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Electrodeposition at the liquid/liquid interface: The chronoamperometric response as a function of applied potential difference

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Dedicated to Prof. D.J. Schiffrin, on the occasion of his 65th birthday

Abstract

The electrodeposition of Pd at the interface between two immiscible electrolyte solutions has been investigated using chronoamperometric techniques, under conditions of variable applied overpotential. An alumina membrane-templated interface has been used as a means to circumvent the agglomeration phenomena shown previously to affect deposit growth at this type of interface. Palladium deposition, from aqueous solutions of tetrachloropalladate, was induced by electron transfer from an organic phase electron donor (butylferrocene). The resultant data has been interpreted in terms of classical models, previously developed for amperometric deposition on solid electrode surfaces.

Keywords: Liquid/liquid interfaces; Metal deposition; Modified interface; Nucleation

1. Introduction

Metal deposition is one of the most thoroughly investigated areas of electrochemistry. This field continues to attract interest, both from a theoretical and an experimental viewpoint, with the underlying scientific aim being to understand the relationship between deposition conditions and the growth and morphology of the resultant deposit. Ultimately, the goal is to derive insight into how solid phases nucleate and grow from solution. The vast majority of experimental studies have dealt with deposition on solid electrode surfaces. The realisation that nucleation was most likely to occur at defect sites on the substrate surface [1] means that knowledge of the sample geometry (and therefore history) has become more important, as one needs to know the density and distribution of defect sites in order to make quantitative comparison between distinct deposition experiments of a given metal on a given conducting substrate. Experimentally, control over defect density is difficult to achieve [2,3]. An exception to this statement is the case of deposition on single crystal substrates, which has given further impetus to this area lately. This renewed interest is coupled to the development of scanning probe microscopy, which allows deposit distribution and morphology to be determined in situ on the nanometre scale [4]. Such experiments are technically difficult, however, and the role of phenomena such as potential-induced surface reconstruction can complicate analysis. To date, there have been a number of reports combining classical and/or atomistic models of cluster growth with studies of well-defined single crystal surfaces [5]. However, even if a single crystal surface is used as the substrate, the issue of parameter generality is not completely resolved, since in many

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cases the substrate stabilises the nascent cluster giving rise to phenomena such as underpotential deposition and, in fact, can influence the geometry and electronic structure of the deposit [6].

In 1996 Cheng and Schiffrin reported another approach to deposition at electrified interfaces, namely the potential-induced deposition of gold at the interface between two immiscible electrolyte solutions (ITIES), using water and 1,2-dichloroethane (DCE) solutions to form the electrified phase boundary [7]. The motivation behind this study was the molecularly smooth nature of the ITIES, which means that a minimal influence of the substrate on the deposit (for example, through epitaxial effects) should result. In fact, the formation of colloidal metal particles at liquid/liquid interfaces has a long pedigree [8], although electrolytic – as opposed to galvanic – deposition at this interface was first reported much more recently [9]. This preliminary communication of 1975 was overlooked until the aforementioned work of Cheng and Schiffrin [7], which suggested that micron-scale gold deposits were formed by the heterogeneous transfer of electrons across the water/DCE interface. Kontturi, Schiffrin and co-workers subsequently described palladium deposition at the water/DCE interface [10]. Analytical models were developed to relate the chronoamperometric response to the nucleation rate, k, and the maximum number of nuclei formed on the surface, N_0. The authors of this work noted the lack of fixed nucleation sites at the liquid/liquid interface made it an “ideal substrate” for interfacial nucleation studies. However agreement between experiment and theory was limited, an observation later attributed to the agglomeration of the metallic particles [11]. To draw an analogy with the deposition of metals on solid surfaces, the liquid/liquid case is closest to the case of deposition of a metal on an “inert” substrate, for example palladium on glassy carbon [12].

We have recently shown that an ensemble of micron-scale liquid/liquid interfaces can be formed by modifying the interface with appropriate membrane materials [13,14]. This process facilitates deposit characterisation, and has been applied to electrolytic deposition of palladium and platinum at the water/DCE interface [15,16]. Specifically, the use of the template allows retention of the particle distribution, which is otherwise lost on transfer to an electron microscope, for example. The presence of the membrane did not catalyse the deposition process for either metal, since the potentials observed for the onset of deposition were identical in the presence/absence of the membrane [15]. We attribute this behaviour to the electronically insulating character of the substrate. Galvanic deposition processes have also been reported using the template [17]. The presence of the template has the advantage of separating diffusion fields to particles growing in distinct pores (see Fig. 1). Furthermore, at longer times the flux imposed by the template will gradually evolve from a (hemi)-spherical to a linear field. Finally, in contrast to earlier experiments on palladium deposition [10,11], we have used an excess of electron donor over the palladium precursor (up to levels dictated by the solubility of the donor), so that mass-transport can be approximated in terms of aqueous phase diffusion only. To ensure that only intra-pore diffusion is significant, we have limited our analysis of the experimental chronoamperometry to the time-scale dictated by diffusion along the pore length, thus [18]:

$$t = \frac{\langle l^2 \rangle}{2D} \tag{1}$$

This approach has the advantage of simplifying the transport analysis of the problem, however the disadvantage is that only the short-time data ($t < 1.8$ s, with l as the membrane length of 60 μm [19], and the diffusion coefficient D as 1×10^{-5} cm^2 s^{-1} [11]) is used. One key assumption here is that transport of the palladium ions is predominantly via volume diffusion, rather than surface diffusion, processes. Surface diffusion effects may indeed contribute, but in the absence of reported data on metal complex diffusion rates on alumina surfaces, the volume coefficient has been taken to hold.

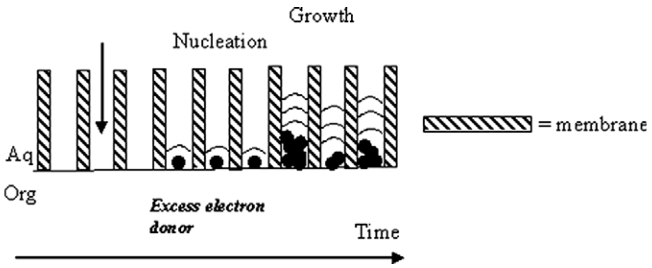

Fig. 1. Schematic of metal deposition at the membrane-templated interface. Use of the hydrophilic γ-alumina membrane constrains the growing deposit within the pores.

Using the assumptions of non-overlapping diffusive transport to the separated growing particles, where the flux is controlled by the supply of the metal precursor, this report attempts to interpret the observed chronoamperometric data for palladium deposition in terms of existing models for metal deposition at the electrode/electrolyte interface. A consistent increase in deposition current with applied overpotential (Galvani potential difference at the ITIES) was observed. The application of progressive nucleation models to the experimental data yields a low (fractional) value for the critical cluster size, N_{crit} (the minimum number of atoms required to form a stable palladium particle). There are prior reports of N_{crit} values tending to zero for electrodeposition on solid substrates, for example for palladium grown on pyrolytic graphite [20]. The experimental data is also interpreted in terms of instantaneous nucleation models, which yielded physically reasonable nucleus density values: the conclusions highlight the need for more work in this area to assess the applicability of classical electrodeposition models to the liquid/liquid interface.