

Electrodeposition of copper on glassy carbon electrodes in the presence of picolinic acid



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ABSTRACT

The electrodeposition of copper on glassy carbon electrodes in the presence of picolinic acid (PA) was investigated by means of voltammetric, chronoamperometric and electrochemical impedance spectroscopy measurements complemented by UV–vis spectroscopy and SEM imaging. Voltammetry shows the appearance of two cathodic current peaks that are assigned to the electroreduction of copper ions and $[\text{Cu}(\text{PA})_2]^{2+}$ soluble complex species. The anodic stripping of the metallic layer shows two electrochemical processes related to the formation of cupric ions that are produced from the electro-oxidation of both the deposited copper layer and the cuprous species that result from the chemical reaction between the metallic layer and cupric ions at the interface. This second contribution appears to be influenced by the initial conditions of the electrode surface and the presence of PA in solution. Voltammetry and potentiostatic current transients show that copper deposition occurs through a nucleation and growth process. From the analysis of the transients an instantaneous nucleation with 3D growth process under diffusion control is concluded, although a deviation in the curves from the model is observed. This deviation from the model, usually found in other systems, is explained in terms of the morphological characteristics of the particles depositing on the electrode surface. SEM images show the formation of nuclei on the glassy carbon surface and a change in the morphological characteristics of the deposit when the reaction occurs in the presence of PA. The Nyquist plots show a single capacitive constant at high frequencies, related to the charge transfer of copper ions, and a Warburg-type contribution at low frequencies, related to the diffusion of copper ions from the solution to the electrode surface. Values of the charge transfer resistance result lower in the presence of PA. The corresponding Bode plots show a good agreement between experimental and fitted data.

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1. Introduction

Electrodeposition of metal films is a viable alternative to vacuum-based deposition processes or chemical vapor deposition not only because of its simplicity but also because of the possibility of working at room temperature and pressure and a fine control of thin film properties. For this purpose, electrodeposition baths usually contain organic compounds with functional groups such as $-\text{SH}$, $=\text{NH}$, $-\text{COOH}$, etc., as the addition of these species improves the smoothness, brightness, hardness and ductility of the resulting films [1–3]. These additives are in small amounts in the electrolyte but their presence change on the characteristics of the deposited particles, such as homogeneity distribution, shape, size and number density.

The electrodeposition of copper is a process of great practical importance, especially in the electronics industry for processes such as manufacturing of printed-circuit boards, in which hard, uniform and bright deposits are desired and the formation of loose deposits has to be prevented. On the other hand, the copper electrodeposition reaction has also been used as a model for fundamental studies of nucleation processes [4]. As a consequence, the electrochemical studies related to the copper electrodeposition have been performed in an ample variety of experimental conditions, including acidic [5–9] and buffered basic mediums, with [10,11] and without [4,6,7] complexation, involving different electrode surfaces such as graphite [6], glassy carbon [4,12,13], HOPG [14], Pt [7,15–17], Cu [8,9,18] and Au [19].

Picolinic acid (2-carboxypyridine (PA), $\text{C}_6\text{H}_5\text{NO}_2$ = pyridine-2-carboxylic acid), one of the most chelating agents present in the human body, is a pyridine compound with a carboxyl side chain at the 2-position. It is an isomer of nicotinic acid, which has the carboxyl side chain at the 3-position. Although few works have been published in relation to its possible use as additive in

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electrodeposition processes [16,20], it is however an interesting alternative due to the fact that it is rather inexpensive and easy to obtain. Furthermore, PA has been reported to be an efficient leveler agent for copper electrodeposition on platinum [16]. In this case, PA appeared a very effective brightener producing highly uniform and smooth surfaces of copper deposits in slightly acidic solutions of copper sulphate. More recently, it has been tested for the case of electrodeposition of silver on HOPG [20].

The aim of this work is to advance in the knowledge of copper electrodeposition in the presence of additives, by studying the electrodeposition of copper on glassy carbon in the presence of PA. Glassy carbon is an interesting substrate for studying electrodeposition processes as it offers an amorphous structure that assumes a random distribution of active sites for the formation of nuclei, a fact that it is usually employed to allow the verification of theoretical models related to nucleation and growth processes. For this purpose, electrochemical studies from cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy, coupled to UV–vis spectroscopy and SEM imaging, were employed to study the initial stages of copper electrodeposition and the steady state growth of the copper film in slightly acid solutions. Studies were also run in PA-free solutions for the sake of comparison for discussing the influence of the additive on the nucleation and growth of copper films.

2. Experimental

Experiments were run employing a typical three electrode glass cell. As a working electrode a 3 mm dia glassy carbon discs embedded in Teflon (Radiometer) or Kel-F (CH Instruments, Inc.) were used. Before each experiment, the electrode surface was mechanically polished using a 0.3 μm alumina suspension. The auxiliary electrode consisted of a platinum foil and the reference electrode was a mercurous sulphate (MSE, 0.650 V vs. SHE). For the EIS measurements a copper wire (-0.385 V vs. MSE) was used as reference in order to avoid the interference of the MSE electrode impedance at high frequencies. Electrochemical measurements were made employing an Autolab 128N, controlled by Nova 1.9 software, for the voltammetric and potential step experiments, and a Zahner IM6d electrochemical workstation for impedance measurements. Analysis of the data obtained during an electrochemical impedance measurement was performed by fitting the experimental data with an equivalent circuit, based on the Boukamp model, using Nova 1.9 software facilities. The morphological characterisation of copper deposits was made using an environmental scanning electron microscope (FEI Quanta 200 ESEM).

Three working solutions were employed: (i) Na_2SO_4 0.1 M + CuSO_4 0.02 M + PA 0.005 M (pH=2.92); (ii) Na_2SO_4 0.1 M + CuSO_4 0.02 M + PA 0.01 M (pH=2.60); and (iii) Na_2SO_4 0.1 M + CuSO_4 0.02 M (pH=4.74). Occasionally, a Na_2SO_4 0.1 M + CuSO_4 0.02 M solution with its pH adjusted to 2.90 was used for comparison purposes. All solutions were saturated with nitrogen before the measurements and a flow of nitrogen was maintained over the surface during the experiments. All measurements were made at 298 K and potentials in the text are referred to the MSE.

3. Results and discussion

3.1. UV–vis spectra

The addition of PA results in a visually marked increase in the blue tinge of the 0.02 M CuSO_4 solution. The corresponding UV–vis spectra show a blue-shift in the maximum absorption from 800 to 750 nm as the PA concentration is increased (Fig. 1). The

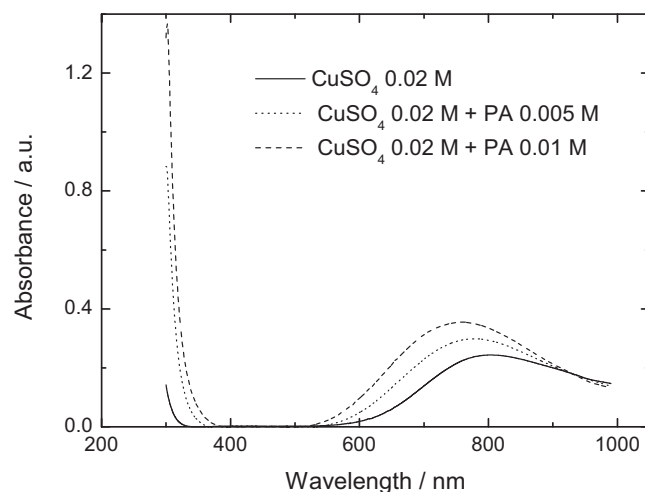
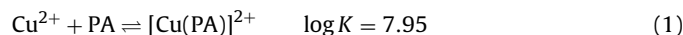


Fig. 1. UV–vis spectra corresponding to the solutions used in the paper.

peak maximum shift to 775 nm has been described as a characteristic of copper(II)–oxygen donor ligand binary complexes [21]. As described further on, the formation of the soluble complex species, as revealed by this absorbance increase, will result in the appearance of a cathodic current peak in the cyclic voltammograms associated to its reduction.

According to the literature, PA can form complex species with transition metals such as Mn, Co, Ni, Cu, etc. [22,23]. Particularly for the case of Cu, PA can form complex species involving either one or two ligands with Cu^{2+} ions [24]:



As a result, the reaction between copper and PA produces the formation of a complex denoted as bispicolate copper (II), where the Cu(II) cation is located at the center of a distorted N_2O_4 octahedron axially elongated by Jahn–Teller distortion. The two ligands coordinate through the nitrogen atom and one of the carboxylate O-atoms in a trans-geometry [25–27]. The electrochemical behaviour of the $[\text{Cu}(\text{PA})_2 \cdot 2\text{H}_2\text{O}]^{2+}$ species was studied in DMF, and results indicated that the electroreduction of the complex proceeded through a quasi-reversible one-electron process producing $[\text{Cu}(\text{PA})_2]^+$ species. The quasi-reversible behavior was associated with the geometry change occurring, i.e. from an octahedral to a tetrahedral environment, around the metal ion [27].

3.2. Voltammetry

Before investigating the different stages related to the electroreduction of copper ions on GC in PA-containing solutions, and their subsequent stripping, voltammograms were run in plain 0.1 M Na_2SO_4 + 0.02 M CuSO_4 solutions for the sake of comparison (Fig. 2). Thus, runs made on a fresh polished electrode at 0.0010 V s^{-1} from 0.1 V downwards, by stepwise increasing the negative potential limit from -0.40 V to -0.95 V, show the progressive appearance of a cathodic current peak (I_c) at ca. -0.49 V followed by a limiting current contribution from -0.8 V downwards. Furthermore, the negative potential scan also shows the presence of a cathodic current loop at ca. -0.50 V that is usually expected when a nucleation and growth process occurs [28]. During the positive potential scan, an anodic current peak I_a at ca. -0.24 V is observed along with a hump I_{IIa} on the positive side of the peak, particularly when the negative potential scan limit is above -0.6 V (Fig. 2). It should be noted that the voltammogram shows a negative displacement of

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