# ELECTRODEPOSITION OF LEAD-TIN ALLOY FROM FLUOBORATE SOLUTION - A VOLTAMMETRIC STUDY

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Lead-tin alloy deposition is done commercially from fluoborate bath. Though the practical aspects of addition agents for producing quality deposits are widely reported, the basic aspects on influence of these addition agents on alloy deposition are important. The techniques of cyclic and linear stripping voltammetry on a copper electrode in a fluoborate solution, with and without addition agents, have been employed to throw light on the basic aspects, with the aim of understanding, optimizing and controlling lead-tin alloy deposition.

Key words: Electrodeposition, lead-tin alloy, fluoborate bath, voltammetry

## INTRODUCTION

Lead-tin alloy deposition, which finds an extensive application in electronics - such as printed circuits and connectors is carried out commercially from a fluoborate bath [1]. Though a number of other baths such as sulfamate [2,3], pyrophosphate [4,5], chloride [6] etc have been reported, they have not gained any significance in industry [7,8]. The desirable composition and control of lead-tin fluoborate solution was reviewed [9-11]. Use of addition agent is essential for producing a good quality deposit of the alloy.

In the present investigation, the electrodeposition kinetics of Pb-Sn alloy from an aqueous solution of fluoborate and the role as well as the mechanism of 1,10 - phenanthroline additive have been studied. The technique of cyclic and linear stripping voltammetry on a copper disc electrode is adopted for the purpose.

## EXPERIMENTAL

Linear stripping voltammetric studies were carried out using a conventional three electrode system with provision for inlet and outlet for deaerating the solution with pure and dry nitrogen gas. A three electrode system consisting of a rotating teflon covered copper disc (6 mm dia) as working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE) was employed. The solutions were prepared from analar grade reagents and double distilled water. The optimum electrolyte composition employed for Pb/Sn alloy plating is [11]: 35 gdm$^{-3}$ of Sn$^{++}$; 17.5 gdm$^{-3}$ of Pb$^{++}$; 246 gdm$^{-3}$ of HBF$_4$ and 25 gdm$^{-3}$ of H$_3$BO$_3$.

The Pb-Sn alloy was deposited on the copper electrode, initially without and then in the presence of additives in solution at -0.800 V (vs SCE) for 2 minutes which was then subjected to anodic sweep followed by cathodic sweep to complete the cyclic voltammogram in the range of -0.8 to 0.0 V. The alloy deposition was carried out at constant potential by rotating the electrode at the rate of 2000 r.p.m. Before depositing the Pb-Sn alloy, the working electrode was polished with emery papers down to 4/0 grade, degreased with acetone and finally washed twice with distilled water.

A Wenking potentiostat coupled with a Wenking Scan generator was used for controlling the inputs. A rotating electrode (Tacussel) set up was used for controlling the rotation of the working electrode. An x-y recorder was used to record the I - E curves. All the potentials were expressed against SCE. The measurements were carried out at 298 ± 1 K.

## RESULTS AND DISCUSSION

Cyclic and linear stripping voltammetric experiments, carried out for the system lead-tin fluoborate on copper disc electrode in the presence and absence of additives, yielded well defined and reproducible current- potential curves.

Fig.1 shows the typical current - voltage (CV) response of a Pb-Sn fluoborate solution in HBF$_4$ acid recorded at the sweep rate of 20 mVs$^{-1}$. The response of the deposition and dissolution of Pb-Sn alloy shows the involvement of single step reduction and oxidation on copper as evidenced by one cathodic and anodic peak in the CV (see Fig. 1).

The effect of the additive 1,10 phenanthroline, on the CV response at the sweep rate 40 mVs$^{-1}$ is given in Fig.2. For comparison the CV curve recorded under identical conditions for a solution containing no organic additive is also given in Fig. 2A.

The effect of sweep rate on the cyclic voltammograms obtained for the system Pb-Sn fluoborate in HBF$_4$ acid are also studied. The resultant $E_p$ and $i_p$ values obtained for different sweep rates are given in Table 1. The peak potential values of the cathodic peak $E_p$ (C) is found to shift with increasing sweep rate for a given concentration. But the cathodic shift of peak potential, $E_p$ (C), value in the presence of 1, 10 phenanthroline is observed for a given concentration and sweep rate employed. The peak potential values of the anodic peak $E_p$ (a) are constant and occur over the potential range of -0.340 to -0.370 V.

The cathodic peak current values $i_p$ (c) are found to increase with increase in sweep rate while the anodic peak currents, $i_p$ (a) seem to be constant in the presence of additive. However, in the absence of additive $i_p$ (a) values are increased with increasing sweep rate.
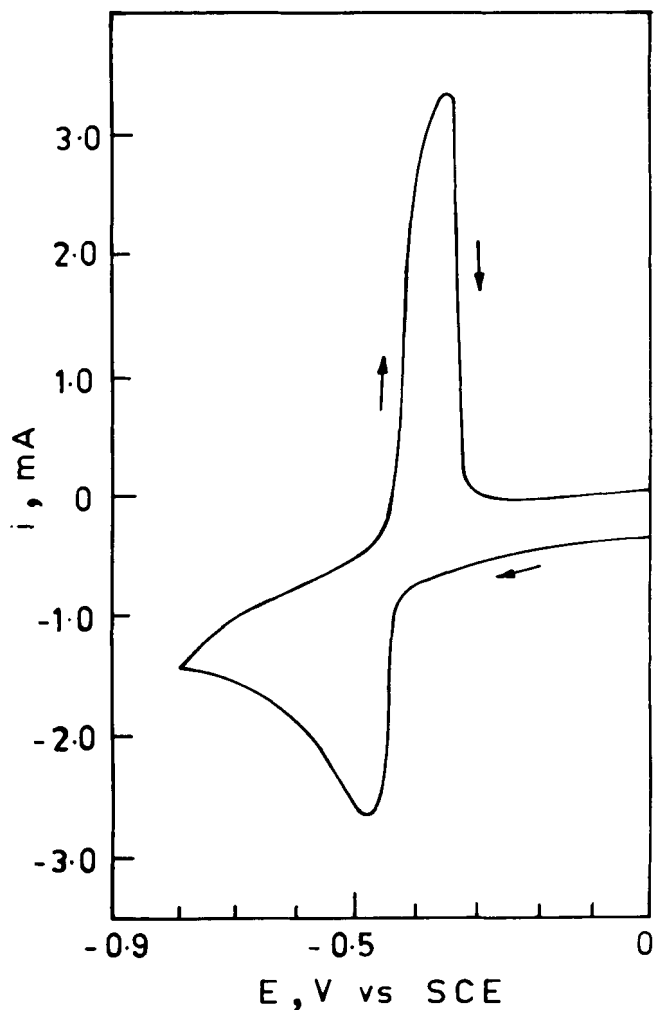
Fig. 1: Typical cyclic voltammetric response of a Pb-Sn fluoborate in HBF$_4$ acid on copper electrode. Sweep rate 20 mVs$^{-1}$; Range of potential sweep -0.8 to 0.0 V (SCE)
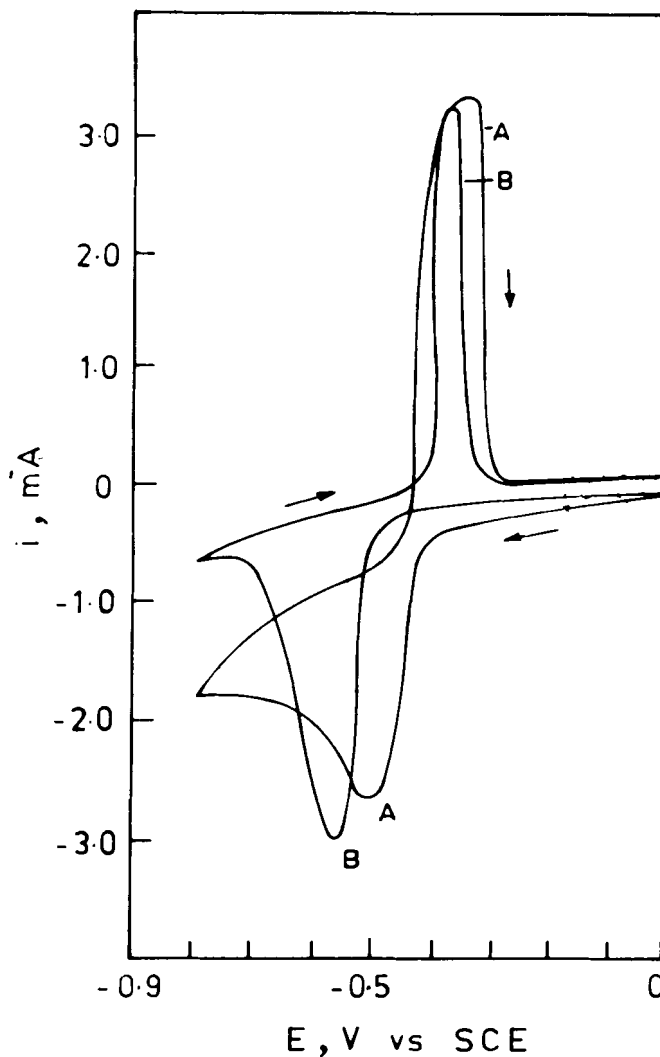
Fig. 2: Typical cyclic voltammetric response of a Pb-Sn fluoborate in HBF$_4$ acid solution on copper electrode without (A) and with (B) 1, 10 - phenanthroline (0.5 gdm$^{-3}$) as additive. Sweep rate 40 mVs$^{-1}$; Range of potential sweep -0.8 to 0.0 V (SCE)

TABLE-I: The peak potential values of E$_p$ (c) and E$_p$ (a) and the peak current values of i$_p$ (c) and i$_p$ (a) obtained with and without the additive 1,10 - phenanthroline and under different sweep rates V/mVs$^{-1}$

| V/mVs$^{-1}$ | i$_p$(c)/cm | Without additive | | E$_p$ (a) | i$_p$ (c)/cm | With additive | | E$_p$ (a) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | i$_p$ (a)/cm | E$_p$ (c) | | | i$_p$ (a)/cm | E$_p$ (c) | |
| 10 | 3.0 | 7.1 | -0.48 | -0.34 | 4.5 | 6.5 | -0.54 | -0.37 |
| 20 | 4.0 | 7.5 | -0.49 | -0.34 | 5.5 | 6.7 | -0.54 | -0.37 |
| 40 | 4.4 | 7.5 | -0.51 | -0.34 | 5.7 | 6.7 | -0.59 | -0.37 |
| 60 | 4.6 | 8.3 | -0.52 | -0.34 | 5.8 | 6.7 | -0.58 | -0.37 |
| 80 | 4.8 | 8.5 | -0.53 | -0.34 | 6.0 | 6.7 | -0.57 | -0.34 |
| 100 | 5.0 | 8.9 | -0.54 | -0.34 | 6.1 | 6.7 | -0.55 | -0.34 |

The observation on $E_p$ shift with sweep rate together with the data on the large peak potential difference between $E_p$(a) - $E_p$ (c) which is greater than 140 mV, and also increases with increasing sweep rate, suggests the deposition and dissolution of the alloy on copper to be irreversible under the voltammetric conditions studied.

The voltammograms generally exhibit an enhancement of the cathodic peak currents in the presence of additive in comparison with the system containing no additive in solution. But on reversing the scan, only a small increase in the anodic peak is noted (Table I).

The enhancement of the reduction current in the presence of 1,10 - phenanthroline may be attributed to the fact that the initial adsorption of the additive on the electrode surface presents an energy barrier for the reduction of approaching metal ion. The interactions between the approaching $Sn^{2+}$ and $Pb^{2+}$ ions could be understood by the fact that the metal ions become activated by the surface potential when they are approaching the electrode surface. The interactions of these activated metal ions and adsorbed phenanthroline on the reacting surface should be quite significant. It is difficult at the moment to give a more detailed mechanism to explain the reduction and deposition of metal species from a mixed ion solution. The mechanism, involved in mixed solution should be studied in more detail with the help of the techniques like AC impedance [12] and coulostatic [13] which are capable of throwing more light on the properties of solution-electrode interface.

The utility of the linear stripping voltammetric technique has also been explored by studying the effect of organic additive (1,10 - phenanthroline) Pb-Sn ions reduction on copper electrode in fluoborate bath. The Pb-Sn alloy was deposited onto the rotating copper electrode in the presence of organic additive in solution at -0.8V for 1 minute which was then subjected to anodic sweep. The amount of charge under the stripping peak is calculated with increasing additive concentrations and tabulated in Table II.

TABLE II: The amount of charge obtained under anodic stripping peak, mC.cm$^{-2}$, for different additive concentrations

| Sl.No. | Concentration of 1,10 - phenanthroline (gdm$^{-3}$) | Quantity of stripping peak charge (mC.cm$^{-2}$) |
|---|---|---|
| 1 | 0.00 | 402.8 |
| 2 | 0.25 | 471.7 |
| 3 | 0.50 | 816.2 |
| 4 | 0.75 | 222.6 |
| 5 | 1.00 | 127.2 |
| 6 | 1.25 | 106.0 |

The amount of charge is found to increase with increase in 1,10 phenanthroline concentration upto 0.5 gdm$^{-3}$ and then decreases. This indicates that the phenanthroline concentration needed for Pb-Sn alloy deposition in fluoborate bath is about 0.5 gdm$^{-3}$.

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