

ELECTROCHEMICAL BEHAVIOUR OF TIN IN GLUCONATE SOLUTIONS

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SUMMARY

Voltammetric studies revealed that under transient conditions in neutral pH gluconate solutions, the electroactive species are $\text{Sn}(\text{GH}_4)^+$. The formation of monovalent species is slow. Gluconate prevents the formation of $\text{Sn}(\text{OH})_2$. In high alkali solutions, the adsorbed monovalent species obey to a non activated Temkin adsorption isotherm and the first electron transfer is slow. The gluconates interact with $\text{Sn}(\text{OH})_2$ and hinder the participation of OH^- ions in the deposition process.

INTRODUCTION

The search for ecofriendly and economical plating baths for the development of tin plating on steel resulted in the gluconate as the complexing agent for tin plating. Tin was deposited on steel from gluconate bath in the neutral pH range with a throwing power comparable to stannate baths [1]. The potential-pH diagram of tin- H_2O reveals that SnO or $\text{Sn}(\text{OH})_2$ are the predominant species formed in the pH range of 3 to 10 [2]. Gluconic acid is represented by HGH_4 [3, 4] where the first H refers to the carboxylic acid hydrogen and H_4 refers to the four hydrogen on the secondary alcohols. The anion of the gluconic acid is represented as GH_4^- . The dissociation constants of gluconic acid and the stability constants of divalent and tetravalent tin gluconate

complexes was found to be $\text{Sn}(\text{GH}_4)^+$ [5]. This paper presents the electrochemical behaviour of tin in gluconate solutions in a wide range of pH 3 to 10 and also in higher alkali solutions.

EXPERIMENTAL

Triangular potential sweep voltammetric experiments were carried out in Bio Analytical Systems 100A, USA using a conventional three electrodes cell assembly of glassy carbon as working electrode, platinum as counter and S.C.E. as reference electrodes respectively. The solutions under study were deoxygenated for one hour using purified hydrogen. The temperature of the cell was kept at $30 \pm 0.01^\circ\text{C}$.

Solutions were made from analar chemicals SnSO_4 solutions ($2.5 \times 10^{-2}\text{M}$ to $2.5 \times 10^{-1}\text{M}$) and sodium gluconate solutions ($2.5 \times 10^{-2}\text{M}$ to $7.5 \times 10^{-1}\text{M}$) were used. The pH of the solutions were adjusted using digital pH meter (± 0.01 accuracy). The alkali concentrations were established by titrating against standard mineral acid.

RESULTS

(i) Neutral pH Solutions (6.4 to 7.2)

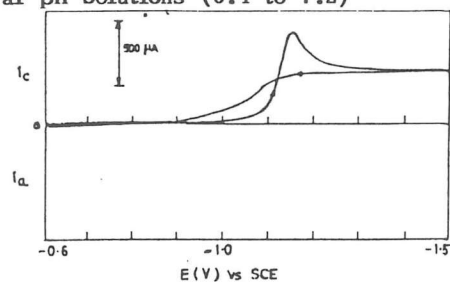


Fig.1 Typical Cyclic Voltammogram in $1.25 \times 10^{-1}\text{M}$ $\text{SnSO}_4 + 3.75 \times 10^{-1}\text{M}$ sodium gluconate at pH 7.2.

$E_{\lambda,a} = -600 \text{ mV}; E_{\lambda,c} = -1500 \text{ mV}; v = 5 \text{ mVs}^{-1}$

Figure 1 presents the electrochemical spectrum of deposition and dissolution of tin from $1.25 \times 10^{-1}\text{M}$ SnSO_4 containing gluconate solutions at pH 7.2. The forward scan exhibited a cathodic peak at -1153 mV vs SCE. The reverse scan intersected the forward scan. The cathodic peak potential varied with log sweep rate with a slope of $120 \text{ mV decade}^{-1}$ and with pH a value of 30 mV/pH change was observed (Figures 2 and 3).

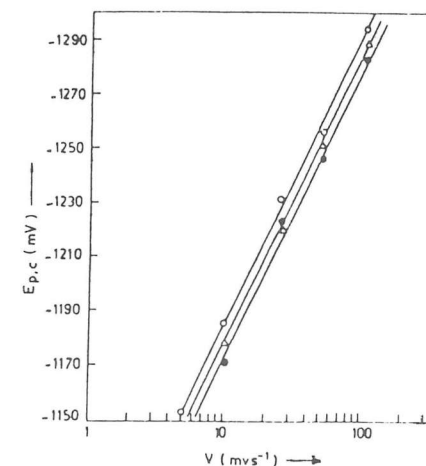


Fig.2 Variation of cathodic peak potentials ($E_{p,c}$) with sweep rate in different gluconate solutions.

- $1.25 \times 10^{-1}\text{M}$ $\text{SnSO}_4 + 3.75 \times 10^{-1}\text{M}$ sodium gluconate
- $1.25 \times 10^{-1}\text{M}$ $\text{SnSO}_4 + 3.25 \times 10^{-1}\text{M}$ sodium gluconate
- △-△-△ $1.25 \times 10^{-1}\text{M}$ $\text{SnSO}_4 + 5 \times 10^{-1}\text{M}$ sodium gluconate

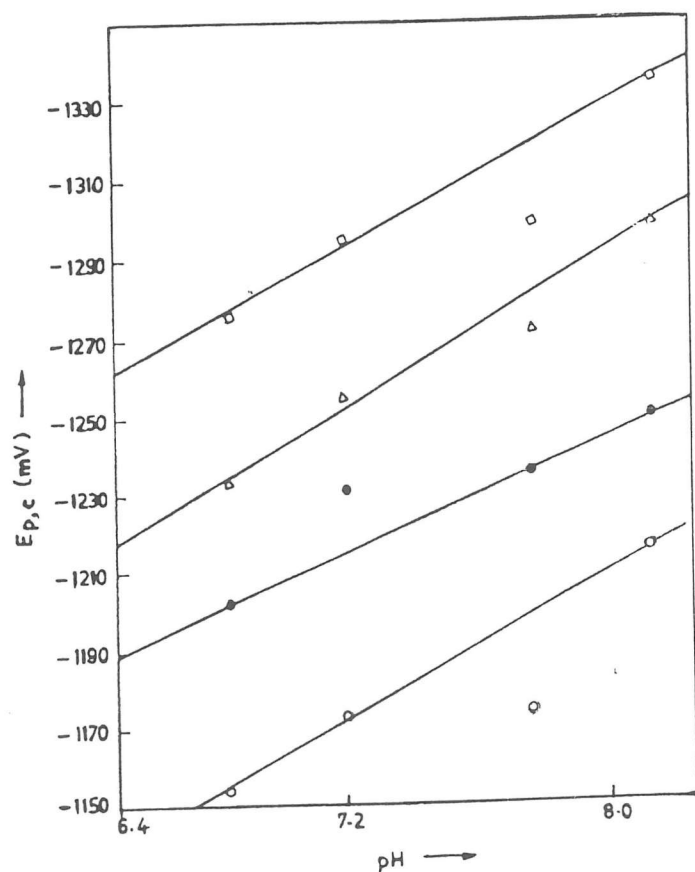


Fig.3 Variation of cathodic peak potentials with pH at different sweep rates

○-○-○ 10 mVs^{-1} ; ●-●-● 25 mVs^{-1} ;
 △-△-△ 50 mVs^{-1} ; □-□-□ 100 mVs^{-1} ;

The cathodic peak currents were invariant with pH. Gluconate concentrations did not influence the cathodic peak currents and potentials at all sweep rates from 5 mVs^{-1} to 100 mVs^{-1} .

(ii) Higher pH solutions ($\text{pH} > 8.2$)

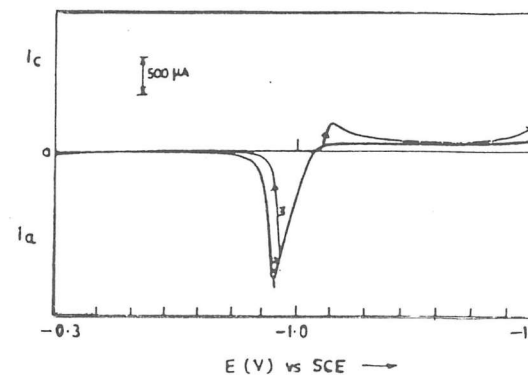


Fig.4. Typical cyclic voltammogram for the deposition and dissolution of tin in $2.5 \times 10^{-2} \text{M SnSO}_4 + 1 \text{M NaOH}$ solutions. 1, 2, 3 scan numbers.

$$E_{\lambda,a} = -300 \text{ mV}; \quad E_{\lambda,c} = -1700 \text{ mV}; \quad v = 10 \text{ mVs}^{-1}$$

When polarised from -300 mV, the forward scan exhibited a cathodic peak at -1100 mV (Figure 4). Beyond -1700 mV, hydrogen evolution takes place. The reverse scan exhibited an anodic peak at -960 mV. Increase of scan rate shifted the $E_{p,a}$ to more negative values suggesting that the dissolution was favoured with continuous cycling.

The charges flowed under the cathodic peak (Q_c) was found to remain constant while the charges flowed under the anodic peak (Q_a) decreased with cycling. The $E_{p,a}$ varied with sweep rate with a slope of $60 \pm 5 \text{ mV decade}^{-1}$ and $60 \text{ mV decade}^{-1}$ was observed from $E_{p,c}$ vs $\log v$ plots (Figure 5).

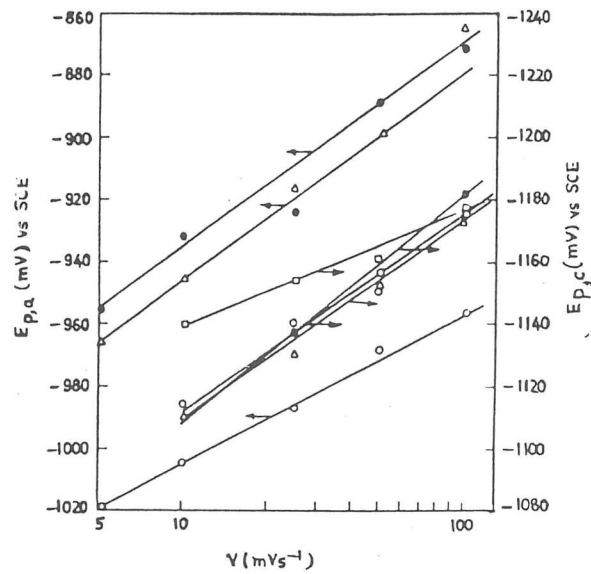


Fig.5. Variation of anodic peak potentials ($E_{p,a}$) and cathodic peak potentials ($E_{p,c}$) with sweep rate in different SnSO_4 solutions in 2M NaOH solutions.

- $2.5 \times 10^{-2} \text{M}$
- $5 \times 10^{-2} \text{M}$
- △-△-△ $7.5 \times 10^{-2} \text{M}$
- 10^{-1}M

The cathodic peak currents were found to increase with Sn(II) concentration with a slope of 1, while they decreased with $\log \text{OH}^-$ ion concentration with a slope of -2 (Figures 6 & 7).

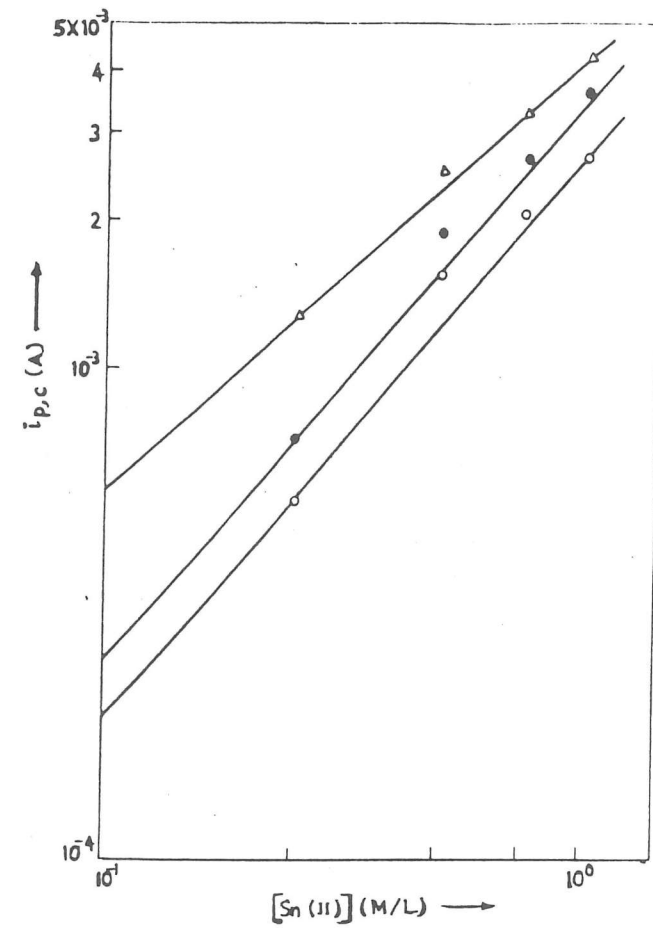


Fig.6. Variation of cathodic peak currents with Sn(II) concentration in 2M NaOH solutions at different sweep rates.

- 5 mVs^{-1} ; ●-●-● 70 mVs^{-1} ;
- △-△-△ 25 mVs^{-1}

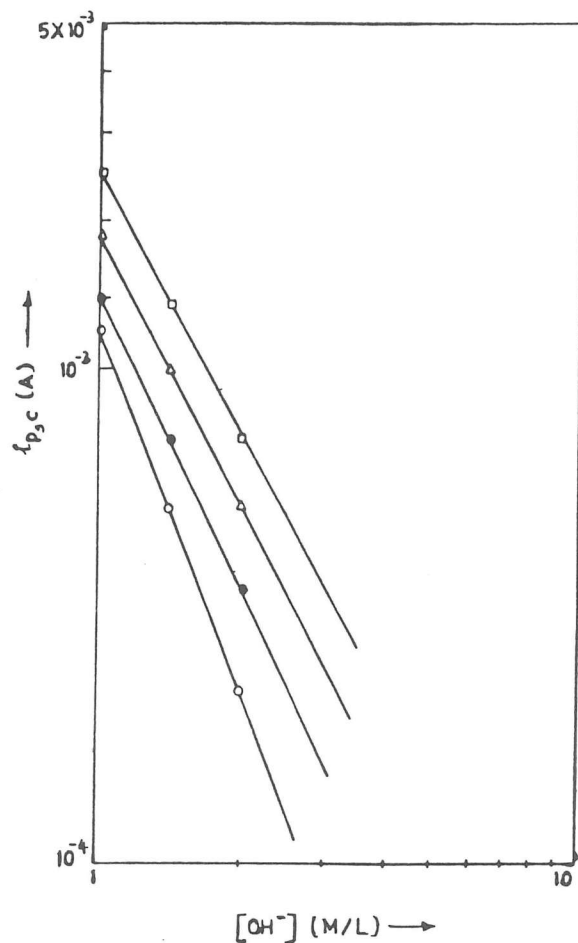


Fig.7. Variation of cathodic peak currents with hydroxyl ion concentration $5 \times 10^{-2} \text{M}$ SnSO_4 solutions.

$\circ-\circ-\circ$ 5 mVs^{-1} $\triangle-\triangle-\triangle$ 25 mVs^{-1}
 $\bullet-\bullet-\bullet$ 10 mVs^{-1} $\square-\square-\square$ 50 mVs^{-1}

(iii) Higher pH solutions ($\text{pH} > 8.2$) containing gluconates

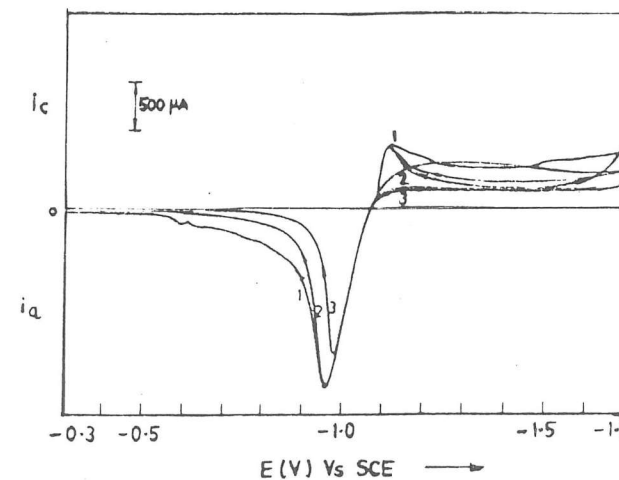


Fig.8. Typical cyclic voltammogram in $5 \times 10^{-2} \text{M}$ SnSO_4 + $2.5 \times 10^{-2} \text{M}$ sodium gluconate in 2M NaOH solutions. $E_{\lambda,a} = -300 \text{ mV}$; $E_{\lambda,c} = -1700 \text{ mV}$; $v = 10 \text{ mVs}^{-1}$
1, 2, 3 scan numbers.

The presence of gluconates has no effect on the electrochemical spectrum (Figure 8). The anodic and cathodic peak potentials varied with sweep rate, each with a slope of $60 \pm 5 \text{ mV decade}^{-1}$. Gluconate concentration increased the cathodic peak currents while increase of OH^- ion concentration decreased them.

DISCUSSIONS

In aqueous solutions, tin forms simple hydrated ions Sn^{2+} , Sn^{4+} and the complex ions like HSnO_2^- , SnO_2^{2-} in alkaline solutions [2]. The assumed equilibria in the potential-pH diagram of $\text{Sn-H}_2\text{O}$ ceases to exist in the presence of ions which could react with tin.

In neutral pH solution, the deposition of tin under transient conditions (5 to 100 mVs⁻¹) may involve the formation of adsorbed Sn⁺ ion, e.g.



If the first electron transfer is slow,

$$i_c = k_1 [\text{Sn}^{2+}] \exp - \frac{\alpha_c F \Delta \phi}{RT}$$

Where α_c is the cathodic transfer coefficient; $\Delta \phi$ is the interfacial potential difference; k_1 is the rate constant; $[\text{Sn}^{2+}]$ is the concentration of Sn²⁺ ions in solution.

This suggests that

$$\left[\frac{d \log i_c}{d \log (\text{Sn}^{2+})} \right]_E = \text{order of the reaction with respect to}$$

Sn²⁺ ions = 1 and the cathodic currents were independent of OH⁻ ions and of gluconate concentration.

For an irreversible process [6]

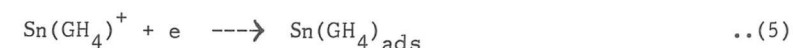
$$E_p = E^0 + \frac{RT}{F} \left[\ln \frac{K^0}{\sqrt{D}} - 0.5 \ln \frac{\alpha F v}{RT} - 0.78 \right] \quad \dots(3)$$

$$i_p = nFA C_{\text{ox}}^0 D_{\text{ox}} \left(\frac{\alpha F v}{RT} \right) \lambda \left(\frac{\alpha F}{RT} \right) (E_i - E) \quad \dots(4)$$

Where E_i is the initial potential; C_{ox}^0 is the concentration of the species undergoing reduction; D_{ox} is the diffusion coefficient of Sn²⁺ ions and K^0 is the specific rate constant. Therefore one can derive

the dependencies of peak potentials on sweep rate and various dependencies either on OH⁻ ions concentration or Sn(II) concentrations at constant sweep rate. The observed cathodic Tafel slope of 120 mV decade⁻¹ (Figure 2) confirms the first electron transfer to be slow in the reduction process.

In order to prevent the precipitation of Sn(OH)₂ and to obtain clear solutions tin:gluconate concentration ratios of 1:3 were used. This excess gluconate caused the invariance peak currents and potentials in the range of sweep rates studied. However, one may assume the reduction to take place as

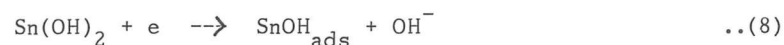


In the solution there exists a dynamic equilibrium between Sn(OH)₂ and Sn (GH₄)⁺ and this was seen by the dependencies of cathodic peak potentials on the pH.

In high alkali solutions

A review on the dissolution of tin and cathodic processes occurring on tin was published [7], and the nature of the stannite ionic species resulting from the dissolution of tin in NaOH solutions was found to be Sn(OH)₃⁻. The mechanism of dissolution was found to involve Sn(OH) and Sn(OH)₂ as adsorbed intermediates on the electrode [8]. The anodic dissolution of tin in alkaline solution was found to have a Tafel slope of 57 mV decade⁻¹ and the reaction order with respect to OH⁻ ions was 2. A quasi-reversible

charge transfer followed by a chemical reaction to form HSnO_2^- was proposed [9]. Under transient conditions (5 to 100 mVs^{-1}) the observed cathodic Tafel slope of 60 mV decade⁻¹ suggests the following mechanism:



In the reduction of Sn(OH)_2 would be slow and the coverage of the surface by adsorbed SnOH to be negligible ($\theta \ll 1$), one would obtain a cathodic Tafel slope of 120 mV decade⁻¹ for adsorbed Sn(OH) obeying Langmuir isotherm [10]. The observed Tafel slope of 60 mV decade⁻¹ suggests that $\theta \gg 0.1$ and the interaction between adsorbed monovalent species become appreciable and different sites on the metal may have different free energies of adsorption. Hence in terms of the non activated Temkin isotherm one would obtain a cathodic Tafel slope of 60 mV decade⁻¹ and the reaction orders with respect to Sn^{2+} of +1 and with respect to OH^- ions of -1.5 respectively.

In the presence of gluconate, the anodic and cathodic Tafel slopes remain unaffected. These cathodic peak currents increased with gluconate ion concentration with a slope of +1.0 suggesting the following mechanism:



The presence of gluconate influences the participation of OH^- ions. For the adsorbed Sn(OH) obeying non activated Temkin isotherm,

$$\text{the } \left[\frac{d \log i}{d \log (\text{OH}^-)} \right]_{v, a_{\text{Sn}^{2+}}, a_{\text{GH}_4^-}} = 0.5$$

This was observed experimentally.

CONCLUSIONS

Voltammetric studies revealed that under transient conditions in neutral pH gluconate solutions the electroactive species is $\text{Sn(GH}_4\text{)}^+$. The formation of monovalent species is slow. Gluconates prevent the formation of Sn(OH)_2 . In high alkali solutions, the adsorbed monovalent species obey non activated Temkin adsorption isotherm and the first electron transfer is a slow step. The gluconates interact with Sn(OH)_2 and hinder the participation of OH^- ions in the deposition process.

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(Received, 24 August 1994

Revised form, 27 December 1994)