

The equilibrium potentials of the zinc electrode were then calculated for the equilibrium concentrations of uncomplexed zinc cations. The obtained results were −1.03 ± 0.02 V (vs. Ag/AgCl) and were in agreement with the experimental results.

The cathodic currents recorded between the nucleation potential E_n and the equilibrium potential E_f were higher for the reverse sweep than for the forward sweep in all systems. This is obvious, since the energy required for the zinc overpotential deposition on the glassy carbon substrate is higher than that for the metal deposition on the native zinc layer formed during the previous scan [16].

An interesting effect was observed on the anodic branches of the CV curves for the 0.25 M zinc solutions (Fig. 1a). The previously deposited metal dissolved faster in the sulphate and chloride-sulphate solutions during anodic process running in a potential range from E_f to the third crossover potential E_c. The E_c potential of −0.93 V was the same for all solutions. Such behaviour was not observed for more concentrated electrolytes.

It is believed that the formation of ZnSO$_4$ complexes (being more stable than ZnGlu$^+$ in the chloride-sulphate bath) facilitates the dissolution of the metal for potentials up to E$_c$, but then the development of the anodic peak A$_{Zn}$ is governed by the amount of the previously deposited zinc. This effect was not as emphatic at higher Zn(II) concentrations, due to the fact that there were no differences in the concentrations of both free Zn^{2+} ions (10^{-2} M) and ZnSO$_4$ complex (10^{-1} M) in both sulphate-containing solutions. However, in this case, another phenomenon was observed, related to the development of anodic peak A$_{Zn}$. The maximum of the anodic peak was at about −0.72 V in the chloride bath, it was shifted to −0.55 V in the sulphate bath, while a not very well-defined double peak was developed in the intermediate potential range for the chloride-sulphate bath. This shows that the anodic dissolution of zinc is directly related to the formation zinc complexes. Thus, it is assumed that the following reaction:

$$Zn + Glu^- \rightarrow ZnGlu^+ + 2e \qquad (2)$$

takes place at less positive potentials, while at more positive potentials zinc oxidation occurs via:

$$Zn + SO_4^{2-} \rightarrow ZnSO_4 + 2e \qquad (3)$$

The observed behaviour is opposite to the statement reported for sulphate-gluconate solutions by Torrent-Burguès and Guaus [11]. They investigated the electroreduction of zinc ions (0.01 M) on a glassy carbon electrode and found double reduction peaks during voltammetric studies associated with a competition in the complexing action of zinc ions by sulphate and gluconate anions. In the anodic scan, the principal oxidation peak also appeared as a double peak. As the first anodic peak was situated at a potential similar to that in the absence of gluconate, this peak was assigned to oxidation via sulphate anion complexation, while the second peak (at more positive potential) to the zinc oxidation via gluconate anion complexation. In turn, Esfahani et al. [11] found single cathodic and anodic responses during cyclic voltammetry in sulphate and sulphate-gluconate solutions. They observed zinc deposition at slightly more positive potentials (−1.08 V vs. Ag/AgCl) and zinc dissolution at more negative potentials (−0.7 V vs. Ag/AgCl) in the presence of gluconate in a comparison with pure zinc sulphate baths. Such a phenomenon may confirm the conclusions of the present work.

3.2. Potentiostatic polarization curves

Electrodeposition of zinc was performed at various cathodic potentials. Figure 3 shows partial polarization curves calculated from the experimental data, i.e. zinc mass gain m_{Zn} and total electric charge flowed through the circuit during electrolysis.

Partial current densities were calculated as follows:

$$i_{Zn} = \frac{m_{Zn}}{k_{Zn} t S} \qquad (4)$$

$$i_{H_2} = i_{total} - i_{Zn} \qquad (5)$$

where:

t – electrolysis time,
i – current density,
k_{Zn} – zinc electrochemical equivalent,
S – cathode surface area.

The course of the potentiostatic polarization curves, as well as the range of cathodic current densities, is quite different from the potentiodynamic cathodic branches (Fig. 1a) due to a change in the electrolysis conditions (static versus dynamic). This enables deeper analysis of the cathodic process. It was found that the presence of chloride ions enhances the electroreduction of zinc ions as it was started already at −1.1 V (Fig. 3 a, c). In turn, the cathodic process was initiated at more negative potentials as well as being inhibited in the sulphate bath (Fig. 3b). The latter was revealed by the reduction of the zinc ions under limiting current (of about −1.3 A/dm²) in a potential range from −1.4 V to −1.8 V. Such behaviour was related to a release of Zn^{2+} cation from $ZnSO_4$ complex as a rate-determining step of the cathodic reaction. At more negative potential, the deposit's morphology was seriously changed and the formation of columnar structures, being new areas for metal growth, was observed.

In turn, in both chloride-containing electrolytes, the zinc partial polarization curves indicated charge-transfer as a rate-determining step. Analysis of the polarization curves in terms of Tafel plots (insets in Figures 3 a, c) indicated linear dependences of the activation overvoltage η on the current density i:

$$\eta = E_i - E_0 = a + b \log i \qquad (6)$$

For the cathodic reaction, Equation (6) is defined by more specific form:

$$\eta_c = \frac{2.3RT}{\alpha_C zF} \log i_0 - \frac{2.3RT}{\alpha_C zF} \log i \qquad (7)$$

where:

i_0 – exchange current density,
α_C – symmetry factor of energy barrier for cathodic reaction,
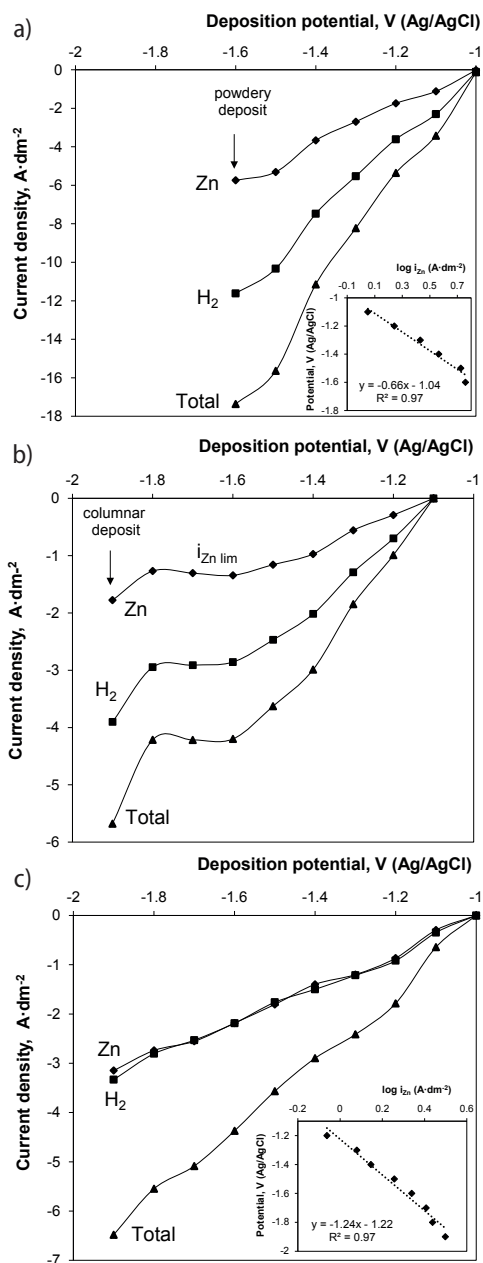R – gaseous constant,
T – temperature.

Fig. 3. Potentiostatic polarization curves registered in 0.25M zinc-gluconate solutions: a) chloride; b) sulphate; c) chloride-sulphate

The slopes of the straight lines were −0.66 V/dec and −1.24 V/dec for the chloride and chloride-sulphate bath, respectively. Symmetry factors for the energy barrier were

then calculated, giving the values: 0.02 and 0.04 for the corresponding solutions. The obtained results confirm the inhibiting effect of the sulphate ions on the reduction of zinc ions as α_C was twice as high as in the chloride bath.

Finally, it is worth noting that the total cathodic current was characterized by the rather high contribution made by hydrogen co-evolution, despite the fact that the pH of the solutions was quite close to neutral. This additionally suggests that the formation of zinc complexes somewhat inhibits the reduction of zinc ions.

3.3. Chronoamperometry

The electrodeposition of metals on a foreign substrate is initiated by the creation of nuclei. Their growth is followed by overlapping to form a continuous deposit. To show the influence of chloride and sulphate ions on the initial stages of the zinc deposition the chronoamperometric measurements were performed. Figure 4 shows current-time transients (left side) and their analysis (right side) in terms of a model developed for three--dimensional nucleation and growth process running under mass transfer control [16]. The increase in the cathodic current on the *i-t* curves corresponds to a growth of the individual zinc nuclei and/or an increase in a number of nuclei, where the transport of the electroactive species to the growing centers occurs through hemispherical diffusion zones formed around a particular nucleus. The maximum cathodic current is related to the moment at which hemispherical metal nuclei are at the point of collision. It is then followed by the falling of the current due to mass transport limitations. The height of the cathodic peaks is clearly dependent on the bath's composition, thus at the same deposition potential the current reached maximal values quite proportionally to the concentration of sulphate species. It confirms previous statements on the inhibiting effect of this anion.

Theoretical models of the metal nucleation describe the formation of nuclei by either a progressive or instantaneous mode. A classification of the nucleation is often realized by a comparison of the experimental results with theoretical predictions plotted in a dimensionless form. During instantaneous nucleation, all nuclei are produced at the same time and they grow further with the same rate. Under these conditions, the following diagnostic equation is fulfilled:

$$\left(\frac{I}{I_{max}}\right)^2 = \frac{1.9542}{\frac{t}{t_{max}}}\left[1-\exp\left(-1.2564\frac{t}{t_{max}}\right)\right]^2 \tag{8}$$

In turn, during progressive nucleation, the nuclei are formed constantly and they grow to different sizes and/or at different rates. In such cases, the following expression is fitted:

$$\left(\frac{I}{I_{max}}\right)^2 = \frac{1.2254}{\frac{t}{t_{max}}}\left[1-\exp\left(-2.3367\left[\frac{t}{t_{max}}\right]^2\right)\right]^2 \tag{9}$$

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Non-dimensional plots for the instantaneous and progressive nucleation models shown in Figure 4 (right side) indicate the formation of zinc deposits according to the instantaneous nucleation model. However, some deviations of the experimental and theoretical curves was observed in the sulphate bath at $t/t_{max} > 3$. The results once more indicate the specific behaviour of this system originating from the presence of the $ZnSO_4$ complex and the inhibition of the metal growth due to complex decomposition as the rate-determining step. Such action was not observed in the remaining solutions as the source of electroactive zinc ions was a labile $ZnGlu^+$ complex.
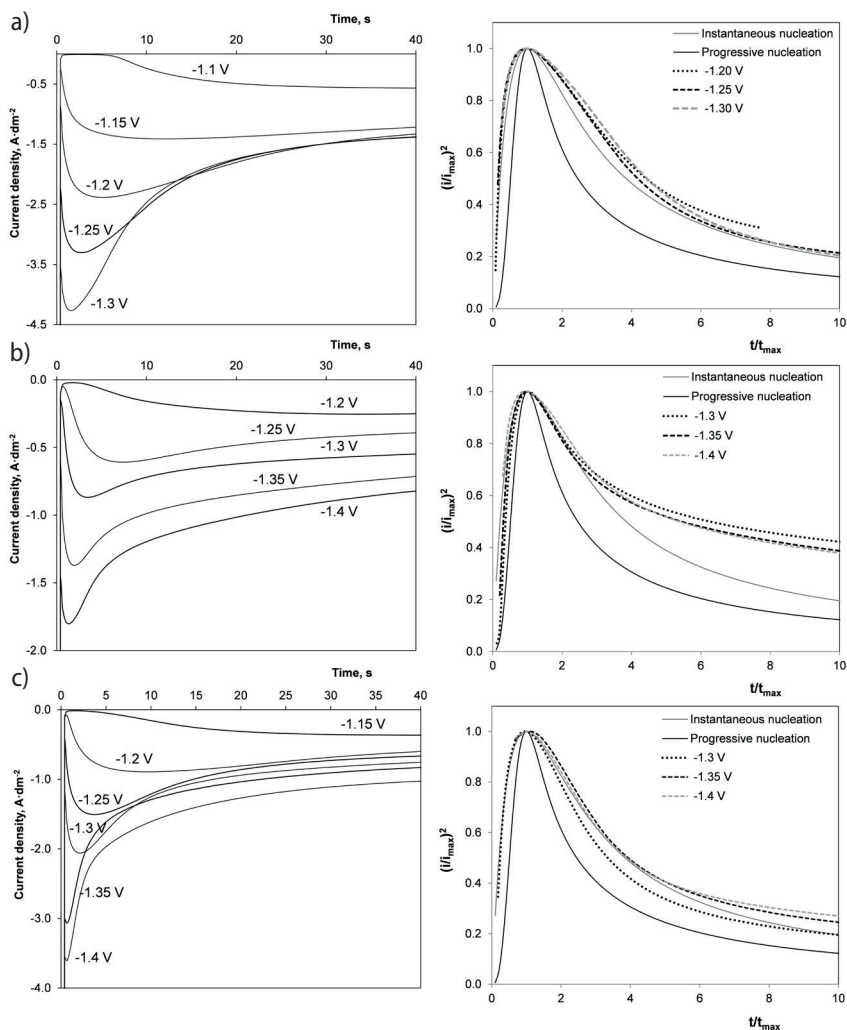

Fig. 4. Chronoamperometric curves and corresponding model curves registered in 0.25M zinc--gluconate solutions: a) chloride; b) sulphate; c) chloride-sulphate

For instantaneous nucleation with diffusion limited growth, the current and time maxima are given by the following expressions [16]:

$$i_{max} = 0.6382zFDc\left(kN_0\right)^{\frac{1}{2}}$$ (10)

and

$$t_{max} = \frac{1.2564}{N_0\pi kD}$$ (11)

where:

D – diffusion coefficient of electroactive species,
c – concentration of metal ions,
N_0 – number density of active sites,
$k = (8\pi cM/\rho)^{1/2}$,
M – molar mass of deposited metal,
ρ – density of metal (7.134 g·cm^{-3}).

The above equations can then be combined to calculate the nucleus density:

$$N_0 = 0.065k^{-\frac{1}{2}}\left(\frac{zFc}{t_{max}i_{max}}\right)^2$$ (12)

Further considerations allow us to determine the diffusion coefficient, which is described in the following way for the instantaneous nucleation:

$$D = \frac{i_{max}^2 t_{max}}{0.1629\left(zFc\right)^2}$$ (13)

Values of i_{max}, t_{max}, N_0 and D at different potentials for various baths are summarized in Table 1. It is evident that with more electronegative potential the current maximum increases and shifts towards shorter times. This is typical for three dimensional nucleation and the growth of a new phase under diffusion control. The number density of active nucleation sites is about 10^5 cm^{-2}, but it increases in the presence of sulphate ions. This is in good agreement with partial polarization curves, which show the inhibition of the hydrogen evolution in both sulphate-containing electrolytes. This favors the formation of the metal instead of the loss of the electric current in the parallel reaction. The average diffusion coefficients of zinc species are 10^{-6} cm^2·s^{-1} and are smaller in the sulphate solution. It is in accordance with the speciation of the baths, as a neutral $ZnSO_4$ complex is less willingly transported towards a negative cathode than a positively charged $ZnGlu^+$ complex.

Table 1. Values characteristic for instantaneous nucleation of zinc from gluconate baths

Bath	Potential [V]	$-i_{max}$ [A·dm^{-2}]	t_{max} [s]	N_0 [cm^{-2}]	D [cm^2·s^{-1}]
Chloride	−1.20	2.385	5.2	0.20·10^5	7.8·10^{-6}
	−1.25	3.303	2.8	0.36·10^5	8.0·10^{-6}
	−1.30	4.266	1.6	0.66·10^5	7.7·10^{-6}
Sulphate	−1.30	0.868	3.4	3.55·10^5	6.7·10^{-7}
	−1.35	1.371	2.0	4.11·10^5	9.9·10^{-7}
	−1.40	1.801	1.4	4.86·10^5	1.2·10^{-6}
Chloride-sulphate	−1.30	2.060	2.2	1.50·10^5	2.5·10^{-6}
	−1.35	3.065	0.6	9.14·10^5	1.5·10^{-6}
	−1.40	3.611	0.6	6.58·10^5	2.1·10^{-6}

4. Conclusions

The influence of chloride and sulphate anions on the cathodic reduction of zinc ions from gluconate solutions was investigated. Cyclic voltamperometry, potentiostatic polarization measurements and chronoamperometric experiments correlated with the speciation of the baths revealed the inhibiting effect of sulphate ions. It originated from the formation of a stable neutral $ZnSO_4$ complex in the sulphate-gluconate bath and the release of zinc ions from the complex as a rate-determining step. In turn, a less stable $ZnGlu^+$ complex predominated in both chloride-containing solutions. It resulted in zinc deposition under activation control. Independently of the solution composition, the nucleation of zinc occurred according to the instantaneous model with an average number of nucleation active sites of 10^5 cm^{-2}.

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