ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Electroanalytical Chemistry 583 (2005) 273–285

Journal of Electroanalytical Chemistry

www.elsevier.com/locate/jelechem

Effect of diffusion in underpotential deposition: Simulated and experimental results

E. Kirowa-Eisner *, R. Gepshtein, E. Gileadi

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, 69978 Tel Aviv, Israel

Received 3 March 2005; received in revised form 27 May 2005; accepted 1 June 2005
Available online 26 July 2005

Abstract

Diffusion limitation can play a role in shaping the CVs during *upd* formation, in spite of the fact that the amount of metal deposited is very small, of the order of 1–2 nmol/cm^2. In this paper, the shapes of cyclic voltammograms are evaluated quantitatively by digital simulation. The Frumkin adsorption isotherm and reversibility are assumed. A dimensionless parameter P is defined, which is proportional to the ratio between the diffusion-limited and the surface-controlled peak current densities. A domain in which diffusion can be neglected is presented by a series of lines of constant P in plots of $\log c_{\mathrm{bulk}}$ vs. $\log |v|$. This will allow one to choose the combinations of concentrations and sweep rates where experiments can be conducted without significant interference by diffusion limitation. The results of simulation were compared for the case of *upd* formation of lead on a polycrystalline silver substrate. Very narrow CV peaks are observed for this system, and the value of the interaction parameter in the Frumkin isotherm is found to be $f = -2.5 \pm 0.1$. Good agreement between experiment and the results of simulation was found when this value was employed.

Keywords: Underpotential deposition; Frumkin isotherm; Diffusion control; *upd* of lead; Polycrystalline silver; Digital simulation

1. Introduction

Underpotential deposition has been studied for many substrate/metal couples [1–5]. As the technology of preparing single crystals of metals and their use as electrodes has developed, the work on *upd* tended to concentrate on formation of such monolayers on different crystal faces [6–11]. It has commonly been observed that the behavior depends on the crystal face exposed to the solution. Employing cyclic voltammetry, the position of the peak potential associated with *upd* formation is found to be different for different crystal faces, and the shape of the voltammogram can also be quite different. The former implies that the energy of adsorption depends on crystal faces. This is not surprising, in view of the well-known observation that both the work function and the potential of zero charge (pzc) are crystal-face dependent. The latter indicates, in the opinion of most authors, that the structure of the monolayer is also different, and the formation of 2-dimensional phases, which would be expected to depend on the specific geometry of each crystal face, has been observed [8,9]. Although it is recognized that *upd* formation is an adsorption process, relatively little attention has been paid to the analysis of the adsorption isotherms involved.

When *upd* is studied on polycrystalline substrates, several adsorption/desorption peaks are observed on some of the metals, but not on others. These peaks can sometimes be associated with a peak observed on one particular crystal face on a single-crystal substrate [11]. For example, employing polycrystalline silver for *upd* lead, one usually observes a single peak, as seen in Fig. 1, while on gold at least two peaks are commonly observed, (cf. [11,12]). Moreover, it was argued that

---

* Corresponding author. Tel.: +972 36408239; fax: +972 36409293.
E-mail address: eisner@post.tau.ac.il (E. Kirowa-Eisner).

0022-0728/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2005.06.010

one of the peaks observed on gold represents the overlap of two types of adsorption sites [11]. This implies that different crystal faces are exposed to the solution for different substrates, but why this should be the case has not generally been discussed. It could be argued that even though gold and silver are mechanically pretreated in an identical manner, the difference in hardness of the two metals could give rise to different surface morphologies. Still, even the best mechanical polishing leaves a rough surface, on the atomic scale, and the usual electrochemical pretreatments cannot eliminate this roughness. Even if one or two crystal faces are predominant on the surface of a polycrystalline substrate, other adsorption sites should be abundant enough to be detected. In other words, it is not surprising that two or three adsorption sites are detected on a polycrystalline gold substrate – it is more surprising that one does not routinely observe many peaks on any polycrystalline substrate in the study of *upd* formation.

In a recent publication we studied the formation of *upd* of lead on polycrystalline gold and silver substrates [12]. Special attention was given to formation of such layers from dilute solutions, under conditions of diffusion limitation, and to the determination of the relationship between the concentrations and sweep rates where diffusion limitation starts to have an effect. Considering that the peak current density controlled by diffusion is proportional to the product $c_{\text{bulk}} \times |v|^{0.5}$, and the peak associated with *upd* formation is proportional to the sweep rate, $|v|$, it was concluded that the influence of diffusion on the surface process would be determined by the ratio $c_{\text{bulk}}/|v|^{0.5}$. For the wider peak of lead on gold this yielded an estimated maximum sweep rate of 1.0 V/s for a 12-mM solution of Pb^{2+}, which could be used without significant diffusion limitation. On a silver substrate, the corresponding concentration of lead would have to be about 0.2 M.

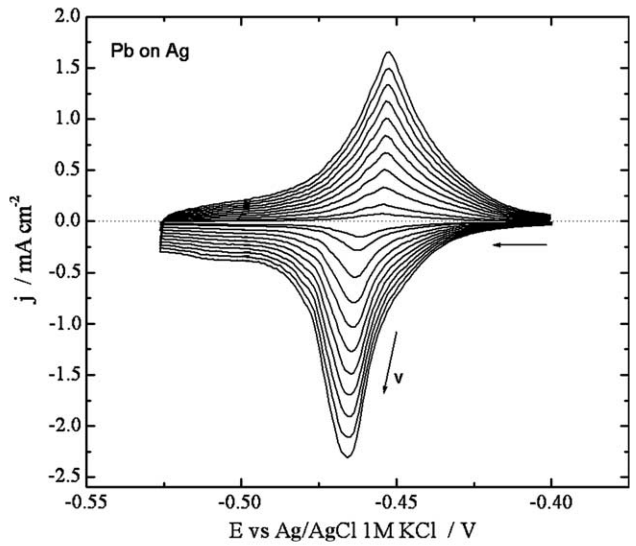

Fig. 1. Cyclic voltammograms for *upd* of Pb on polycrystalline Ag. 10 mM PbCl_2 in 1.0 M HCl; 3.0 M NaCl. $v = 5, 10, 20, \ldots, 100$ mV/s.

In the present work, we conducted numerical simulations for the deposition of lead on silver, in order to obtain quantitative predictions regarding the involvement of diffusion limitation in *upd* formation, and to calculate the height of the peak current and the position of the peak potential, over a wide range of solution concentrations, particularly when diffusion plays a significant role. We chose silver as the substrate, since it yields a single well-defined peak that can be characterized experimentally and compared to the predictions of the simulation.

2. Simulation

2.1. The fundamental equations employed for the simulation procedure

The process we consider is reversible adsorption including charge transfer.

$$M^{n+} + ne\Delta M_{upd}, \tag{1}$$

where M_{upd} refers to a neutral metal atom formed on the surface of a foreign substrate, at potentials positive with respect to the reversible potential for deposition of the metal in the same solution, i.e., in the *upd* region. The adsorption isotherm used is the Frumkin isotherm, which can be written as [13–15]

$$\frac{\theta}{1-\theta}\exp(f\theta) = \frac{c_{\text{bulk}}}{c_{\text{st.s.}}}\exp\left[-\frac{nF}{RT}(E - E^0)\right], \tag{2}$$

where $\underline{f}$, which can assume values of $f \geqslant -4$, is the rate of change of the apparent standard Gibbs energy of adsorption with coverage, in dimensionless form. Positive values correspond to lateral repulsion and/or surface heterogeneity, while negative values imply lateral attraction, which could, in certain cases, lead to two-dimensional phase formation. The standard state is chosen such that for $\theta = 0.5, f = 0$ and $c_{\text{bulk}} = c_{\text{st.s.}} = 1.0$ M, the peak potential is equal to the standard potential E^0.[1] The fractional surface coverage is defined, as usual, as

$$\theta = \Gamma/\Gamma_{\max}. \tag{3}$$

We note that the maximum surface coverage $\Gamma_{\max}$ does not necessarily correspond to the number of substrate atoms on the surface, since there may not be a one-to-one correspondence between the substrate and the adsorbate. For example, it was shown by X-ray scattering that *upd* of lead on Ag(1 1 1) has an incommensurate triangular closed-packed geometry, with the lattice of lead compressed by 1.2%, relative to bulk lead [16].

---

[1] Here E^0 stands for the standard potential for *upd* formation, not the standard Nernst potential for deposition of the same metal.