

# Codeposition of lead and thallium UPD on polycrystalline silver

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The Underpotential Deposit (UPD) of metals on different substrates has been studied in detail. However, the simultaneous UPD of two metals on a single substrate has been very little studied, probably due to the stringent experimental conditions viz. the UPD of two metals has to occur without the bulk deposition of either. In the present study, simultaneous UPD of Pb and Tl on polycrystalline silver has been investigated. Initially the experimental condition satisfying the above requirements has been standardised. Subsequently the influence of scan rates on the simultaneous UPD behaviour of both the metals and also the effect of concentration on one metal on the UPD behaviour of the other have been studied.

**Key words:** Underpotential deposition, codeposition of UPD's, voltammetry

## INTRODUCTION

Underpotential deposition (UPD) of metals on various substrates is gaining importance due to its possible applications in electrocatalysis [1]. The UPD behaviour of a number of metals like Pb, Tl, Cu, etc. on substrates like Ag, Pt etc. has been investigated in detail [2]. However, codeposition of two metals in their UPD state on a single substrate has been very little studied. The only available report [3] on this aspect is rather very sketchy and does not detail the experimental conditions. The obvious difficulty in obtaining the codeposition of UPD's of two metals, arises from the interference caused by the bulk deposition of the more electropositive metal. Taking advantage of the fact that UPD potentials of metals depend on the complexation tendency of the electrolytic medium [4], the background electrolyte can be judiciously chosen so that the UPD's of both metals occur distinctly before the bulk deposition of either. The codeposition of Pb and Tl UPD's on polycrystalline Ag has been investigated and the results are reported in this communication.

## EXPERIMENTAL

An all glass three electrode cell was employed. An Ag disc of 0.196 cm<sup>2</sup> area served as working electrode. The other electrodes were a Pt foil and NCE. Analytical grade chemicals were used and the solutions were deoxygenated before use. Potentiostat and X-Y recorder were used for the voltammetric investigations.

## RESULTS AND DISCUSSION

Detailed investigations have shown that an electrolytic

medium of 0.1M sodium citrate and 0.01M sulphuric acid facilitates the codeposition of Pb and Tl UPD's. The underpotential shifts obtained individually for Pb and Tl in this medium were 160 and 240mV respectively, which agree well with the values reported earlier [5] and are also in agreement with Kolb relationship. Further, the surface coverage in both cases is found to be concentration dependent. Charge calculations reveal sub-monolayer coverage at low concentrations approaching a full monolayer at concentrations greater than 0.0001M.

Cyclic voltammograms describing the codeposition of Pb and Tl are presented in Fig. 1. The salient features of these results are as follows: At a chosen fixed concentration of Tl (0.0001M), variation of Pb concentration from 0.00001 to 0.001M influences the UPD peaks of Tl significantly. At low concentrations, Tl peaks are more predominant, but they are practically absent at high concentrations. In the intermediate range (0.00005 and 0.0001M) UPD peaks of both Pb and Tl are well characterised. Further, in these concentrations, sweep rate is found to influence, markedly, the formation of UPD peaks. When the concentration of Pb is 0.00005M, Tl peaks are observed only at sweep rates higher than 20 mV.s<sup>-1</sup>, while sweep rates larger than 50 mV.s<sup>-1</sup> are needed for the appearance of well defined Tl peaks at 0.0001M concentration of Pb.

The absence of Tl peaks at concentrations of Pb greater than 0.0001M suggests that practically all active sites get occupied by Pb even before the onset of Tl UPD. At lower Pb concentrations, the coverage is incomplete before reaching the Tl UPD peak. This explanation appears to be substantiated by an experiment where ever at low concentrations of Pb (0.00005M) prolonged polarization at Pb UPD potentials for five minutes followed by the potential sweep over the Tl UPD potentials results in the

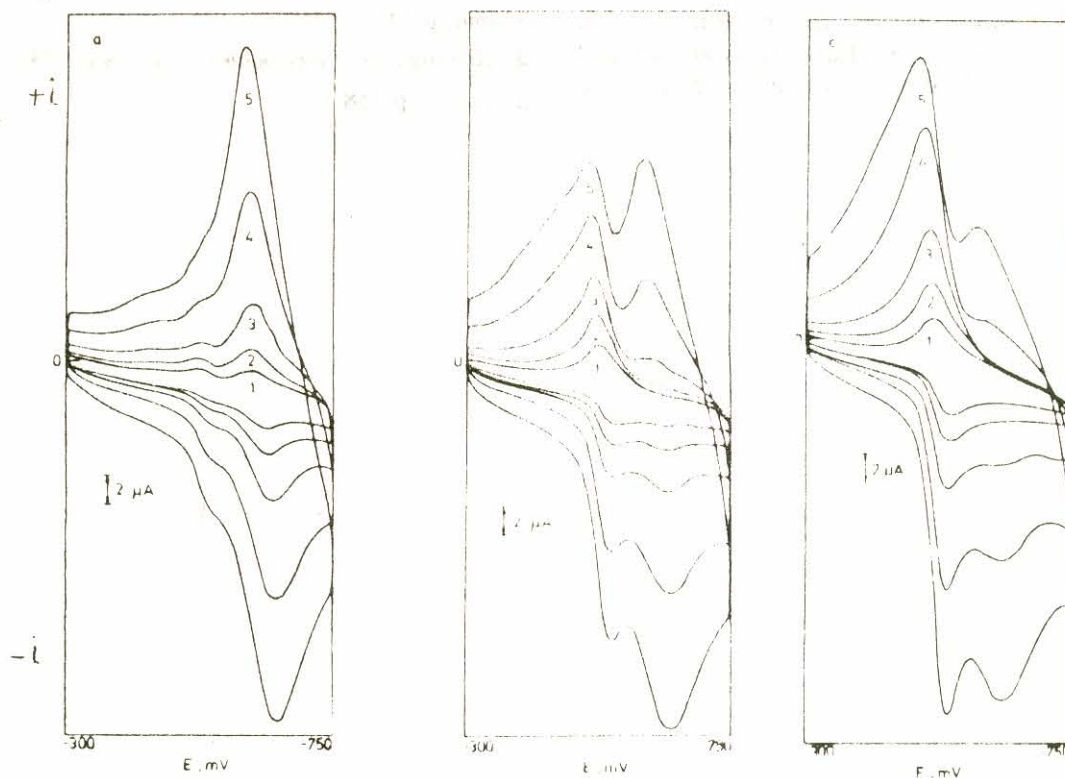


Fig. 1: CV's of pb and Tl UPD's on polycrystalline Ag from 0.1M sod. citrate + 0.01M sulphuric acid containing 0.0001M of Tl(I) and Pb(II) concentration of (a) 0.00001M (b) 0.00005M and (c) 0.0001M at sweep rates of (1) 5 (2) 10 (3) 20 (4) 50 and (5) 100  $\text{mVs}^{-1}$

absence of Tl peaks which would otherwise be observable at this concentration of Pb. These observations indicate that UPDs of Pb and Tl are codeposited adjacent to each other and formation of Tl UPD over Pb layer is not probable.

Further, at intermediate concentrations of Pb, increase of sweep rate results in decrease of Pb coverage and increase of Tl coverage. Interestingly, the total coverage observed under all these sweep rates tends to be a constant value which corresponds to a sub-monolayer coverage ( $120 \pm 15 \mu\text{c.cm}^{-2}$ ). This observation also tends to support the aforementioned view, viz. UPD layers of Pb and Tl on Ag are formed only on adjacent sites and not in the manner of one UPD over the other UPD. Further, the observed influence of sweep rate on the relative coverage can probably arise as follows: The work function difference  $\Delta\phi$ , normally considered to be the driving force for the UPD formation indicates that the UPD kinetics of Ag/Tl ( $\Delta\phi = 0.2\text{eV}$ ), is likely to be faster than that of Ag/Pb ( $\Delta\phi = 0.06\text{eV}$ ). As a result, the relative growth rates and hence the respective coverages for the two metal UPDs could be expected to follow the pattern that is noticed experimentally.

Finally, mention may be made of the interesting observation involving codeposition and stripping in solutions of Tl concentrations beyond 0.0001M. Two peaks

corresponding to Pb and Tl UPD's are observed in the cathodic sweep while only one peak corresponding to that of Pb UPD is noticed during the stripping process. The charge corresponding to this anodic Pb peak is larger than that due to the cathodic Pb peak. Can this observation be attributed to the formation of an intermetallic compound or a two dimensional alloy whose anodic dissolution may account for the increase in charge? Only future investigations should reveal.

## CONCLUSION

(i) The experimental conditions for the codeposition of Pb and Tl UPD's on polycrystalline Ag have been standardized. (ii) UPD codeposition is critically dependent on concentration of Pb and the sweep rate employed. (iii) UPD layers of Pb and Tl appear to form on adjacent sites of the Ag surface rather than one UPD over the other UPD.

## REFERENCES

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