

Mechanisms and Molecular Aspects of Copper Electrodeposition

A.L.Portela, G.I.Lacconi and M.López Teijelo

INFIQC, Depto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Pabellón Argentina, Ciudad Universitaria, 5000 Córdoba, Argentina

SERS (Surface Enhancement of Raman Scattering) has been proved to be a very sensitive and chemically specific tool for probing adsorption of additives at the electrode/solution interface. Since the intensity of SERS signals is related to the surface structure, this method has been nowadays further extended to the in-situ monitoring during electrocrystallization processes. The purpose of the present work is to study the effect of pyridin-carboxylic acids (PCA) upon the mechanism and morphology of copper layers formed in slightly acidic solutions of copper sulphate. The copper electrodeposition process was followed through the analysis of the vibrational bands of the surface active species of PCA.

The electrolytic solutions consisted of 0.01 M CuSO_4 + 0.1 M Na_2SO_4 of different pH with or without PCA added at various concentrations. A three-electrode spectroelectrochemical cell with a Pt disc as substrate, a Pt wire as counter-electrode and a saturated calomel electrode was employed. For the SERS experiments a Raman Renishaw Ramascope spectrometer and an Imaging Microscope 2000 System with a He-Ne laser (633 nm, 3.5 mW on the sample) were used.

Electrochemical results indicate that the addition of nicotinic acid produces an inhibition of current for copper electrodeposition which is related to the additive adsorption. At low potentials copper deposition is accompanied by the formation of Cu(I) complex species with nicotinic acid molecules. These species as well as Cu(II) complex species are electroreduced at more negative potentials. On the other hand, in the presence of picolinic acid the electrodeposition takes place in different potential regions from both Cu(II) free ions and complex species and no evidence of Cu(I) complex formation is obtained.

The surface morphology of copper deposits is strongly dependent on the conditions of deposition. In the absence of PCA, surfaces with high roughness and formation of loose deposits are obtained while with PCA added, deposits are very smooth and bright.

The remarkable differences between solution and surface spectra point to a strong interaction between copper deposits and PCA species. The sharp SERS signal intensity drop at about 1600 cm^{-1} and the absence of the band of $\nu^{\text{C=O}}$ indicate that cations are not adsorbed. The SERS spectra of nicotinic acid obtained at different pH values are clearly related to the anion as the predominant adsorbed species in the interfacial region. Depending on the potential and time values used in the copper deposition, the adsorption of the zwitterion of nicotinic acid also becomes evident. More active surfaces for Raman enhancement of nicotinic adsorbed species are obtained at pH 1.5. In this case both functional groups

(pyridine and carboxylic) are coordinated to the metal surface.

The SERS intensity diminution for nicotinic acid relative to that of the other isomers could be due the molecules interaction with a more uniform and smooth copper surface.

Acknowledgments: We thank CONICET, CONICOR-DAAD and SECYT-UNC for their financial support.