

Studies of Se Deposition and H₂Se Electrocrystallisation on Pt Ultramicroelectrodes

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The electrodeposition of selenium and metal chalcogenides on foreign substrates has received much attention in the last years due to the possibility of forming thin films of semiconductor compounds¹. Those films have found numerous applications in electronic and electro-optical devices and several studies have been reported on their preparation and properties. These films can be obtained using a variety of techniques, but from an economical point of view, electrodeposition is one of most interesting ways to obtain highly ordered films. Despite this, investigations of the initial stages (nucleation and growth mechanisms) for selenium film depositions have remained largely ignored.

This work reports studies of the initial stages of Se deposition and the subsequent H₂Se electrocrystallisation on a disc-shaped Pt ultramicroelectrode (*ume*) carried out by cyclic voltammetry, chronoamperometry and atomic force microscopy (*AFM*).

The electrochemical measurements were performed using a two-electrode cell with a saturated calomel electrode (*SCE*) as auxiliary/reference. The working electrode was a Pt *ume* ($\phi = 50\mu\text{m}$) sealed in glass. Before each measurement, the *ume* surface was polished with emery paper 1200 (3M) and thoroughly washed.

The electrolytic solution was 0.01 M SeO₂ + 0.50 M H₂SO₄. The reagents were from Merck P.A. and water from the Millipore ion-exchange system.

The electrochemical behaviour of selenium is presented in Fig. 1 for different inversion potentials (E_{inv}). The cathodic scan reveals two peaks at around 0.45 (peak I) and 0.28 V (peak II), respectively. Peak I corresponds to the underpotential deposition (*upd*) of selenium while peak II can be ascribed to massive selenium deposition. Re-oxidation of these two species is observed in the same region of the platinum oxidation. Thus, peak I' is due to selenium *upd* dissolution while peak II' is associated at massive selenium dissolution. This last peak only appears when E_{inv} is lower than 0.35 V and increases in intensity, as the E_{inv} is made less positive.

The responses obtained for E_{inv} varying from -0.25 to -0.55 V reveal that selenium deposition completely inhibits hydrogen adsorption/desorption and shift the hydrogen evolution to more negative potentials. The voltammetric response obtained with an E_{inv} of -0.45 V exhibits one additional anodic shoulder at more positive potentials. This is more clear for $E_{inv} = -0.55$ V (peak III) and has been attributed to the dissolution of H₂Se formed in the cathodic scan².

The study the H₂Se electrocrystallisation is important since that species can affect the films formed in the presence of other metals such as Ag, Cu, Cd, Pb, etc. The chronoamperometric experiments were performed from an initial potential of 0.8 V to final values varying from -0.45 to -0.49 V with a intermediate hold at 0.2 V for 2 s to grow a selenium layer.

The current transients exhibit a single maximum with both the peak current and peak time values dependent on the final potential. Analysis of the charge density values for the intermediate potential step indicates the deposition of two selenium monolayers.

The current transients were analysed using the equations below that were previously developed in our laboratories for nucleation processes on disc-shaped *ume*³. They correspond to instantaneous and progressive nucleation processes controlled by diffusion, respectively:

$$I = (4nFDc^{\infty}r + 8nFc^{\infty}r^2 D^{1/2} \pi^{-3/2} t^{-1/2}) [1 - \exp(-N\pi kDt)] \quad (1)$$

$$I = (4nFDc^{\infty}r + 8nFc^{\infty}r^2 D^{1/2} \pi^{-3/2} t^{-1/2}) \times [1 - \exp(-0,5AN_{\infty}\pi k'Dt^2)] \quad (2)$$

where N is the number of nuclei formed, AN_∞ is the rate of nuclei formation and k, k' are experimental constants.

For all final potentials investigated here, a good agreement between the experimental transients and the equation for instantaneous nucleation (1) was observed after application of a non-linear fitting procedure.

The study of H₂Se electrocrystallisation was complemented by *ex situ AFM*. Figure 2 shows *AFM* images (2.5 x 2.5 μm) of the deposit obtained potentiostatically at -0.47 V for 0.29 s. It is possible to observe several growing centres uniformly distributed on the platinum surface thus confirming the instantaneous mechanism derived from the non-linear fitting.

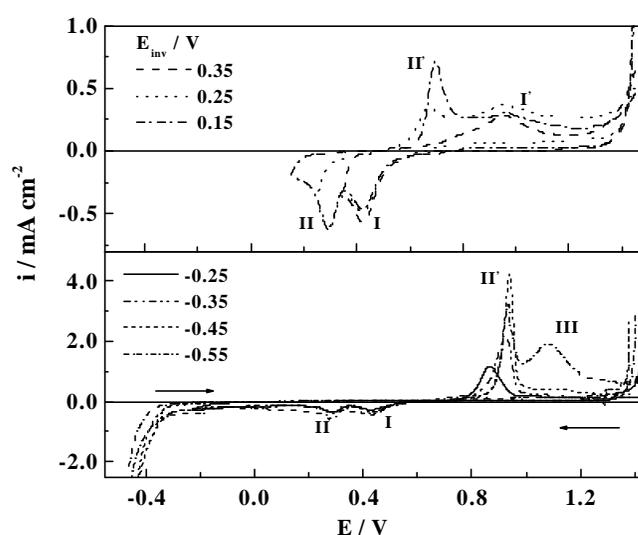


Fig. 1 Cyclic voltammograms for Se deposition and dissolution on Pt *ume* at 5 mV s⁻¹ for different inversion potentials.

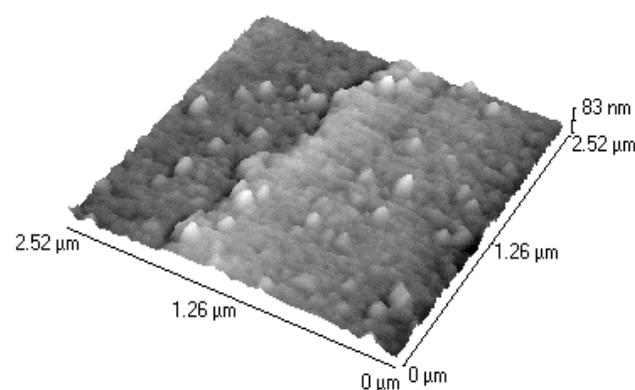


Fig. 2 –AFM of H₂Se deposited at -0.47 V with t=0.29 s.

References:

- 1- Kimmel, M. et al., *Electrochim. Acta*, **45**, 3737 (2000).
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