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Electrode kinetics of antimony in alkaline solutions

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The kinetics of the electro-oxidation and electro-reduction of Sb in alkaline solutions as well as the electrodeposition of Sb(III) on Sb have been studied. The rest potential follows the relation,

$$E_0 = 0.152 - 0.059\,\mathrm{pH} \qquad V \text{ is SHE}$$

which is the equation for the equilibrium potential for the redox reaction,

$$2\mathrm{Sb} + 6\mathrm{OH}^- = \mathrm{Sb_2O_3} + 3\mathrm{H_2O} + 6e^-$$

The rates of anodic dissolution and electro-reduction can be expressed by the following empirical kinetic equations,

$$i_\mathrm{a} = 6F\bar{k}_\mathrm{a}[\mathrm{OH}^-]^2 \exp 0.59FE/RT$$

and

$$|i_\mathrm{c}| = 6F\bar{k}_\mathrm{c} \exp - 1.31FE/RT$$

The empirical kinetic equation for electrodeposition of Sb(III) is

$$|i'_\mathrm{c}| = 3F\bar{k}'_\mathrm{c}[\mathrm{SbO_2^-}] \exp - 0.454FE/RT$$

Mechanisms are proposed to interpret the experimental results.

Nomenclature

b_a	Anodic Tafel slope
b_c	Cathodic Tafel slope
b'_c	Tafel slope for electrodeposition reaction
E	Electrode potential
E^e	Equilibrium potential
E_0	Rest potential
i_a	Anodic current density
i_c	Cathodic current density
i_0	Exchange current density for Sb/Sb(III) reaction
$i_{\mathrm{c,28a}}$	Sb(III) electrodeposition current density for Step 28a
$i_{\mathrm{c,21e}}$	Cathodic current density for Step 21 e
i'_c	Current density for Sb(III) electrodeposition
i'_0	Exchange current density for Sb(III) electrodeposition
$\bar{k}_\mathrm{a}$	Anodic rate constant
$\bar{k}_\mathrm{c}$	Cathodic rate constant
$\bar{k}_{\mathrm{c,28a}}$	Electrodeposition rate constant for Step 28a
$k_{\mathrm{a,21e}}$	Anodic rate constant in Equation 22
$k_{\mathrm{c,21e}}$	Cathodic rate constant in Equation 25
$\bar{k}'_\mathrm{c}$	Electrodeposition rate constant
$\bar{k}'_{\mathrm{a,21e}}$	Anodic rate constant in Equation 23
$\bar{k}'_{\mathrm{c,21e}}$	Cathodic rate constant in Equation 26
R	Gas constant
T	Absolute temperature
α_a	Anodic charge transfer coefficient
α_c	Cathodic charge transfer coefficient
α'_c	Charge transfer coefficient for Sb(III) electrodeposition reaction
β	Symmetry factor

1. Introduction

Antimony has been used as an alloying element to harden and mechanically strengthen soft metals such as tin and lead. For example, it has been used in the support grids of lead acid battery plates [1]. Furthermore, because of its noble character it can increase the corrosion resistance of iron and steel [2, 3].

Applications of the Sb/Sb oxide electrode as a reference electrode have been widely reported. Stock *et al.* [4], and Ives and Janz [5] have reviewed the use of antimony as reference electrodes. Park and Beard [6] attribute the rest potential of the Sb/Sb_2O_3 electrode to the redox reaction,

$$2Sb + 6OH^- = Sb_2O_3 + 3H_2O + 6e^- \quad (1)$$

Edwall [7] has provided an updated review of the literature and has reported on his comprehensive studies of the Sb/Sb oxide electrode using polycrystalline and single crystal Sb. He was primarily interested in physiological applications.

The irregular behaviour of the Sb/Sb oxide rest potential has been attributed to the presence of dissolved oxygen [4, 5, 8–10]. Thus the true equilibrium potential cannot be experimentally measured until virtually all traces of oxygen are removed from the system.

Huq *et al.* [11] determined the anodic dissolution behaviour of monocrystalline Sb in 1 mol dm^{-3} $NaClO_4$ (pH 10.8) and obtained a Tafel slope of 0.10 V dec^{-1}. More recently, Wikstrom *et al.* [12] reported experimental results of the kinetics of Sb electro-oxidation and electroreduction as well as electrodeposition of Sb(III) in HCl solutions. They report that the rest potential of Sb in deoxygenated HCl is the equilibrium potential of the redox reaction

$$Sb + 2H_2O = HSbO_2 + 3H^+ + 3e^- \quad (2)$$

Empirical kinetic expressions for electro-oxidation and electro-reduction are

$$i_a = \bar{k}_a [OH^-][Sb(III)]^{-1} \exp 2FE/RT \quad (3)$$

and

$$|i_c| = \bar{k}_c [H^+]^2 \exp -FE/RT \quad (4)$$

The Sb(III) electrodeposition rate is

$$|i'_c| = \bar{k}'_c [H^+][Sb(III)] \exp -FE/2RT \quad (5)$$

The work reported in this paper is a study of the electro-oxidation and electro-reduction kinetics of Sb in alkaline solutions containing Sb(III). In addition, the electrodeposition kinetics of Sb(III) on Sb in alkaline solutions have been examined.

2. Experimental details

The 1 cm × 1.5 cm planar electrodes were cut from 99.9996% antimony bar stock, and masked with purified paraffin except for surfaces to be exposed to the electrolyte. The electrodes were first etched in CP-4A for 4–8 s, rinsed in distilled water and then immersed in the electrolyte.

The electrolytes were prepared from B&A KCl, KOH and Sb_2O_3. The ionic strength was maintained constant at one i.e. 1 mol dm^{-3} (KOH + KCl). Solutions of pH 11, 12, 13 and 13.7 were prepared. The solutions (23.5 ± 1.0° C) were deoxygenated with prepurified nitrogen which first passed through two scrubbers before the cell. A three-electrode cell was used with a saturated calomel reference electrode. However, all potentials are reported relative to SHE.

The antimony electrodes were galvanostatically polarized at each current density for 2 min as steady state potentials were attained within $1\frac{1}{2}$ min. Prior to polarization and subsequent to immersion in the electrolyte, the rest potential of antimony was monitored until a steady state was achieved.

3. Results

The pH dependence of the rest potential (E_0) in alkaline solutions (pH 11, 12, 13 and 13.7) is shown in Fig. 1, where

$$\frac{\partial E_0}{\partial pH} = -0.059\,V \quad (6)$$

The rest potential is independent of Sb(III) for

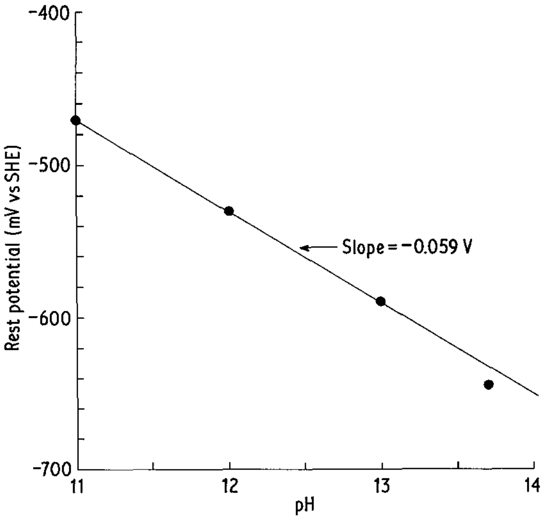

Fig. 1. Rest potential of antimony vs pH in alkaline solutions.

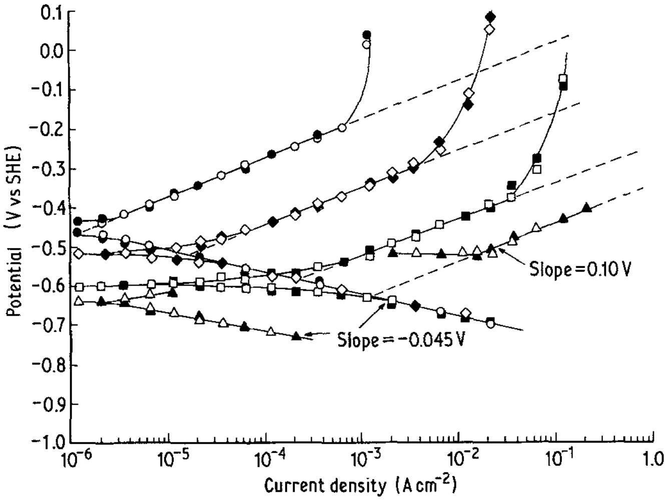

Fig. 2. Polarization behaviour of antimony in alkaline solutions. Open – 0 mmol dm^{-3} Sb(III), closed – 2 mmol dm^{-3} Sb(III); ○ pH 11.0, ◇ pH 12.0, □ pH 13.0, △ pH 13.7.

concentrations ranging from 0.2 to 2 mmol dm^{-3} in pH 11, 12, 13 and 13.7 solutions,

$$\left[\frac{\partial E_0}{\partial \log[\mathrm{Sb(III)}]}\right]_{\mathrm{pH}} = 0 \tag{7}$$

Fig. 2 shows that the anodic dissolution of Sb increases with increasing pH but that the reduction reaction is independent of pH (except for pH 13.7). It is also observed that both anodic dissolution and the reduction reaction are independent of the Sb(III) in the electrolyte. Anodic Tafel slopes of 0.10 V decade^{-1} (potentials > -0.52 V for pH 13.7) and cathodic Tafel slopes of 0.045 V decade^{-1} were obtained.

The polarization data for pH 13.7 are anomalous. There is a horizontal potential plateau of about $1\frac{1}{2}$ decades in current density at -0.52 V during anodic polarization (complete set of anodic polarization data for pH 13.7 is not shown); this behaviour was not observed for Sb in solutions of lower pH. Furthermore, the cathodic Tafel line for pH 13.7 is shifted to more negative potentials of about 0.14 V than the cathodic Tafel line for pH 11, 12 and 13. Extrapolation of the anodic Tafel line (> -0.52 V) for pH 13.7 to the cathodic Tafel line for pH 11, 12 and 13 solutions gives a potential of -0.64 V and a current density of 1.2 mA cm^{-2} at the intersection. The former value is the measured rest potential of Sb in pH 13.7 solutions. If it is assumed that the mechanism for Sb anodic dissolution in pH 13.7 solutions above the current plateau (> -0.52 V) is the same as for Sb anodic dissolution in pH 11, 12 and 13 solutions, the current density of 1.2 mA cm^{-2} at the intersection, as described above, can be taken as the exchange current density for the Sb/Sb(III) reaction in pH 13.7 solutions consistent with those obtained for Sb in the other alkaline solutions. These exchange current densities are plotted versus pH in Fig. 3 and,

$$\frac{\partial \log i_0}{\partial \mathrm{pH}} = 1.1 \tag{8}$$

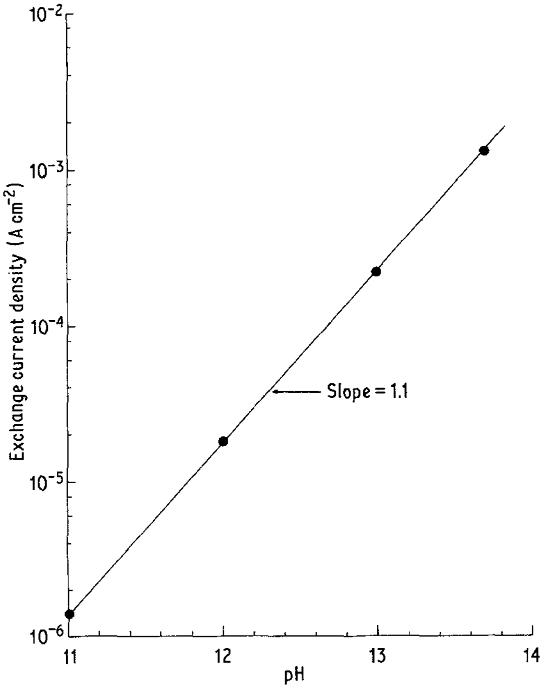

Fig. 3. Exchange current vs pH for the Sb redox reaction in alkaline solutions.

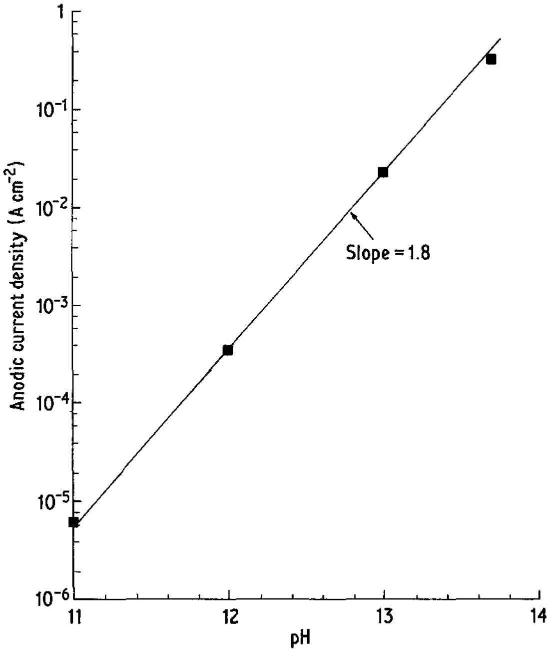

Fig. 4. The pH reaction order plot of anodic dissolution of antimony in alkaline solutions. $E_a = -0.4$ V.

It is seen that the exchange current density of pH 13.7 obtained at the intersection of the extrapolation of the upper anodic Tafel line and the cathodic Tafel line for pH 11, 12 and 13 correlates well with the exchange current densities for the other alkaline solutions.

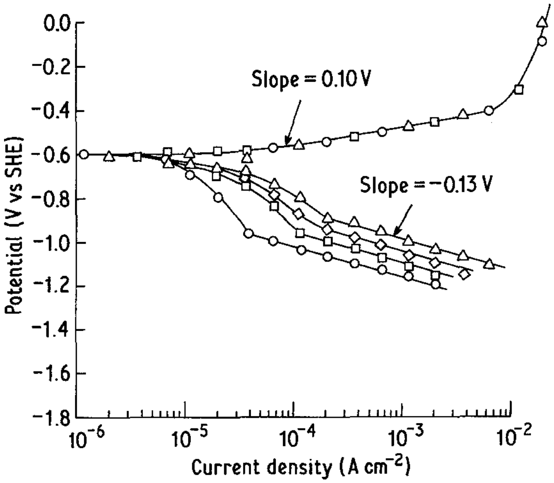

Fig. 5. Effect of Sb(III) on the polarization behaviour of antimony in pH 13 solutions. ○ 0.0 mmol dm^{-3} [Sb(III)], □ 0.2 mmol dm^{-3} [Sb(III)], ◇ 0.6 mmol dm^{-3} [Sb(III)], △ 2.0 mmol dm^{-3} [Sb(III)].

The pH reaction order plot for anodic dissolution in alkaline solutions is given in Fig. 4. A reaction order of 1.8 is obtained,

$$\left(\frac{\partial \log i_a}{\partial \mathrm{pH}}\right)_{-0.4\,\mathrm{V}} = 1.8 \qquad (9)$$

indicating that anodic dissolution of Sb in alkaline solutions is approximately second order with respect to hydroxyl ions. The pH reaction order for reduction of the Sb/Sb(III) reaction is zero order, as shown in Fig. 2. The empirical rate expressions for the anodic and cathodic reactions are

$$i_a = 6F\overline{k}_a[\mathrm{OH}^-]^2 \exp \alpha_a FE/RT \qquad (10)$$

where

$$b_a = 2.303RT/\alpha_a F = 0.10\,\mathrm{V\,dec}^{-1} \qquad (11)$$

and

$$|i_c| = 6F\overline{k}_c \exp -\alpha_c FE/RT \qquad (12)$$

where

$$b_c = -2.303RT/\alpha_c F = -0.045\,\mathrm{V\,dec}^{-1} \qquad (13)$$

Figs. 5 and 6 show the effect of Sb(III) on the anodic and cathodic polarization of Sb in pH 13 and 13.7 solutions, respectively, where cathodic polarization below −1.0 V is also obtained. Sb(III) concentrations of 0.0, 0.2, 0.6 and 2.0 mmol dm^{-1} were examined. Anodic dissolution is independent of Sb(III), as also shown in Fig. 2. For Sb in pH 13.7 solutions, the current plateau at −0.52 V is clearly shown with a lower anodic Tafel line of slope 0.05 V decade^{-1} and an upper anodic Tafel line of slope 0.10 V decade^{-1}. At potentials below −1.0 V, there is a clear dependence of cathodic polarization on Sb(III). In the absence of Sb(III) only hydrogen evolution through water discharge occurs. In the presence of Sb(III), both hydrogen evolution and electrodeposition of Sb(III) occur. In all cases, the cathodic Tafel slopes are −0.13 V decade^{-1}. The polarization behaviour of Sb in pH 11 and 12 solutions are similar to Sb in pH 13 solutions.

The rate of Sb(III) electrodeposition is determined by subtracting the rate of hydrogen evolution obtained in the absence of Sb(III) from the cathodic polarization in the presence of Sb(III). These results are given in Fig. 7, which shows that the rate of Sb(III) electrodeposition is independent of pH and increases with increase in Sb(III) concentration. The cathodic Tafel slopes representing Sb(III) electrodeposition are −0.13 V

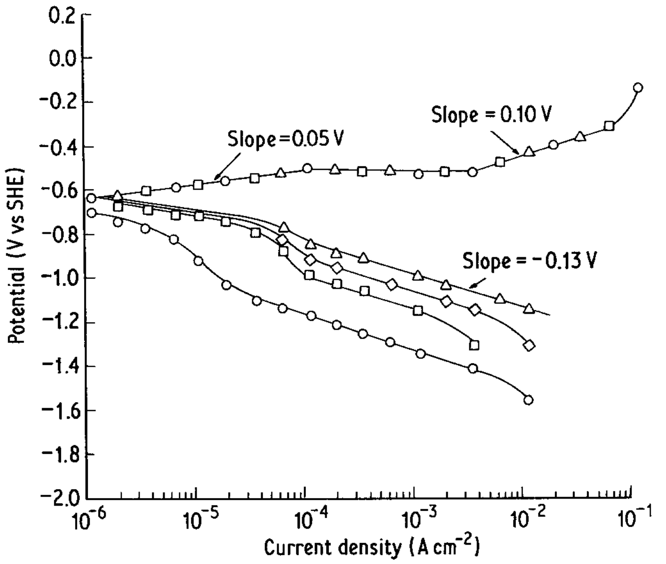

Fig. 6. Effect of Sb(III) on the polarization behaviour of antimony in pH 13.7 solutions. ○ 0.00 mol dm^{-3} [Sb(III)], □ 0.2 mmol dm^{-3} [Sb(III)], ◇ 0.6 mmol dm^{-3} [Sb(III)], △ 2.0 mmol dm^{-3} [Sb(III)].

decade^{-1}. Fig. 8 shows that the electrodeposition of Sb(III) in alkaline solutions is first order with respect to Sb(III).

According to Park and Beard [6] Sb(III) is in the form of $\mathrm{SbO_2^-}$ in alkaline solutions. Thus, when $\mathrm{Sb_2O_3}$ is dissolved in alkaline solutions, $\mathrm{SbO_2^-}$ forms,

$$\mathrm{Sb_2O_3 + 2OH^- = 2SbO_2^- + H_2O} \qquad (14)$$

The electrodeposition reaction is assumed to be

$$\mathrm{SbO_2^- + 2H_2O} + 3e^- = \mathrm{Sb + 4OH^-} \qquad (15)$$

where $E^e = 0.446 - 0.079\mathrm{pH} + 0.02\log[\mathrm{SbO_2^-}]$ V vs SHE.

The exchange current densities for the reaction (Equation 15) determined from the experimental results are given in Figs. 9 and 10 as functions of pH and Sb(III) concentrations, respectively. The plots give,

$$\left(\frac{\partial \log i'_0}{\partial \mathrm{pH}}\right)_{[\mathrm{Sb(III)}]} = 0.5 \qquad (16)$$

and

$$\left(\frac{\partial \log i'_0}{\partial \log[\mathrm{Sb(III)}]}\right)_{\mathrm{pH}} = 0.9 \qquad (17)$$

The empirical rate expression for Sb(III) electrodeposition is

$$i'_c = 3F\overleftarrow{k}'_c[\mathrm{SbO_2^-}]\exp-(\alpha'_c FE/RT) \qquad (18)$$

where

$$b'_c = -2.303\frac{RT}{\alpha'_c F} = -0.13\,\mathrm{V\,decade^{-1}} \qquad (19)$$

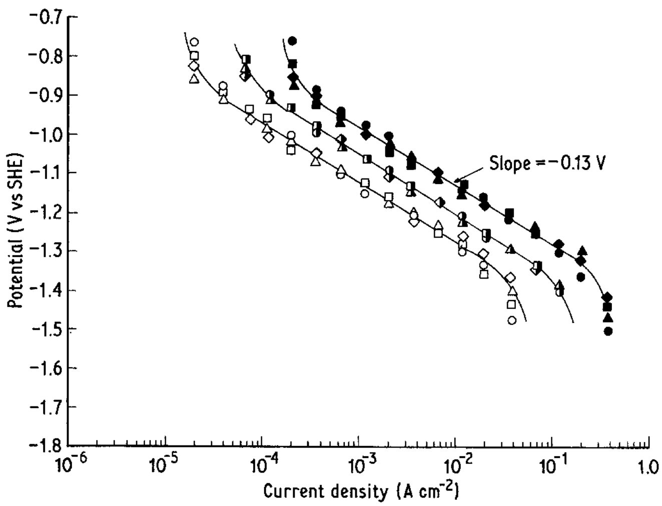

Fig. 7. Rate of electrodeposition of Sb(III) on antimony in alkaline solutions. Open – 0.2 mmol dm^{-3} [Sb(III)], half-closed – 0.6 mmol dm^{-3} [Sb(III)], closed – 2.0 mmol dm^{-3} [Sb(III)]; ○ pH 11.0, □ pH 12.0, ◇ pH 13.0, △ pH 13.7.

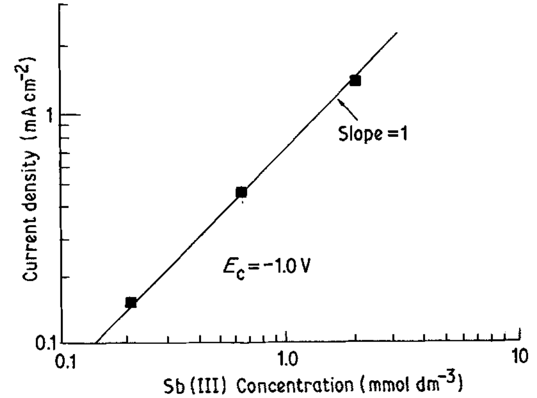

Fig. 8. Sb(III) reaction order plot for electrodeposition of Sb(III) on antimony in alkaline solutions.

4. Discussion

The rest potentials (Fig. 1) closely follow the equilibrium potential for the reaction,

$$2Sb + 6OH^- = Sb_2O_3 + 3H_2O + 6e^- \quad (1)$$

where

$$E^e = 0.152 - 0.059\,\mathrm{pH} \qquad V \text{ vs SHE} \quad (20)$$

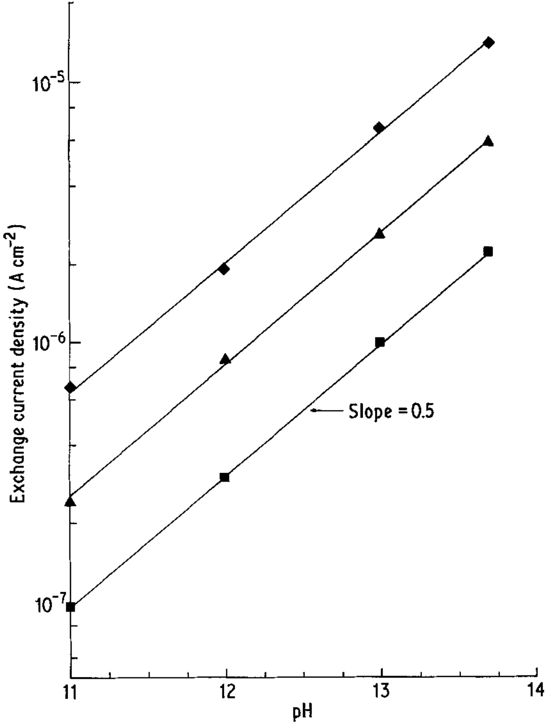

Fig. 9. Exchange current vs pH for the electrodeposition of Sb(III) on antimony in alkaline solutions, ■ 0.2 mmol dm^{-3} Sb(III), ▲ 0.6 mmol dm^{-3} Sb(III), ◆ 2.0 mmol dm^{-3} Sb(III).

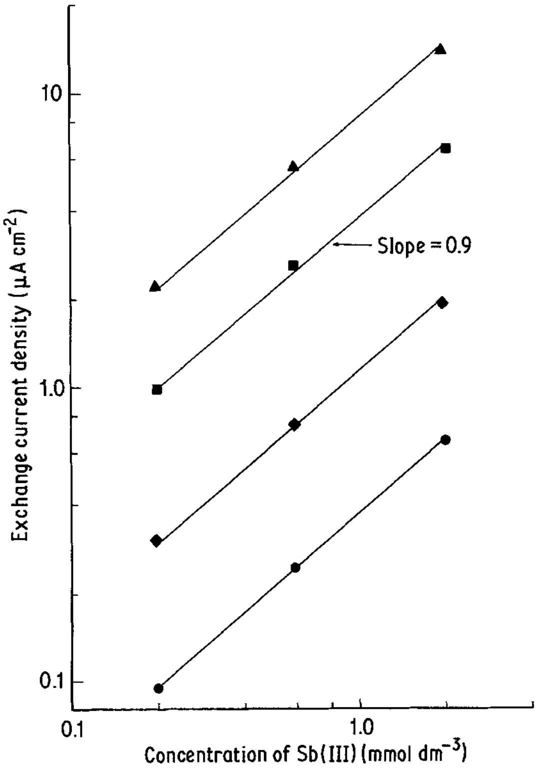

Fig. 10. Exchange current vs Sb(III) concentrations for the electrodeposition of Sb(III) on antimony in alkaline solutions. ● pH 11, ◆ pH 12, ■ pH 13, ▲ pH 13.7.

If it is assumed that the Sb/Sb(III) reaction can be represented by Equation 1, the following mechanism is proposed to interpret the experimental data:

$$Sb + OH^- = SbOH^- \quad (21a)$$

$$SbOH^- = Sb(OH) + e^- \quad (21b)$$

$$SbOH + OH^- = Sb(OH)_2 + e^- \quad (21c)$$

$$Sb(OH)_2 + OH^- = Sb(OH)_3^- \quad (21d)$$

$$Sb(OH)_3^- + OH^- \xrightarrow{\text{rds}} Sb(OH)_4^- + e^- \quad (21e)$$

$$Sb(OH)_4^- + Sb = 2Sb(OH)_2 + e^- \quad (21f)$$

$$Sb(OH)_2 + OH^- = HSbO_2 + H_2O + e^- \quad (21g)$$

$$2HSbO_2 = Sb_2O_3 + H_2O \quad (21h)$$

For the rate determining Step 21e, the anodic rate is

$$i_{a,21e} = F\vec{k}_{a,21e}[Sb(OH)_3^-][OH^-]\exp \beta FE/RT \quad (22)$$

If it is assumed that all steps other than Step 21e are then at quasi-equilibrium, that surface coverages of adsorbed intermediates $Sb(OH)^-$, $Sb(OH)$ tend to very small values, and that $\theta_{Sb(OH)_2} \rightarrow 1$. Equation 22 becomes

$$i_{a,21e} = F\bar{k}'_{a,21e}[OH^-]^2 \exp \beta FE/RT \quad (23)$$

Therefore, for $\beta = 0.5$ the rate of Sb electrodissolution is

$$i_a = 6F\bar{k}_a[OH^-]^2 \exp FE/2RT \quad (24)$$

The cathodic rate for Step 21e is,

$$|i_{c,21e}| = F\bar{k}_{c,21e}[Sb(OH)_4^-] \exp -(1-\beta)FE/RT \quad (25)$$

With the same assumptions as given above for Equation 22, Equation 25 becomes

$$|i_{c,21e}| = F\bar{k}'_{c,21e} \exp -(2-\beta)FE/RT \quad (26)$$

Thus, the rate of Sb(III) reduction is,

$$|i_c| = 6F\bar{k}_c \exp -3FE/2RT \quad (27)$$

The rate expressions (Equations 24 and 27) developed from the above mechanism approximate well the empirical rate expressions given in Equations 10 and 12, respectively.

For electrodeposition of Sb(III) in alkaline solutions (potentials < -1.0 V), Equation 15 is taken as the reaction,

$$SbO_2^- + 2H_2O + 3e^- = Sb + 4OH^- \quad (15)$$

where $E^e = 0.446 - 0.079\text{pH} + 0.02 \log [SbO_2^-]$ V vs SHE.

The following mechanism is proposed for the electrodeposition of Sb(III) in alkaline solutions.

$$SbO_2^- + 2H_2O + e^- \xrightarrow{\text{rds}} Sb(OH)_3^- + OH^- \quad (28a)$$

$$Sb(OH)_3^- = Sb(OH)_2 + OH^- \quad (28b)$$

$$Sb(OH)_2 + e^- = SbOH + OH^- \quad (28c)$$

$$SbOH + e^- = SbOH^- \quad (28d)$$

$$SbOH^- = Sb + OH^- \quad (28e)$$

If Step 28a is assumed as the rate determining step,

$$i_{c,21a} = F\bar{k}_{c,28a}[SbO_2^-] \exp -(1-\beta)FE/RT \quad (29)$$

Therefore, for $\beta = 0.5$, the rate of Sb(III) electrodeposition ($|i'_c|$) is,

$$|i'_c| = 3F\bar{k}'_c[SbO_2^-] \exp -FE/2RT \quad (30)$$

The rate expression for Sb(III) electrodeposition (Equation 30) developed from the above mechanism is in accord with the empirical rate expression (Equation 18).

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References

[1] H. E. Haring and K. G. Compton, *Trans. Electrochem. Soc.* **68** (1935) 283.

[2] M. Pourbaix, 'Atlas of Electrochemical Equilibrium in Aqueous Solutions', Pergamon Press, Oxford (1966).

[3] R. M. Burns and W. W. Bradley, 'Protective Coatings for Metals', Reinhold Pub., New York (1955) 274.

[4] J. T. Stock, W. C. Purdy and L. M. Garcia, *Chem. Rev.* **58** (1958) 611.

[5] D. J. G. Ives and G. J. Janz, 'Reference Electrodes', Academic Press, New York (1961) p. 351.

[6] L. R. Park and H. C. Beard, *J. Phys. Chem.* **37** (1933) 822.

[7] G. Edwall, Dissertation, Royal Institute of Technology, Stockholm, Sweden (1976).

[8] L. R. Park and H. C. Beard, *J. Amer. Chem. Soc.* **54** (1932) 856.

[9] G. A. Perley, *Ind. Eng. Chem., Anal. Edn.* **11** (1939) 319.

[10] A. R. Tourky and A. Mousa, *J. Chem. Soc.* (1948) 756.

[11] A. K. M. S. Huq, A. J. Rosenberg and A. C. Makrides, *J. Electrochem. Soc.* **111** (1964) 278.

[12] L. L. Wikstrom, N. T. Thomas and Ken Nobe, *ibid.* **122** (1975) 1201.