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Nucleation and growth of silver nanostructures onto HOPG electrodes in the presence of picolinic acid

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ABSTRACT

Silver electrodeposition onto HOPG electrodes in the presence of picolinic acid (PA) has been studied by cyclic voltammetry and chronoamperometry. Changes in the nucleation and growth mechanisms, which are dependent on the PA concentration and solution pH, have been observed. Formation of complexes with Ag^+ ions and adsorption of the additive molecules on both, the substrate and the growing silver crystallites can be correlated with the potential dependence of the kinetic parameters, N_0 and A. The amount, distribution (random or localized on the defects sites) and size of the crystallites on the substrate are influenced by the composition of the solution (PA concentration and pH) when the control of the nucleation and growth processes is regulated by application of a double potential program.

1. Introduction

For many years, use of electrodeposition methods in metal coating research has intensified with growing technological interest to acquire a better understanding of the role played by the additives in the global process. At a macroscopic level, it is well known that the organic additives fulfill functions as leveling and brightening agents [1–3]. Organic molecules containing functional groups have a strong influence on the kinetics of the first stages of the electrocrystallization process, thereby promoting the formation of metallic films with different properties and morphology [4–6]. Despite the diversity of studies conducted in this area, only limited amounts of information about the activity of additives during electroformation of nanodimensional metal structures are currently available. When the dimension of the deposited metal structures approaches the nanometer range, the initial stages of electrocrystallization, i.e. the nucleation and growth, become very important [7–9]. Nuclei formation can be regarded as the most critical stage in the process mechanism for establishing the final particle properties [9,10].

Silver nucleation mechanisms on different electrodes from various electrolytes have been extensively studied [10–15]. The surface state of the substrate, and the temperature and composition of the electrolyte play an important role in the mechanism of silver nanoparticles deposition. Most research has shown that silver deposition in additive-free electrolytes occurs by an instantaneous nucleation mechanism [16–18], whereas the mechanism of silver growth on substrates such as crystalline silicon or highly oriented pyrolitic graphite (HOPG) corresponds to the Volmer–Weber growth, which is very important to induce only the formation of 3D crystallites [10,19]. When the electrolyte contains small amounts of organic compounds, changes on the characteristics of the deposited particles (homogeneity distribution, shape, size, and number density) are observed. The resulting morphology of the crystallites is generally related to the adsorption of the additive molecules on the electrode or on the growing clusters, and the additive adsorption process has been shown to have an important influence on the electron transfer kinetics and, consequently, on the nucleation of the metallic clusters [20].

Picolinic acid (PA) is an organic compound with chemical structure simple, inexpensive and easy to obtain, however there are currently very few publications concerning to the use of pyridine–carboxylic acids, as additives in plating process. For example, PA was demonstrated to be an efficient leveler agent in copper electrodeposition, mainly for its tendency to form complexes with metallic ions and its adsorption capacity on various surfaces, via their functional groups [21,22]. In the present study, we have used PA as an additive to establish its influence on the initial stages of Ag crystallites electrodeposition onto HOPG surfaces.

The aim of this work is to provide a better understanding of the underlying mechanisms of silver electrodeposition on HOPG electrodes on the basis of electrochemical results from cyclic voltammetry and chronoamperometry in the presence of picolinic acid (PA). The influence of different acid–base species of the additive, and the corresponding complexes with Ag^+ ions in solution, on the nucleation and growth kinetics of silver nanostructures is discussed in detail.

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2. Experimental

All solutions were prepared from analytical grade reagents and purified water by a Millipore Milli-Q system. The electrolyte employed was 1 mM $AgClO_4$ (BDH Chemicals Ltd.) in 0.5 M $HClO_4$ (J.T. Baker) at pH 0.3, or in 0.1 M $KClO_4$ at pH 3.0 and 6.5. Picolinic acid (Sigma–Aldrich) was added to the electrolyte, and solutions with concentrations ranging from 0.5 to 5.0 mM were prepared. The pH of the electrolyte was adjusted by addition of $HClO_4$ or KOH concentrated solutions. The aqueous solutions were freshly prepared and saturated with purified nitrogen before every experiment.

Analytical determinations of the species in solution were carried out by Nuclear Magnetic Resonance spectroscopy (NMR) with a BRUKER 400 MHz spectrometer (Advance II) containing a BBI inverse detection probe. The ^{1}H NMR spectra were recorded for 5.0 mM PA solutions, after addition of different amounts of $AgClO_4$ at pH 3.0 and 6.5 (10% deuterated water) with a constant ionic strength of 0.1 M. Benzene was added as an internal standard.

Electrochemical measurements were carried out in a conventional three-electrode glass cell system at room temperature. HOPG plates (SPI Supplies, Brand Grade SPI-1, 10×10 mm^2), previously cleaved with adhesive tape and introduced in a Teflon holder were used as working electrodes. A platinum foil and a silver wire directly immersed in the electrolyte were used as counter and quasi-reference electrodes, respectively. All potentials are reported vs. Ag°/Ag^+ (1.0 mM) reference electrode ($E_{Ag^\circ/Ag^+} = -0.30$ V vs. SCE).

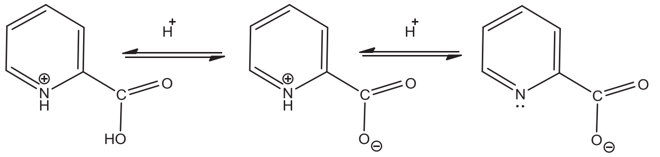
Potentiodynamic experiments were recorded at a scan rate of 0.02 V s^{-1} in the potential range from +0.5 to −0.4 V with a computer-controlled potentiostat Autolab PGSTAT with GPES software (ECO CHEMIE B.V.). Prior to each electrochemical experiment, a reproducible state of the HOPG surface was produced by polarization of the electrode at 0.4 V for about 3 min in the electrolyte [23]. Application of this conditioning pretreatment is necessary due to the initial presence of a cathodic current given by the intrinsic nucleation sites on the freshly cleaved graphite surface at open circuit potential [24]. The deposition of silver crystallites was carried out under potentiostatic conditions by application of either a single or double potential step. All current densities were normalized in terms of the apparent geometric area of the HOPG electrode.

The morphology of Ag crystallites was examined using a scanning electron microscopy (SEM) JEOL JSM-7401F Field Emission Gun Scanning Electron Microscope (FEG-SEM), with data acquired in the LEI mode, with a gun tension of 5 kV.

3. Results and discussion

3.1. Composition of the PA electrolyte

Picolinic acid has two acidic functions with thermodynamic dissociation constants of $pK_1 = 1.03$ and $pK_2 = 5.21$ [25], corresponding to the dissociation of the carboxyl group and the protonated ring nitrogen, respectively. Reaction scheme (1) shows the different acid–base species of PA, labeled as ***H₂Pic***$^+$ (protonated), ***HPic*** (zwitterion) and ***Pic***$^-$ (anion).



H₂Pic⁺ *HPic* *Pic⁻*

(1)

It is noteworthy that depending on the solution pH, the PA species in solution can form soluble complexes with the Ag^+ ions. For example, the relevant PA chemical species in solution are the protonated ***H₂Pic***$^+$ at pH 0.3, the zwitterion ***HPic*** at pH 3.0 and the anion ***Pic***$^-$ at pH 6.5. It is important to notice that the concentration of $[\boldsymbol{Ag}(\boldsymbol{L})^+]$ complexes in solution, with ***HPic*** and ***Pic***$^-$ species as ligands, can be regulated by changing the pH. In the present case, the formation of complexes with the protonated species ***H₂Pic***$^+$ is not considered because it has not available functional groups.

In order to study the silver electrodeposition mechanism in the presence of PA, knowledge of the stability constants for the silver complexes with the different PA species was required. In this work, the formation constants were determined by analysis of solution nuclear magnetic resonance (NMR) spectra. The chemical shifts from ^{1}H NMR spectra provide an estimate for the degree of electronic perturbation of the ligand species caused by the Ag^+ ions, thereby allowing the chemical structures and stability constants of silver complexes to be determined [26–29].

The comparative analysis of the spectra (results not shown) of 5 mM PA solutions supported the following statements regarding the complexes' chemical structure:

- The $[\boldsymbol{Ag}(\boldsymbol{HPic})^+]$ and $[\boldsymbol{Ag}(\boldsymbol{Pic})]$ species at pH 3.0 and 6.5, respectively, are formed by the interaction between Ag^+ ions and the carboxylate group of the PA species.
- Evidence of silver complexes formation was obtained by monitoring the changes in the chemical shifts (around 0.2 ppm) when titration of PA ligands (at every pH), with Ag^+ ions is performed [28,29].
- The values of calculated constants in concentrations (Kc) for $[\boldsymbol{Ag}(\boldsymbol{L})^+]$ complexes with 1:1 stoichiometry are given by reactions (2) and (3).

$$\boldsymbol{Ag}^+ + \boldsymbol{HPic} \rightleftarrows [\boldsymbol{Ag}(\boldsymbol{HPic})^+] \quad K_{1:1}(\text{pH } 3.0) = (11.5 \pm 0.6)\ \text{M}^{-1} \tag{2}$$

$$\boldsymbol{Ag}^+ + \boldsymbol{Pic}^- \rightleftarrows [\boldsymbol{Ag}(\boldsymbol{Pic})] \quad K_{1:1}(\text{pH } 6.5) = (800 \pm 100)\ \text{M}^{-1} \tag{3}$$

From the complexation constants, the chemical composition of the electrolytes at three pH values can be established.

3.2. Potentiodynamic deposition of silver from PA containing solutions

In order to establish the potential region for silver deposition onto HOPG electrodes, the voltammetric behavior in aqueous solutions containing PA was analyzed. The potentiodynamic profiles of HOPG in 1.0 mM $AgClO_4$ aqueous solutions in the absence (red curves) and presence (black curves) of 0.5 mM PA at pH 0.3 (a), 3.0 (b) and 6.5 (c), are shown in Fig. 1. The comparison between the j/E potentiodynamic profiles recorded in the absence of additive shows similar behavior, irrespective of the solution pH. There is one well-defined current peak for silver electrodeposition and the corresponding anodic peak, due to the silver dissolution process. The cathodic peak at around −0.23 V corresponds to the electroreduction of silver ions on the HOPG, according to the reaction:

$$Ag^+ + 1e \rightarrow Ag^\circ \tag{4}$$

Regardless of the pH, the potential of the cathodic and anodic peaks does not change with the pH. It is due to the same process is occurring in all solutions. However, the charge involved in the whole voltammogram (mainly in the dissolution process) diminishes notably as the pH is increased [30]. Furthermore, evidence of the process irreversibility is shown by the anodic peak shifting to more positive potentials, a feature that some authors have related to the silver oxidation with the formation of Ag(OH) species or silver oxide complexes with perchlorate ions [30–32].