Electrochimica Acta 156 (2015) 154–162

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Spectroelectrochemical study of picolinic acid adsorption during silver electrodeposition

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ARTICLE INFO

Article history:
Received 6 October 2014
Received in revised form 31 December 2014
Accepted 9 January 2015
Available online 12 January 2015

Keywords:
Surface-Enhanced Raman Spectroscopy
silver electrodeposition
picolinic acid
adsorption

ABSTRACT

The adsorption of picolinic acid (PA) onto HOPG electrodes during silver electrodeposition at pH 3.0 was examined using conventional electrochemical techniques: cyclic voltammetry and impedance measurements (differential capacity-potential plots) and Surface-Enhanced Raman Spectroscopy (SERS), through a wide range of electrode potentials. The spectroelectrochemical results indicate that the electroactive species for silver electrodeposition are Ag^+ ions and [Ag(Pic)] complexes, in spite of the predominant species in solution being the zwitterion (HPic). Adsorption of the anion (Pic^-) occurs through a wide potential range where the electrode surface charge density is positive. However, HPic deprotonation, hydrogen formation and Pic^- desorption, with the consequent decrease in SERS intensity, occur at the zero-charge potential (pzc) for HOPG.

1. Introduction

Metal electrodeposition stands out between the most significant applications of electrochemistry as a technique that enables the deposition of a wide variety of nanostructures onto conductor and semiconductor substrates at ambient temperature. The quality of the deposits depends on experimental conditions such as electrode potential, current density, surface pretreatment, electrolyte composition, and the presence of organic additives in the bath [1,2]. Adsorption of molecules with different functional groups at the deposited metal surface influences for example, the nucleation rate, thereby resulting in different deposit morphologies, surface distribution on the surface, and properties at the nanoscale [3–6].

Obtaining information about the electrode/electrolyte interface during the electrodeposition process is very important for both technological applications and fundamental research. Surface-Enhanced Raman Spectroscopy (SERS) has been extensively used to study different processes through identification of various organic addition agents and corrosion inhibitors [7,8]. Detection and identification of adsorbates are feasible when a SERS-active substrate is available. However, a quantitative analysis of the surface concentration is not easy because the orientation of the adsorbed molecules is related to the selection rules for active Raman vibrational modes and the dependence of surface coverage on electrode potential. An approach based on combining Raman spectroscopy and electrochemical techniques, such as cyclic voltammetry and impedance measurements, can provide information concerning direct adsorbate interactions at metal/electrolyte interface during the electrodeposition process [9].

In this work, we investigate silver deposition onto HOPG electrodes with picolinic acid (PA) as an additive in the electrolyte. Use of this organic molecule as a non-toxic addition agent in metal electrodeposition is of particular interest, because of its tendency to coordinate with metal ions and its ability to be adsorbed onto different surfaces via carboxylate and pyridinic-nitrogen functional groups [10,11]. In a recent investigation of PA-influenced copper electrodeposition on vitreous carbon, Bolzán found two cathodic contributions which were assigned to the electroreduction of copper ions and $[Cu(PA)_2]^{2+}$ soluble complex species [12]. Our own investigations have examined the influence of pyridine-carboxylic acids on nucleation and growth mechanism in silver and copper electrodeposition, and have shown that PA species can be strongly

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http://dx.doi.org/10.1016/j.electacta.2015.01.034

adsorbed on the growing nuclei surface, thereby inhibiting its reactivity and providing a mechanism for dendritic growth [10,13]. In addition, we have also explored the influence of solution pH on voltammetric response, SERS spectra, and silver crystallites morphology, and we have found that the PA anion species is adsorbed at pH values higher than 3.0, while adsorption of both anion and zwitterion species occurs at a pH value of 0.3 [14].

Since the mechanism of silver electrodeposition onto HOPG in the presence of PA is already known [13,14], the focus of the present study lies on investigate the adsorption process of additive molecules on growing crystallites over a wide range potential, in solutions of pH 3.0. SERS spectroscopy with potentiodynamic control of the electrode/solution interface has been shown to be a powerful tool for the sensitive detection of different species of PA on the electrode surface. In addition, differential capacity behavior exhibits strong correlations with spectroelectrochemical experiments.

2. Experimental Section

2.1. Chemicals

All electrolytic solutions used in this work were freshly prepared with analytical grade reagents, without further purification and ultrapure water from a Millipore-Milli-Q system with 18.2 MΩ·cm resistivity. Chemical reagents were silver perchlorate (BDH Chemicals Ltd. 98%), picolinic acid (Sigma-Aldrich, 99%) and potassium perchlorate (J.T. Baker). All solutions were degassed with N_2 for 20 minutes before use, and the pH was adjusted by addition of perchloric acid.

2.2. Electrochemical procedures

Electrochemical measurements were carried out at room temperature in a conventional three-electrode glass cell. Highly oriented pyrolytic graphite (HOPG SPI Supplies, Brand Grade SPI-1, $10 \times 10\,mm^2$) in a Teflon holder with an exposed circular region of $0.283\,cm^2$ was used as working electrode. The basal plane surface of HOPG crystal was cleaved using adhesive tape immediately prior to use. A Pt wire was the counter electrode and a silver wire immersed in the electrolyte was the quasi-reference electrode. All potentials are reported vs. Ag/Ag$^+$ (1.0 mM) reference electrode (E_{Ag/Ag^+} = -0.30 V vs. SCE).

Prior to each electrochemical experiment, a reproducible state of the HOPG surface was attained by polarization of the electrode at 0.4 V for about 3 min [15,16]. Cyclic voltammetry was performed by scanning from 0.4 V towards negative potentials with an Autolab (PGSTAT ECO CHEMIE) electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were acquired with a Solartron 1260 electrochemical interface in the 10^{-1} to 10^5 Hz frequency range with 0.01 V signal amplitude. The differential capacity experiments were recorded at 20 Hz with a scan rate of $10\,mV\,s^{-1}$. Capacity-potential curves were obtained by fitting the ac impedance measurements with a simple RC equivalent circuit representing the electric double layer model.

2.3. SERS experiments

Spectroelectrochemical SERS measurements were performed with a Renishaw InVia microRaman spectrometer, equipped with a Leica microscope and 63x water immersion objective (NA = 0.9). The 632.8 nm line of a He-Ne Coherent 31-2140-000 laser with a power of 3.5 mW and 1.0 μm^2 illuminated area on the sample was used. In-situ SERS measurements were carried out in a homemade-Teflon cell with the HOPG electrode in the bottom (exposed area was $0.40\,cm^2$), a Pt wire loop as counter electrode, and Ag/Ag$^+$ quasi-reference electrode. The spectra were obtained during a potentiodynamic scan at a rate of $1\,mV\,s^{-1}$; with the acquisition mode consisting of 10 s accumulation at each point during the scanning process and resulting in a scan time of ca. 60 s for spectrum. The electrochemical potential in the SERS experiments was applied with a potentiostat/galvanostat EG&G PAR-273 interfaced to a computer. The reported potential values were taken at the end of each SERS spectrum.

2.4. Morphological characterization

Scanning electron microscopy (SEM) images were taken with a JEOL Field Emission Gun model JSM-7401F, with an acceleration voltage of 5 kV and a filament current of 10 μA.

3. Results and Discussion

3.1. Silver electrodeposition onto HOPG in the presence of PA

Picolinic acid (2-pyridine carboxylic acid) has two functional groups, the carboxylic group in the α-position and the pyridinic-nitrogen site, whose acid equilibrium constants are $pKa_1 = 1.03$ and $pKa_2 = 5.21$, respectively [17]. The predominant chemical species in aqueous-PA solution are $\mathbf{H_2Pic^+}$ (protonated) at pH < 1.03, **HPic** (zwitterion) at pH around 3.0, and **Pic**$^-$ (anion) at pH > 5.21. From a chemical structure viewpoint, only the latter two species have functional groups available for coordination with silver ions present in the electrolytic solution. The stability constants for the corresponding 1:1 complexes are given by reactions (1) and (2) at pH 3.0 and 6.5, respectively [13,14].

$$Ag^+ + HPic \rightleftarrows [Ag(HPic)]^+ \quad K_{[Ag(HPic)]^+} = (11.5 \pm 0.6)\,M^{-1} \qquad (1)$$

$$Ag^+ + Pic^- \rightleftarrows [Ag(Pic)] \quad K_{[Ag(Pic)]} = (800 \pm 100)\,M^{-1} \qquad (2)$$

In order to study the effect of PA during silver electrodeposition onto and stripping from HOPG, j/E potentiodynamic profiles were obtained in both presence and absence of 0.5 mM PA in 0.1 M $KClO_4$ and 1.0 mM $AgClO_4$ solution at pH 3.0, with the predominant additive species under these conditions being **HPic**. In the cathodic scan of the first potentiodynamic cycle recorded in 0.5 mM PA solution (Fig. 1), the onset potential for silver deposition is -0.15 V

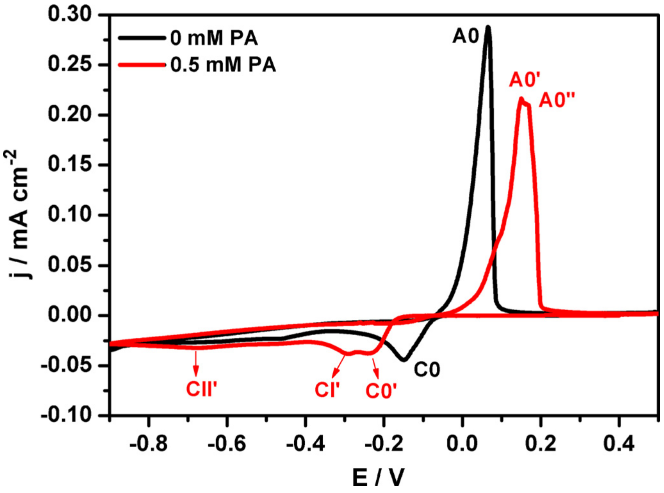

Fig. 1. Potentiodynamic j/E profiles of silver deposition onto HOPG in 0.1 M $KClO_4$ + 1.0 mM $AgClO_4$ solutions at pH 3.0, in the absence (black line) and presence of 0.5 mM PA (red line). Scan rate: $1\,mV\,s^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)