

METHODOLOGICAL ASPECTS FOR THE STUDY OF NUCLEATION AND GROWTH MECHANISMS OF METALS FROM DEEP EUTECTIC SOLVENTS BASED ON CHOLINE CHLORIDE

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Abstract. This paper presents a methodology for studying nucleation and growth mechanisms of metals onto a glassy carbon electrode in a deep eutectic solvent (DES), a mixture of choline chloride and urea at a molar ratio of 1:2. Characteristics and composition of Co(II) complexes formed with the DES were evaluated by means of UV-vis measurements, which confirmed the good stability of these species at room temperature. To elucidate the methodology, kinetic and mechanistic aspects of the early stage of cobalt electrodeposition were studied using cyclic voltammetry and chronoamperometry onto glassy carbon electrode from the DES. From the voltammetric study, typical reduction and oxidation stages were identified. From the behavior of experimental current density transients, it was found that the Co electrodeposition could be described by a model comprising Co three-dimensional nucleation and diffusion-controlled growth taking into account the induction – time. The diffusion coefficient of cobalt ions in DES was determined by two methods: cyclic voltammetry and kinetic parameters obtained from model fitting. Moreover, the dimensionless analyses of the experimental current density transients have shown the dominance of progressive nucleation type during the electrodeposition of cobalt. Characterization techniques such as scanning electron microscopy, energy-dispersive X-ray spectroscopy, and elements mapping were used to verify the presence and the nucleation type of cobalt onto the glassy carbon electrode surface, showing a good agreement with the prediction made from the proposed model. This also corroborates the feasibility of the proposed methodology for studying the electronucleation of metals.

Keywords: electronucleation and growth, physical-mathematical model, deep eutectic solvent.

Classification numbers: 2.2.1, 2.5.3, 3.7.1.

1. INTRODUCTION

Electrodeposition is a well-established method to obtain metals from an aqueous solution [1]. Using this principle, electrowinning has become a widely used technology in the modern metal recovery and refining industry as well as wastewater treatment applications [2]. The most common metals obtained from electrowinning can be mentioned such as gold, silver, copper, lead, zinc, chromium, cobalt, nickel, manganese, etc. [3]. However, the electrolytic processes from aqueous media cause many technological problems, such as the liberation of hydrogen during electrodeposition, low stability due to evaporation, which hinders the metal electrodeposition efficiency and environmental concerns (toxic solutions, soil pollution, difficult waste treatment) [4]. Other metals, such as alkali metals (which react strongly with water), are commercially produced by electrolysis of their pyrochemical molten salts at high temperatures (about 450 - 600 °C) [5]. For aluminum, it is required even higher temperature, thus, the industrial production process is carried out at approximately 980 °C to electrolyze aluminum from alumina dissolved in molten cryolite (Na_3AlF_6) [6]. These high energy demands and the aforementioned limitations prompt researchers to search for novel “green” and “more economic” solvents to substitute the traditional electrodeposition process. Dealing with these problems, the deep eutectic solvent (DES) [7] has demonstrated useful for the electrodeposition of various metals and alloys such as Ni [8], Zn [9], Co [10, 11], Fe [12], Al [13], and Fe-Co [14]. It can be figured out that the nucleation and growth processes of metals are the key phenomena in the theory of phase transitions [15]. Future advances in the control of materials and processes at the nanoscale depend strongly on understanding the fundamental aspects of nucleation and growth such as thermodynamics and kinetics of nucleation, size distribution, and growth rate of nanoclusters since they determine the initial stages of the formation of nanomaterials and nanostructures [15]. In this regard, the use of electrochemical means such as cyclic voltammetry (CV) and chronoamperometry (CA) are highly convenient [10-15]. Although the theory of nucleation is widely publicized, the methodology of these phenomena seems to be limited, particularly in the case of electrodeposition of metals from the DES. Therefore, the purpose of this paper is to provide the methodological aspects on studying mechanisms and kinetics of the metal's electrodeposition onto glassy carbon from DES using CV and CA techniques. The use of physical-mathematical models to describe the nucleation and growth phenomena on the surface electrode is also presented.

2. MATERIALS AND METHODS

2.1. Materials

Choline chloride (99 %, Sigma Aldrich), urea (98.6 %, Sigma Aldrich), and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99 %, Sigma Aldrich) were used as received. The mixture of choline chloride and urea with a molar ratio of 1:2 was stirred with a magnetic stirrer at 100 °C in order to create reline DES. The electrolyte solution was obtained by adding 50 mM CoCl_2 to the DES and kept stirring with a magnetic stirrer for 12 hours at 50 °C.

2.2. Methods

The study of cobalt nucleation and growth mechanisms onto glassy carbon electrode (GCE) from DES was performed by CV and CA techniques under ambient conditions (25 °C, 1 atm). These experiments were carried out in an electrochemical cell (three electrodes) using a VersaSTAT Potentiostat/Galvanostat, coupled with the VersaStudio software installed in a PC for control and data collection. The used (electrochemical) cell consisted of a mirror-polished glassy carbon bar with a surface area of 0.0707 cm² as the working electrode, a platinum wire as the counter electrode, and a silver wire as quasi reference electrode. The GCE surface was characterized using a field emission SEM (FESEM JEOL 7000). The chemical composition and elemental mapping were obtained by EDS techniques of the SEM equipment. The measurements of UV-Vis spectra of the electrolytes with different Co(II) concentrations were performed in a UV-Vis spectrophotometer (UV-6850, JENWAY).

2.3. Methodological aspects

CV and CA are two common techniques for the study of the nucleation and growth of metals mechanism. While the CV can give important information related to the electrochemical processes occurring on the electrode surface such as the oxidation-reduction reactions, which are represented through the reduction-oxidation peaks, some kinetic parameters such as frequency of nucleation, A , and density number of active sites, N_0 , can be determined from the CA by fitting theoretical models to experimental data [16, 17]. Based on these techniques, some steps to follow for the study of electronucleation and growth of metals are:

2.3.1. Potentiodynamic study

- 1) Identification of different processes occurring in the CV: this step consists of performing a CV in the selected electrochemical system. According to the shape of CV, it can be divided into different regions from (1) to (5), as shown in Figure 1.
- 2) Determination of the nucleation region: Once the position of the reduction peak in the CV has been located, the nucleation region can be defined between E_0 (equilibrium potential) and $E_{nucleation}$ (it is the potential at which the current density starts to increase, that records the formation of metal's nuclei onto GCE), $E_{nucleation} < E_0$.
- 3) Determination of the diffusion-controlled region: This region is located at the potentials ranging between $E_{nucleation}$ and E_{peak} (massive electrodeposition), $E_0 < E_{nucleation}$, that records the crystallization or subsequent growth of metallic nuclei onto GCE surface and previously formed metallic nuclei, simultaneously.
- 4) Scan rate study: a series of CVs at different scan rates in the range from 5 to 100 mVs⁻¹ are usually performed. The current density of cathode peak (j_{cp}) will be plotted as a function of the square root of the scan rate ($v^{1/2}$) to check the agreement with Eq. (1), Randles – Sevcik equation [18]. If a linear behavior is fulfilled, it demonstrates that the metal electrodeposition process follows a diffusion-controlled mechanism [18].

$$j_{cp} = \frac{0.4463(nF)^{3/2}C_0D^{1/2}}{(RT)^{1/2}}v^{1/2} \quad (1)$$

where n is the total number of electrons transferred during the overall electrochemical process, C_0 (mol cm⁻³) is the reduced species bulk concentration, D (cm² s⁻¹) is the diffusion coefficient of metal ions.

- 5) Diffusion coefficient calculation: From Eq. (1), considering m as the slope of the ($j_{cp} - v^{1/2}$) plot, it yields,

$$D = \frac{m^2 RT}{0.1992 (nF)^3 C_0^2} \quad (2)$$

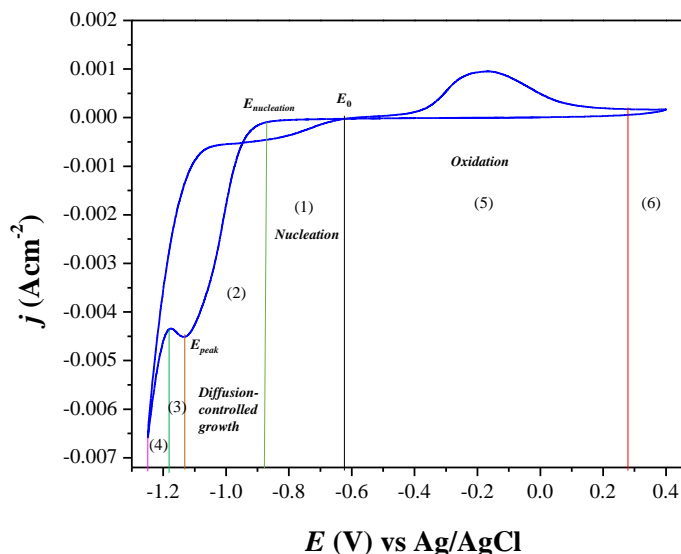


Figure 1. Illustration of different processes observed in a CV recorded in the system GCE/50 mM Co(II) DES. The potential scan started at -0.3 V in the negative direction with a scan rate of 80 mVs⁻¹.

2.3.2. Potentiostatic study

- 6) *Chronoamperometry*: From CV, one can see that to observe both nucleation and growth phenomena, different potentiostatic current density transients have to be measured using potentials from the region (1) to (2), see for example an experimental CA obtained in this potential range shown in Fig. 2.

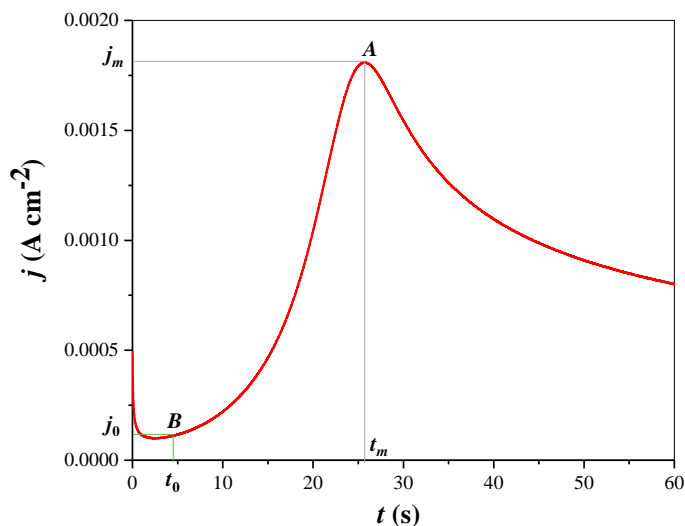


Figure 1. Illustration of an experimental CA recorded in the system GCE/50 mM Co(II) DES at -0.9 V.

- 7) *Dimensionless analysis*: from the experimental CA data, the maximum of current densities for each curve, $A(t_m, j_m)$, are determined (see Fig. 2) and normalized according to the theoretical models (Eq. (3) for instantaneous nucleation and Eq. (4) for progressive nucleation) proposed by Scharifker and Hills [16].

$$\left(\frac{j}{j_m}\right)^2 = 1.9542 \left(\frac{t}{t_m}\right)^{-1} \left(1 - \exp\left[-1.2564 \left(\frac{t}{t_m}\right)\right]\right)^2 \quad (3)$$

$$\left(\frac{j}{j_m}\right)^2 = 1.2254 \left(\frac{t}{t_m}\right)^{-1} \left(1 - \exp\left[-2.3367 \left(\frac{t}{t_m}\right)^2\right]\right)^2 \quad (4)$$

by plotting the normalized experimental CA together with plots obtained from theoretical models, Eq. (3) and (4), one can select which model can be used to describe the experimental data. Thus, if the normalized CA resides within the region generated by the theoretical curves, the three-dimensional nucleation and diffusion-controlled growth developed by Scharifker and Mostany (SM) [17] are appropriate. Then, the SM model is given as:

$$j(t)_{3D} = \frac{nFD^{\frac{1}{2}}C_0}{\pi^{\frac{1}{2}}} t^{-\frac{1}{2}} \left(1 - \exp\left\{-N_0\pi D(8\pi MC_0/\rho)^{1/2} \left[t - \frac{1 - \exp(-At)}{A}\right]\right\}\right) \quad (5)$$

where ρ is the density of the Co deposit and M is its atomic mass, N_0 is the number density of active sites on the electrode surface, and A is the nucleation frequency per active site.

Otherwise, another one must be proposed. Commonly, in a specific case, a modification based on the SM could be useful. For example, in this case, the induction-time is observed at point B(t_0, j_0) of Fig. 2. Therefore, the correction of t_0 must be done by substituting $t = t - t_0$ in Eq. (3) and (4), and Eq. (5), see details in [12]. By fitting Eq. (5) to experimental CAs, one can obtain some kinetic parameters of interest such as A , N_0 , and D .

- 8) *Experimental validation*: a physical-mathematical model such as SM could be useful to describe and predict the behavior of an electrochemical system. However, its result depends strongly on the data and the data processing method. Because the nature of the problem tends to be more complex, it requires experimental observation and visualization to obtain correct data. Therefore, visual methods such as SEM or TEM to observe the surface of deposits and EDS or XPS to determine its chemical composition are recommended to validate the results from the model (i.e. comparing A and N_0 with the SEM image of the surface deposit).

3. RESULTS AND DISCUSSION

3.1. UV-vis measurements

Figure 3a reveals that the Co (II)/DES electrolytes exhibit two absorption peaks within the range of 200 nm and 900 nm in the ultraviolet-visible region. The first peak (λ_1) located in the range of 200 nm – 300 nm at $\lambda = 235.5$ nm, approximately, presents much higher intensity compared to the second one (λ_2) located between 530 nm to 750 nm. However, the intensity of the first peak seems to increase slowly at higher concentrations of Co(II), while for the second one it increases gradually with Co(II) concentration. A strong agreement of the linear dependence between absorbance and Co(II) concentration is observed for the second peak (Figure 3b), which follows the behavior of the Beer-Lambert equation [19]. The presence of

peak λ_1 can be associated with the effect of the conjugate formed between carbonyl and amino in the urea of the DES, while the other peak can be attributed to the formation of $[\text{CoCl}_4]^{2-}$ and $[\text{CoCl}_3(\text{H}_2\text{O})]^-$ species of the cobalt complexes [20]. These UV-vis spectra results indicate that the characteristics and the composition of the Co(II) complexes remain unchanged (negligible change with temperature) under the conditions of the present study. It also comes to support the correctness of the proposed model under the experimental conditions of this study.

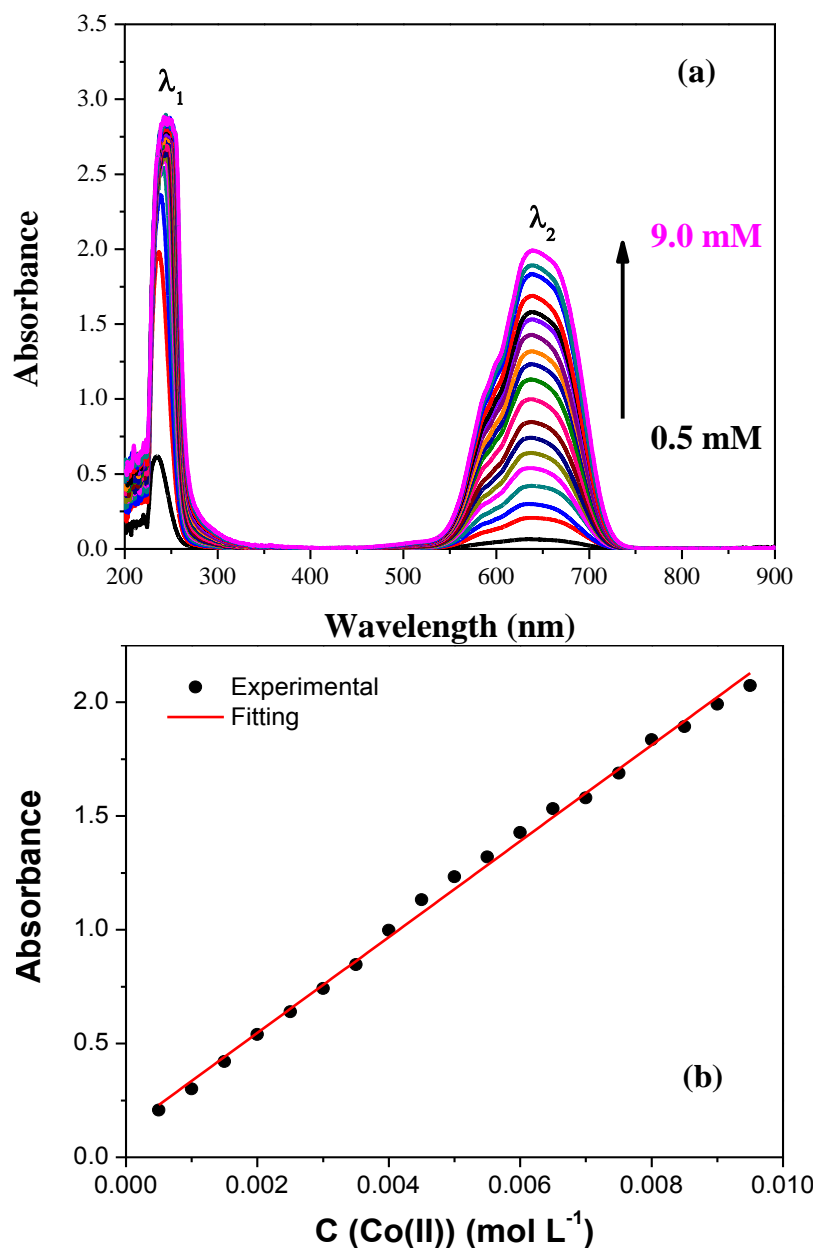


Figure 3. a) Absorption spectra of Co(II) in DES at different concentrations; b) the absorbance (A) as a function of the concentration (C). The linear fit equation is $y = 210.90175 x + 0.1246$.

3.2. Potentiodynamic study

To illustrate the methodology given in section 2.3 for the case of Co nucleation and growth phenomena from DES, some important results are presented below. Typical CV recorded in the system GCE/50 mM Co(II) DES at room temperature is shown in Figure 1. In the CV forward scan, the reduction peak is situated at the potential ranging from -0.9 V to -1.15 V. Whereas, in the opposite direction, the oxidation peak is located in the potential range of -0.45 V to 0.4 V. This peak can be attributed to the oxidation of Co metallic nuclei previously formed during the forward scan into Co(II) ions. The large increase of current density at the potentials lower than -1.20 V after the reduction peak can be related to the reduction of the solvent [21].

To evaluate the electrochemical behavior of Co(II) ions in the DES, CVs were performed at different scan rates as shown in Fig. 4a. Fig. 4b indicates that the current density of cathode peak (j_{cp}) displays a linear behavior with the square root of the scan rate ($v^{1/2}$), which demonstrates that the Co nucleation onto the GCE from the DES follows a diffusion-controlled mechanism described by Eq. (1) for 25 °C.

From Eqs. (1) – (2), D was calculated to be $2.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is consistent with our previous results [10, 11] in this medium. Also, the 3D nucleation behavior can be described by the model developed by Scharifker – Mostany (SM) [17].

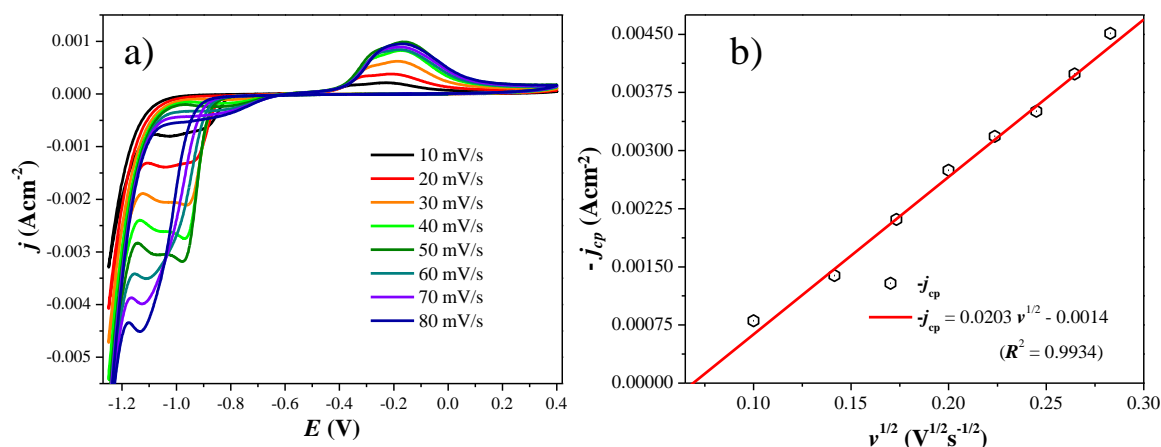


Figure 2. a) CVs recorded with different scan rate (v), and b) The plot displays j_{cp} of the CVs as a function of $v^{1/2}$.

3.3. Potentiostatic study

From CVs, the experimental CA curves were recorded at different applied potentials (-0.90 V, -0.91 V, and -0.92 V) at room temperature. The CA data recorded from the experiments were normalized through the maximum current density for each curve (t_m , j_m) and then compared with theoretical plots for instantaneous and progressive nucleation (Scharifker - Hills model, see Ref. [16]) to investigate the Co nucleation and growth mechanism. Figure 5 shows the influence of the induction time by comparing the experimental normalized plot and the theoretical one in both cases (with and without t_0). If ignoring the influence of t_0 , the normalized experimental curve is under the progressive curve (Figure 5), out of the validated zone that follows the behavior of the 3D nucleation and diffusion-controlled growth described by the SM model [17].

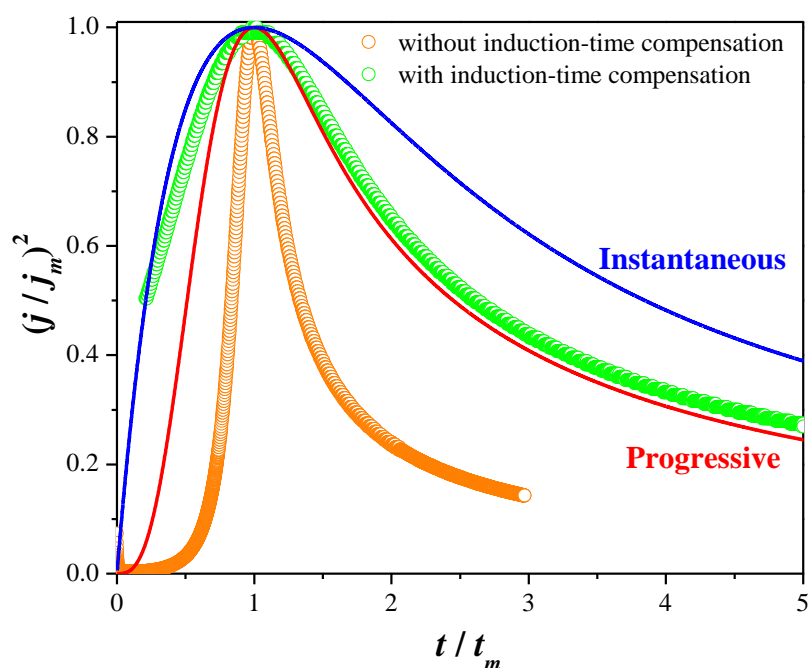


Figure 3. Comparison between the non-dimensional plots of the experimental current density transients without induction-time compensation (orange curve) and with induction-time compensation (green curve) and the theoretical ones for instantaneous (blue) and progressive (red) nucleation at 25 °C and – 0.92 V.

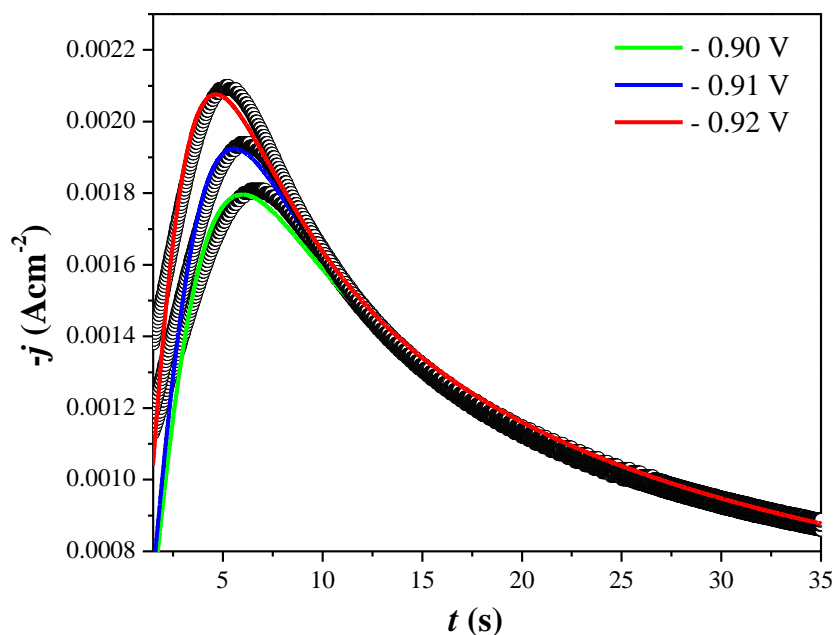


Figure 4. Comparison between the experimental CAs obtained in the system GCE/50 mM Co(II) in DES at room temperature (25 °C) and the theoretical ones (solid lines) fitting to the experimental data using Eq. (4).

Table 1. Kinetic parameters obtained by fitting Eq. (5) to experimental CAs.

$-E$ (V)	A (s^{-1})	$N_0 \times 10^{-6}$ (cm^{-2})	$D \times 10^7$ ($cm^2 s^{-1}$)
0.90	0.278	2.584	8.750
0.91	0.228	3.389	8.974
0.92	0.366	3.149	9.095

Figure 6 depicts the comparison between the experimental CA with the theoretical one plotted using Eq. (5), showing excellent agreement in shape and magnitude. This validates the use of the SM with t_0 correction to fit the data. Some kinetic parameters of interest are obtained by fitting Eq. (4) to experimental data (Figure 6) as shown in Table 1. It reveals that the number of active sites, N_0 , is high (in order of $10^6 cm^{-2}$), while the nucleation frequency is a little bit lower than the values reported in references [10, 11], which is expected as it has been performed at room temperature. However, this kinetics is acceptable for massive electrodeposition from DES under ambient conditions. The obtained results remark the vital importance of this kind of analysis in the studied medium that provides details of kinetic aspects of the Co electrodeposition and its practical feasibility.

3.4. Surface characterization

Figure 7 depicts the evidence of the Co electrodeposition performed onto GCE at different applied potentials ($-0.9 V$ and $-0.92 V$) under ambient conditions. The dark color region corresponds to the GCE surface, while the bright one indicates the formation of the metallic Co on the GCE, which can be verified by the presence of the Co peak shown in the EDS spectrum as can be seen in Figure 8d and the elements (C and Co) mapping in Figures 8a – 8c. In a qualitative manner, the density number (N_0) of cobalt particles in Figure 7b is much higher than that of Figure 7a. This agrees with the prediction from the SM model that the product AN_0 (a robust criterion to evaluate the model for nucleation with diffusion-controlled growth [11]) increases with the increase in the applied potential (Table 1).

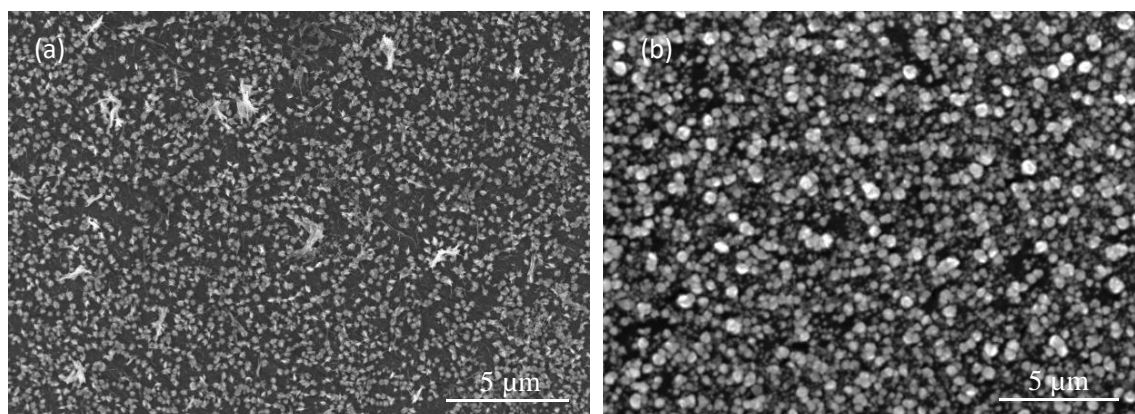


Figure 7. SEM images of Co deposit at different potentials, a) $-0.90 V$ and b) $-0.92 V$ within 50 s.

Furthermore, Fig. 7b reveals that the cobalt hexagonal particles exhibit a relatively homogeneous distribution (see the mapping of Co particles distribution in Figure 8c), while Figure 7a presents a much smaller particle size. For both cases, the Co particles appear in different sizes, meaning that the nuclei are formed with different ages. The observed behavior corresponds to progressive nucleation, which also agrees with the results reported in [20]. This

helps to validate the use of the SM to describe the Co electrodeposition from DES at room temperature.

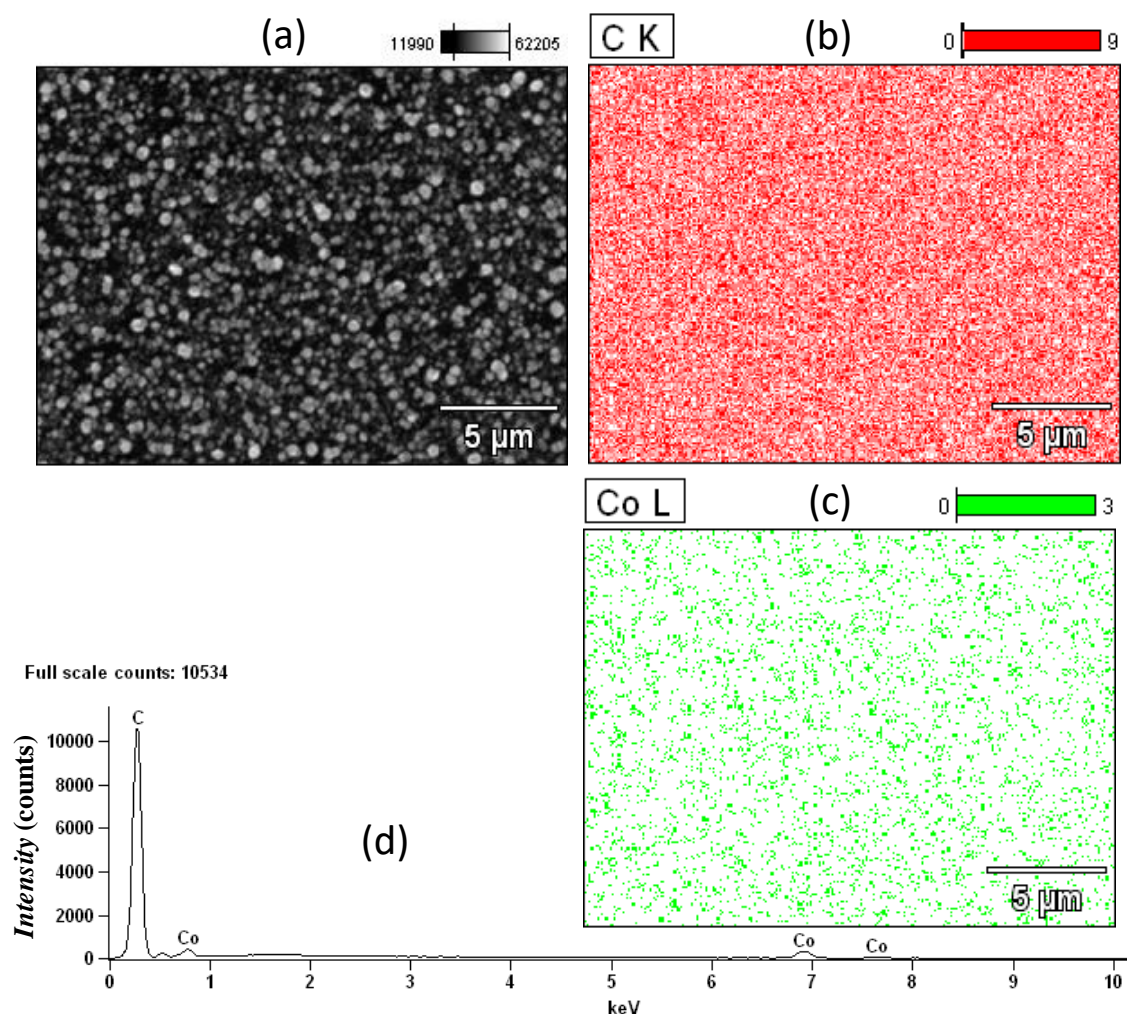


Figure 5. Element mapping using EDS technique of Co deposit: a) selected zone from the sample, which applied -0.92 V to perform EDS, b) distribution of carbon (C) and c) distribution of cobalt, and d) the EDS spectrum obtained on the GCE surface.

4. CONCLUSIONS

A methodology for the nucleation and growth of cobalt onto GCE from DES has been presented. The particularity of the Co electrodeposition under ambient conditions onto glassy carbon from a mixture of choline chloride and urea was studied to validate the proposed methodology. It was found that the Co nucleation onto the GCE from the DES occurred by a 3D nucleation and diffusion-controlled mechanism, which can be described by adding the contribution of the induction time. Based on the results, it can be concluded that the early stage of the Co electrodeposition is dominated by progressive nucleation mechanism under ambient conditions. Finally, the ability of Co electrodeposition in reline DES at room temperature can

expand the potential applications of DES for cleaner production of metals in different engineering fields.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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