

Emergency of electrochemical bistability in the cathodic deposition of copper

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Abstract

Electrodeposition of copper from acidic aqueous solutions is modified by the addition of small amounts of o-phenanthroline giving rise to bistability. A physical-chemical mechanism is proposed in order to explain which species act as surface-blocking agents.

Key words: electrodeposition, nonlinear dynamics, bistability.

Introduction

Nanostructured metallic multilayers in the electrodeposition of copper can be spontaneously synthesized when the system is kept far from thermodynamic equilibrium. We have focused on the understanding of how adsorption of a blocking agent can tune the electrodeposition behavior by altering the total surface area¹. For this purpose, we perturbed the electrodeposition of copper in acid media with small amounts of o-phenanthroline (*phen*).²

Results and Discussion

Negative Differential Resistance (NDR) and hysteresis are observed in the cyclic voltammograms (Fig. 1) when 2.0 mmol.L⁻¹ *phen* is added. The appearance of the NDR is attributed to adsorption of some species which suppresses the electrodeposition of copper. The hysteresis indicates that the system has two stable steady states (SSI and SSII) for the same set of controlling parameters, the so-called bistability (BS).

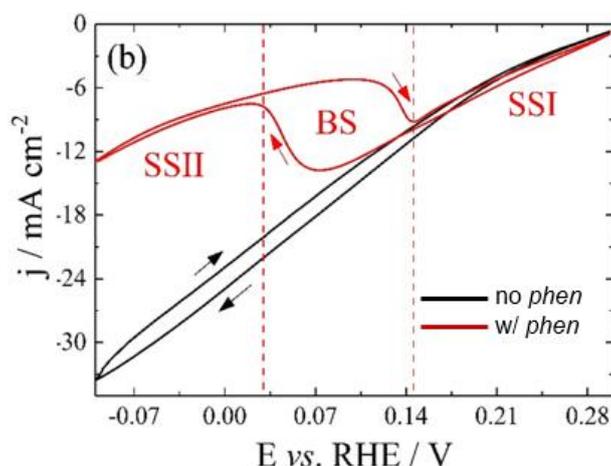


Figure 1. Cyclic voltammograms with and without addition of *phen*. We used a 3-electrode array with WE: Pt-poly plate (1.41 cm²), RE: reversible hydrogen electrode and CE: Pt-poly plate. The scan rate was 0.01 V.s⁻¹, [H₂SO₄] = 0.5 mol.L⁻¹, [CuSO₄] = 0.5 mol.L⁻¹, [*phen*] = 2.0 mmol.L⁻¹. Potential limits were -0.1 V and +0.3 V vs RHE.

In order to further investigate the phenomena involved in the appearance of the NDR and bistability region, we have performed a series of experiments, including:

- Cyclic voltammetry measurements varying the values of (a) an external resistance between the working and counter electrode, (from 0 to 25 ohm), and (b) concentration of *phen* (from 0.5 to 2.0 mmol.L⁻¹), in order to construct bifurcation diagrams. We have found that the bistability region increases as the resistance is increased or the concentration of *phen* is decreased.

- Gravimetric monitoring via Electrochemical Quartz Crystal Nanobalance (EQCN) measurements, in order to evaluate mass changes occurring at the electrode surface during the electrodeposition of copper. In the presence of *phen*, sharp mass/charge (m/q) peaks appear, which indicates adsorption of blocking species.

- Electrochemical Impedance Spectroscopy (EIS) measurements under potentiostatic control, so as to evaluate the dynamics of the electrochemical processes. At 0,12 V vs RHE (that is, in the bistability region), the obtained Nyquist plot in the presence of *phen* is consistent with a HN-NDR process (N-shaped, hidden NDR).

- Imaging analysis using Scanning Electron Microscopy (SEM) in order to observe and compare the morphology of the copper deposits. This work is still in progress, but so far, we have observed that the surface of the deposits is very different between SSI, SSII and the bistability region.

Conclusions

Electrodeposition of copper in acidic aqueous solutions was modified by the addition of small amounts of o-phenanthroline giving rise to bistability. We were able to tune bistability by varying the external resistance and concentration of *phen*. Mass/charge values obtained via EQCN measurements are in agreement with the proposed mechanism, which indicates adsorbed and inhibiting metallic copper complexes with *phen* as ligands. With EIS and SEM measurements it was possible to access the very contrasting features of the steady states and the bistability region.

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¹ Koper, M.; *Electrochimica Acta*. **1992**, *37*, 1771.

² Nakanishi, S.; Sakai, S.I.; Nishimura, K.; Nakato, Y.; *J. Phys. Chem. B* **2005**, *109*, 18846.