

UPD COMPOSITES — AN OVERVIEW

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Systematic experiments have shown that codeposition of Pb and Tl UPDs on silver can be obtained successfully from solution containing Pb(II) and Tl(I) in presence of suitable complexing ligands like citrate, tartrate or EDTA. The UPDs of lead and thallium resulting through codeposition are found to be mutually influenced by the concentration of the Pb(II) and Tl(I) in the media. Voltammograms have further revealed the influence of sweep rate on the coverage of Pb and Tl UPDs. Besides, voltammetric studies with programmed potential inputs indicate that the Pb and Tl UPDs are formed only on adjacent sites and the two UPDs tend to interact resulting in the formation of an alloy. Analysis of the codeposition experimental data shows the inadequacies of the existing models that have been primarily developed for single UPD systems.

INTRODUCTION

Underpotential deposition (UPD) of a metal over foreign metallic substrate is an area of study presently pursued with a view to exploit the possible application of such modified electrodes in electrocatalysis [1-4]. Besides, it can provide insight into the phenomenon of electrocrystallisation associated with the electrodeposition of metals [5-6]. The influence of metallic UPD layers on electrocatalytic reactions has been reviewed [2,4,7]. However reports of attempts to codeposit UPD's of two metals on single metallic substrate have been scarce [8-10] although binary and ternary bulk metal depositions are well known. Studies of codeposition of two metals in their UPD state on a single metallic substrate help in understanding surface processes such as adsorbate-substrate interaction in the presence of another adsorbate and adsorbate-adsorbate interaction between the two UPDs, in addition to elucidating their role in the bulk deposition of mixed metals and/or alloys. Further, this codeposition approach may be explored to study the feasibility of formation/characterisation of two-dimensional alloys involving mono/submonolayer UPDs and potentialities for designing bimetallic catalysts. Codeposition of UPDs has not received attention, perhaps, mainly due to the difficulty arising out of interference caused by the bulk deposition of the more electropositive metal with the UPD of the less electropositive one. We have evolved a strategy to overcome this difficulty. It consists in selective shifting of the UPD potentials of the two metals to within a narrow potential window wherein the UPD's of both the metals occur free from interference due to the bulk deposition of either. Lead (II) is known to form more stable complexes with different complexing ligands than Tl(I). It may, therefore, be expected that in such a background of complexing ions, a shifting of Pb UPD potential may take place to a relatively more cathodic value close to the Tl-UPD potential. The use of complexing anions along with a judicious choice of cationic concentration is expected therefore, to facilitate codeposition of UPDs. We have demonstrated this in our recent communications [11-13]. The present paper highlights the significance of these results and reports more recent observations on these systems.

EXPERIMENTAL

An all-glass three-electrode cell described elsewhere [11] was employed in these studies. The working electrode was a polycrystalline silver disk of 0.378 cm². A Pt foil and a

normal calomel electrode (NCE) served as counter and reference electrodes respectively. All potentials are referred to NCE. The working electrode was polished well using alumina slurry (particle size of 0.05 μm) supplied by Bio Analytical System Inc., USA and subsequently cleaned under sonication.

All the chemicals used were of analytical grade and were used without further purification. Prior to experiments, the solutions were purged with pure nitrogen for an hour. A Wenking potentiostat(model POS 73) coupled with a Rikadenki X-Y-t recorder (model RW 201 T) was employed for recording cyclic voltammograms(CV). In the case of experiments with specially programmed potential inputs, a digital potentiostat (EG&G PAR model 273) was employed.

RESULTS AND DISCUSSION

Codeposition behaviour

Cyclic voltammograms describing the codeposition of Pb and Tl UPDs from citrate solutions are presented in Fig. 1 (curve 1). For easy comparison the CVs obtained for the individual UPDs of Pb and Tl are also presented in the same figure (curves 2 and 3). Two redox peaks could be seen in the figure, one at -510 mV and the other at -600 mV. By comparing the potential values of lead and thallium UPDs obtained from the single salt solutions, these two peaks can be assigned to Pb and Tl UPDs, respectively. This figure further explains that the UPD potential ranges of Pb and Tl can be swept without the interference of the bulk metal deposition of either under the experimental conditions. Use of the tartrate solution also yields similar behaviour for the codeposition of Pb-Tl UPD [14].

Effect of concentration of Pb(II) and Tl (I)

It is well known [15] that the extent of UPD coverage depends upon the concentration of the cations in the solution. Hence in these codeposition systems, the chosen concentration of the two cations should mutually influence the UPD behaviour of the two metals through their concentration-dependent coverage. The influence of Pb(II) concentration on Tl UPD and that of Tl(I) concentration on Pb UPD are described below.

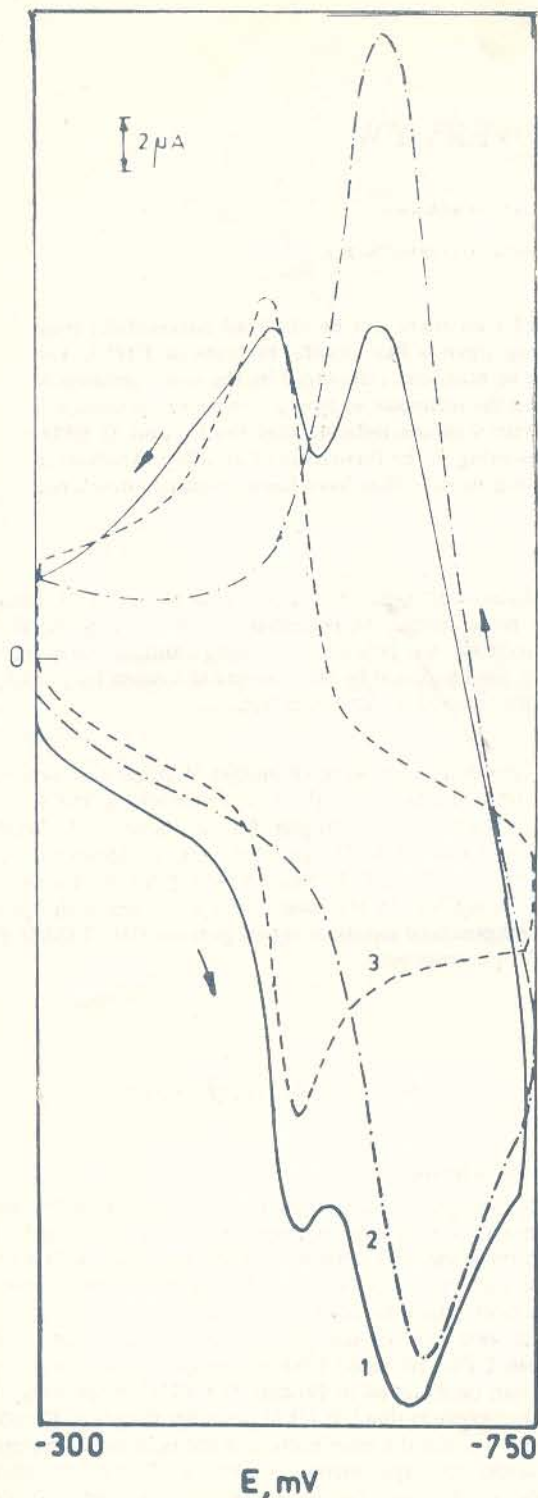


Fig. 1: Cyclic voltammetric response of polycrystalline silver from solutions containing (a) 0.05mM of Pb(II) and 0.1mM of Tl(I) [curve-1]; (b) 0.1mM of Tl(I) [curve-2]; and (c) 0.05mM of Pb(II) [curve-3]. Background electrolyte is 0.11M of sodium citrate and 0.01M of sulphuric acid. Scan rate 100 mV.s^{-1}

During codeposition, underpotential deposition of lead (-510 mV) precedes that of thallium (-600 mV). Hence the presence of Pb-UPD on silver substrate is expected to influence the UPD behaviour of Tl. To have more insight, codeposition experiments

have been carried out keeping Tl(I) concentration constant at 0.1 mM and varying the Pb(II) concentration from 0.01mM to 1mM. At low Pb(II) concentrations (i.e. below 0.05mM) Tl UPD is predominant as evidenced by its well-defined peaks. The UPD behaviour of lead is less marked by the presence of a small hump at a potential of -500 mV . The absence of a well-defined peak for the Pb UPD is obviously due to its low concentrations. However, at higher Pb(II) concentrations (above 0.5mM), UPD of Tl is completely masked by the presence of Pb UPD. In the intermediate concentrations, the UPD corresponding to both Pb and Tl are well marked. Pb UPD tends to predominate when its concentration is increased, resulting in a lower coverage by thallium. Typically, for a thallium concentration of 0.1mM, the charge due to Tl UPD coverage (Q_{Tl}) is found to be 200, 120, and $75 \mu\text{C.cm}^{-2}$, at Pb(II) concentrations of 0, 0.05 and 0.1mM, respectively. This observation indicates that at lower concentrations of lead, the lead ad-atoms do not cover the silver surface completely. Thallium can be deposited on those vacant sites as observed in the experiments. However, when the concentration of lead ion is increased to more than 0.1mM, a complete monolayer of lead is formed leaving no site for Tl deposition. Further, in these higher concentrations of Pb(II), complications due to bulk deposition of lead also occur. The results presented above indicate that Pb and Tl UPDs on silver substrate occur only on adjacent sites and that the formation of Tl monolayer over lead UPD is unlikely. This result is further supported by the absence of either reports[1] on Tl UPD on Pb or the successful efforts [16] to obtain the same in our laboratory.

Experimental data on the variation of Tl(I) concentration keeping the Pb(II) concentration constant have revealed the following:

- (i) At lower Tl(I) concentration (below 0.01mM), the UPD behaviour of Tl is distorted by diffusion limitations and only Pb UPD is predominant.
- (ii) In the range of 0.05mM to 0.5mM, the deposition and dissolution peaks for both lead and thallium could be noticed as long as the Pb(II) concentration does not exceed 0.1mM.
- (iii) At Tl(I) concentrations greater than 0.5mM, peaks corresponding to the deposition of lead and Tl UPD are observed, but on the dissolution side only one peak corresponding to Pb UPD is observed. This behaviour is further found to be influenced by the sweep rate.

Effect of scan rate

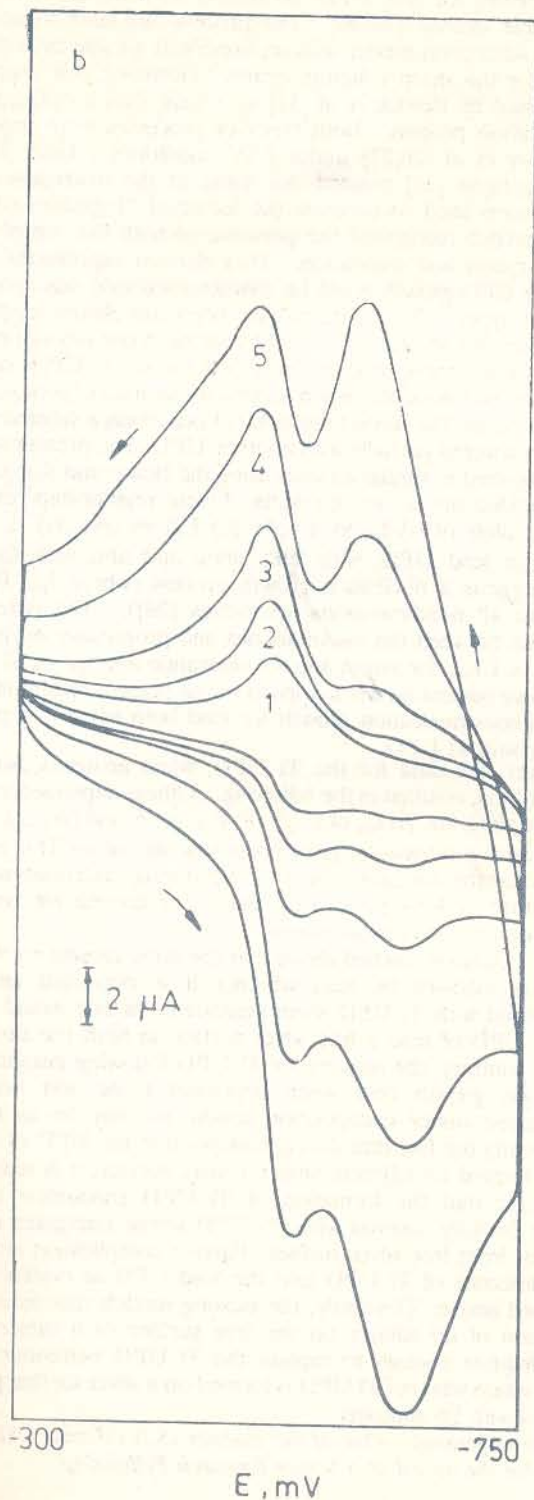
In codeposition systems, such as the one described above, if the kinetics of the two UPDs were to be different, then one may expect the codeposition behaviour to be markedly influenced by the scan rate. This is amply proved by the experimental results described below.

Figure 2 gives the effect of sweep rate on the codeposition behaviour of Pb and Tl UPDs from citrate solutions containing Pb(II) and Tl(I) at 0.05mM and 0.1mM respectively. It can be seen from the figure that well-defined UPD peaks for both Pb and Tl occur at sweep rates greater than 20 mV s^{-1} . The charges corresponding to the Pb and Tl UPD dissolution peaks are computed for each sweep rate from the CVs and are presented in Table I. The data show that as the scan rate is increased, the charge corresponding to Pb UPD decreases while that due to Tl UPD increases. However, the total charge corresponding to Pb and Tl UPDs remains constant and independent of the scan rate. These experiments further support the view that Pb and Tl UPDs are codeposited only on adjacent sites and do not grow over the other. This view is substantiated by an experiment under conditions where both UPD peaks corresponding to Pb and Tl could be seen; for example, at 0.05mM of Pb(II) and 0.1mM of Tl(I), prolonged polarisation at Pb UPD potentials (in this case -510 mV) for five minutes followed by a potential sweep results in the absence of Tl UPD and dissolution which would be otherwise observable at these

concentrations (if no preconcentration of Pb UPD is effected over prolonged periods).

TABLE-I: Influence of sweep rate on UPD coverage of lead and thallium on silver

V (V.s ⁻¹)	Q _{Pb} (μC.cm ⁻²)	Q _{Tl} (μC.cm ⁻²)	Q _{Pb} + Q _{Tl} (μC.cm ⁻²)
0.005	130.0	—	130.0
0.010	112.0	42.5	154.5
0.020	105.0	50.0	155.0
0.050	95.5	61.5	157.0
0.100	75.0	68.3	143.3



due to kinetic effects, then it should also be the case in the absence of Pb UPD. However, this is not true. Hence, these results suggest the possible formation of a new phase containing both Pb and Tl in the underpotential states. This fact is further supported [17] from the fact that lead can dissolve nearly 87 atomic per cent of Tl giving rise to a solid solution, while the reverse is not possible. Hence, experiments carried out using programmed potential inputs [12,14] to understand the role of "time" factor have shown that, given sufficient time, the two UPD metals interact to form an alloy. This is well substantiated by voltammetric experiments in which the codeposition behaviour of Pb and Tl are recorded at two different scan rates. It can be observed from Fig. 3 that deposition and dissolution peaks due to both Pb and Tl occur at a higher sweep rate (50 mV.s⁻¹) while at a lower sweep rate (5 mV.s⁻¹) only one dissolution peak corresponding to Pb UPD occurs despite the presence of both the deposition peaks. Further, any interaction between the substrate (Ag) and adsorbate (Pb and Tl) at the underpotentials being studied, is unlikely because a limiting and constant coverage is reached in the above experiments (unlike in the case of Ag/Cd and Au/Cd where the UPD metal can diffuse into the substrate resulting in the formation of a surface alloy whose coverage increases with time of deposition and often exceeds a monolayer [18,19]). Moreover, work reported on individual Pb and Tl UPDs on silver in other acidic media too gave no evidence for surface alloy [20,21]. These observations suggest that UPD alloying between Pb and Tl adsorbates takes place and surface alloying involving substrate and adsorbate is improbable.

Effect of anions

The UPD of single metals is found to be strongly influenced by the nature of anions present in the electrolytic medium. Hence it is but natural to expect the codeposition behaviour too to depend on the nature of the anion in the background solution. Accordingly, the above codeposition systems have been studied from two other anionic ligands viz. tartrate and EDTA. The experimental results obtained for single UPD systems in solutions containing complexing ligands show UPD peaks at more cathodic potentials than in perchlorate solutions. Besides, the peak becomes sharper. It is also interesting to observe that the peak separation is influenced by the nature of the anion. Thus during codeposition, the deposition sequence of Pb and Tl UPDs is found to be reversed i.e. in EDTA background electrolyte, Tl UPD precedes the Pb UPD during deposition unlike in citrate and tartrate media where Pb UPD occurs prior to Tl UPD. Thus, the results, (discussed in detail elsewhere [22]) point to the possibility of employing suitable complexing ligands to advantageously manipulate the UPD behaviour of metals.

Irreversible UPD

The phenomenon of UPD has fascinated many researchers since modification of electrode surface with mono/submono layers of metals can significantly enhance its catalytic activity [2].

Fig. 2: Influence of sweep rate on voltammetric pattern of polycrystalline silver from solution containing 0.05 mM of Pb(II) and 0.1mM of Tl(I) (1) 5 (2) 10 (3) 20 (4) 50 (5) 100 mV.s⁻¹

The results presented above clearly show the interaction between Pb and Tl UPDs and the time dependent nature of the interaction. The absence of a separate dissolution peak for Tl UPD could not be ignored as due to kinetic effects. Because, if the above result is

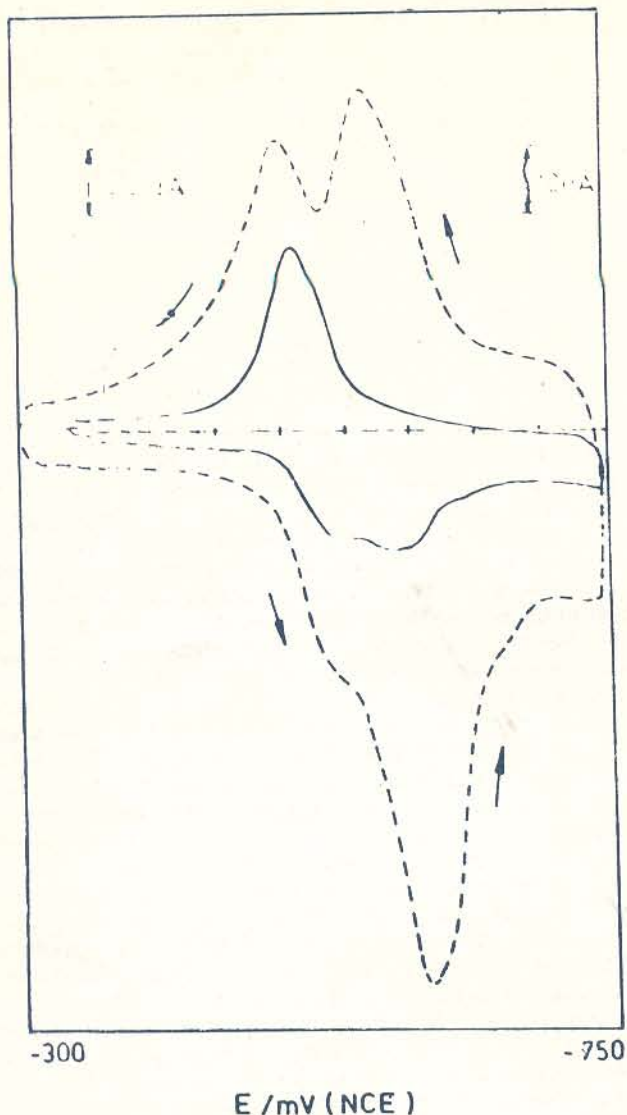


Fig. 3: Cyclic voltammograms showing the codeposition behaviour of lead and thallium from solution containing a mixture of 0.05 mM of Pb(II) and 0.5 mM of Tl(I) at a sweep rate of (i) 5 mVs⁻¹ (—) and (ii) 50 mVs⁻¹ (.....)

Considerable amount of work has been reported, describing the enhanced catalytic activity of electrodes modified with UPD [7]. In such studies, the UPD modification is brought about *insitu* i.e. the UPD modification is reversible and allowed to take place during the course of the reaction itself. On the other hand, if the substrate modification with UPD can be made irreversible, then the modification can be done *exsitu* and the modified electrode can be used for catalysis. Attempts to obtain such irreversible UPD layers through chemical procedures have been described [23,24]. An electrochemical approach capable of yielding an irreversible submonolayer of Pb and Pb-Sn on a polycrystalline silver has been achieved for the first time in our laboratories. This irreversible UPD layer is obtained through a potential cycling in a suitable potential range from a solution containing a suitable cation and a complexing anion like citrate or tartrate. Analysis of voltammetric peaks indicates only a submonolayer coverage with charge equivalent of $80 \pm 30 \mu\text{C.cm}^{-2}$. Further details are discussed elsewhere [22].

Models for UPD

The modelling of the UPD formation and its growth is of considerable interest [25-30]. The process has been treated by the pure adsorption model with an abnormal g -value in order to account for the sharp voltammograms. However, this approach was criticised by Bewick *et al.* [31] who have shown evidence for the nucleation process. Both types of processes were modeled by Conway *et al.* [26,27] under LSV conditions. Later Bosco and Rangarajan [28] pointed out some of the discrepancies in the equations used to describe the assumed "Ingestion effect". Their approach recognised the presence of both the components i.e. adsorption and nucleation. They derived expressions using which the UPD growth could be characterised into adsorption or nucleation types. Those criteria have been successfully employed in characterising several single UPD systems in our laboratory [32-35]. However, these models developed for single UPDs can be expected to be inadequate when applied for analysis of codeposition systems wherein the second metal UPD occurs on a substrate that is already covered partially with another UPD. The present system when subjected to similar analysis using the Bosco and Rangarajan model yielded the following results. Linear relationship resulting from the plots of (i) I_{pn} vs $1/\sqrt{v}$, (ii) E_{pn} vs \sqrt{v} , (iii) $\Delta E_{1/2n}$ vs \sqrt{v} , for lead UPD, with lead alone and also with thallium UPD, suggests a nucleation growth process (where I_{pn} , E_{pn} , $\Delta E_{1/2n}$ are all nondimensional quantities [28]). The criteria to distinguish between the instantaneous and progressive nucleation, viz. I_{pn} vs $1/E_{pn}$ for instantaneous nucleation and I_{pn} vs $1/E_{2pn}$ for progressive nucleation when applied to the present system indicate instantaneous nucleation growth for lead both when it is present alone or with Tl UPD.

However, the data for the Tl UPD, when analysed using the above criteria, resulted in the following. A linear dependency for all the three plots, viz. (i) I_{pn} vs $1/\sqrt{v}$ (ii) E_{pn} vs \sqrt{v} and (iii) $\Delta E_{1/2n}$ vs \sqrt{v} indicates a nucleation growth kinetics only when Tl is present alone while the formation of Tl UPD during codeposition from the mixture of Pb(II) and Tl(I) defies the criteria for both the nucleation and adsorption models.

The conclusions reached above that the same growth mechanism is always followed by lead whether it is deposited alone or codeposited with Tl UPD seem reasonable as one would expect for the UPD of lead a free silver surface in both the situations. On the contrary, the reasons for Tl UPD following instantaneous nucleation growth only when deposited alone and becoming complicated under codeposition conditions may be as follows. Considering the fact that during codeposition the UPD of Pb and Tl are formed on adjacent sites on silver surface, it is reasonable to assume that the formation of Tl UPD encounters a silver surface partially covered with Pb UPD whose energetics may be different from free silver surface. Further complication arises out of coalescence of Tl UPD into the lead UPD as evidenced and discussed above. Obviously, the existing models that assume the formation of an adlayer on the free surface of a substrate are not adequate enough to explain the Tl UPD behaviour during codeposition wherein Tl UPD is formed on a silver surface partially covered with Pb adatoms.

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