AN ELECTROCHEMICAL STUDY OF THE COBALT ELECTRODEPOSITION ONTO A CARBON FIBER ULTRAMICROELECTRODE

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ABSTRACT

A kinetic study of the cobalt electrodeposition onto a carbon fiber ultramicroelectrode of 11 μm of diameter was conducted in overpotential conditions from an aqueous solution containing 0.01 M CoCl₂ + 0.1 M NH₄Cl. From the voltamperometric and chronoamperometric studies, it was found that the value of the diffusion coefficient is 1.2x10⁻⁷ cm² s⁻¹. The analysis of the current density transients suggests that cobalt electrodeposition onto a carbon fiber electrode follows an instantaneous nucleation process controlled by spherical diffusion mass transport. Also, the number of active nucleation sites increases as the applied potential decreases.

Keywords: Cobalt, electrodeposition, ultramicroelectrode, carbon fiber.

INTRODUCTION

Cobalt electrodeposits have received considerable attention due to their potential applications in scientific and technological fields related to the storage of digital information.¹ They have been used in the fabrication of sensors,² heterogeneous catalysis,³ and in the synthesis of intercalation compounds for energy storage⁴ among others. Here, it is interesting to mention that during the cobalt electrodeposition process it is possible to optimize parameters such as temperature, applied current density, and electrolyte composition.¹ In this sense, Co electrodeposition has been studied on different substrates as such: GCE,⁵ Cu,⁶ Cu₁₋ₓ Au,⁷ stainless steel,⁸ Al⁹-¹² and Pt⁹,²³ and from plating baths based on sulfates,⁴,¹³-¹⁵,¹⁷ chloride,¹⁶,¹⁸-²² and citrates¹ solutions, mainly. The results obtained from different systems indicate that cobalt electrodeposition follows a progressive nucleation, but it may switch to instantaneous if ultrasound is employed to improve the mass transfer,²⁶ or increasing the cobalt concentration in the plating bath.²⁷ Also, cobalt electrodeposition may also occur via a nucleation process under charge transfer control.²⁸ Thus, cobalt electrodeposition is diffusion controlled, but a mixed control has been found as well²². In addition, different shape morphologies, such as fractals, butterfly, dendrites, snowflake-like, which exhibit different properties may be obtained.²² Here it is interesting to mention that materials based on cobalt has been scarcely synthesized onto nano or ultramicroelectrodes (UME’s) by electrodeposition,²⁵,²⁶ despite their advantages. For example, the UME’s reduced dimensions allow cobalt to be deposited onto a carbon fiber well synthesized onto nano or ultramicroelectrodes (UME’s) by electrodeposition,²⁵,²⁶ despite their advantages. For example, the UME’s reduced dimensions allow cobalt to be deposited onto a carbon fiber well.
In order to determine the type of kinetic control during the cobalt electrodeposition process, the cathodic peak current was plotted against the scan rate at \( n_s \), see Figure 3. A linear relationship was found indicating a diffusional-controlled process. From the slope of the \( j_p \) vs \( v^{1/2} \) plot and the Berzins–Delahay’s equation it was possible to evaluate the diffusion coefficient value as \( 1.2 \times 10^{-5} \) \( \text{cm}^2 \text{s}^{-1} \).

Also, the kinetic parameters associated with the Co\(^{2+}\) + 2\(e^-\) \(\leftrightarrow\) Co\(^0\) process in the present system were evaluated by means the Tafel equations, equation (2) and (3).

\[
\ln j_c = \ln j_0 - \frac{\alpha_c nF}{RT} v^{1/2}
\]

\[
\ln j_a = \ln j_0 + \frac{(1-\alpha_a) nF}{RT}
\]

In these equations \( j_c \) and \( j_a \) are the cathodic and anodic current respectively, \( j_0 \) is the exchange current, \( \alpha_c \) is the cathodic transfer coefficient, while the anodic transfer coefficient is \( \alpha_a = 1 - \alpha_c \). In Figure 4 are depicted the plots of the logarithm of the cathodic and anodic current vs. the applied potential according to equations (2) and (3). The anodic and cathodic branch data were obtained from a linear voltammogram recorded at a scan rate 1 mV s\(^{-1}\) from the C-UME//0.01 M CoCl\(_2\) + 0.1 M NH\(_4\)Cl system. Fitting the linear part of these branches to the Tafel equations, yielded a value of the cathodic transfer coefficient of 0.23, while the anodic transfer coefficient is 0.77. The above suggests that the anodic process is favored in the present system.

\[ j(t) = (4nFDc^{\infty} r + 8nFc^{\infty} r^2 D^{1/2} \pi^{-3/2} t^{-1/2})[1 - \exp(-NnFRDc)] \]

Thus, the experimental transients (solid lines) represented in Figure 5 were fitted from a nonlinear fit to equation (5). From Figure 5 it can be seen that the theoretical transients (dashed lines) generated through equation (5) compare favorably with the experimental ones obtained at different potential steps, suggesting that this model is able to predict the overall behavior of the experimental transient.
From these fittings, the values of the kinetic parameters associated with the nucleation and growth process of Co on the C-UME were determined and they are reported in Table 1. Note that, as the potential values decrease, the number of active sites, \( N_a \), increases. However, the value of the diffusion constant remains constant, with an average value of \( 1.2 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \). This coefficient diffusion value compares favorably with the obtained from the voltamperometric study.

Table 1. Kinetic parameters of Co electrodeposition from the C-UME/0.01 M CoCl₂ + 0.1 M NH₄Cl system.

| E / V | \( N_a \times 10^4 \) / cm² | \( D_s \times 10^5 \) / cm² s⁻¹ |
|---|---|---|
| -0.81 | 0.270 | 1.315 |
| -0.83 | 0.916 | 1.198 |
| -0.87 | 2.081 | 1.130 |
| -0.89 | 1.874 | 1.335 |
| -0.91 | 3.558 | 1.140 |
| -0.94 | 4.857 | 1.038 |

CONCLUSIONS

An electrochemical study on the cobalt electrodeposition process onto a carbon fiber microelectrode from an aqueous solution containing 0.01 M CoCl₂ + 0.1 M NH₄Cl in overpotential conditions has been carried out through voltammetric and potentiostatic studies. The analysis of the voltammetric curves at different scan rates potential indicated that the cobalt electrodeposition process is diffusion controlled and the value of the diffusion coefficient is \( 1.2 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \). It was also possible to evaluate the anodic \( (\alpha_a) \) and cathodic \( (\alpha_c) \) transfer coefficients; a higher value of \( \alpha_a = 0.77 \) compared to \( \alpha_c = 0.23 \) means that the anodic process is favored in the present system. The potentiostatic study indicated that the electrodeposition of cobalt on a carbon fiber electrode follows an instantaneous nucleation process, which is controlled by spherical diffusion mass transport to the ultramicroelectrode. Also, the number of active nucleation sites increases with the decrease of the applied potential.

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