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Inhibition of PbO_2 formation during lead electrowinning

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The effect of the addition of arsenic compounds on the inhibition of PbO_2 formation on the anode, thus promoting oxygen evolution in the electrowinning process of lead, has been investigated. Various possible anode reactions involving arsenic have been discussed. Preferential adsorption of arsenic compounds on the electrode surface seems to be the most probable reason for the inhibition of PbO_2 formation.

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1. Introduction

Electrowinning of lead from acid solutions has been carried out for many years. Several electrolytes, notably fluoborate, silicofluorides and sulphamate baths, have achieved technical importance for commercial electrodeposition; however, the deposition of PbO_2 on the anode has been an obstacle. Since it is difficult to evolve oxygen at the anode at the lower current densities normally employed in electrowinning, PbO_2 is deposited on the anode at the same time as Pb is deposited on the cathode. Operations such as thermal reduction and leaching have to be carried out for reprocessing of the anode product. Application of higher current densities, and the use of unbalanced electrode arrangements have been suggested to facilitate oxygen evolution in place of PbO_2 formation, but none of these measures is entirely satisfactory.

Addition of arsenic compounds to lead electrowinning electrolytes has been reported [1] with the object of reducing PbO_2 formation. The arsenic compounds which are found to be effective are those which have sufficient solubility in the electrolytes employed. Arsenic content in the range of 250–650 ppm has been found to produce significant gassing at the anode thus eliminating PbO_2 formation. Addition of arsenic compounds such as AsF_3, As_2O_3, $AsCl_3$ and As_2O_5 has been found to be effective. Generally, there is no need to supply additional arsenic during electrowinning since it is not consumed in the process. However, due to the possibility of entrapment of some arsenic either in PbO_2 or the lead deposit, occasional replenishment may be necessary.

2. Experimental details

Potentiodynamic studies were carried out with platinum foil of $5.2\,cm^2$ surface area as working and auxilliary electrodes using a Wenking potentiostat, a Wenking scan generator and an x–y recorder. An H-type glass cell of $200\,cm^3$ capacity was used. Polarization studies were carried out in $0.5\,mol\,dm^{-3}$ HBF_4 and $0.3\,mol\,dm^{-3}$ and $0.03\,mol\,dm^{-3}$ $Pb(BF_4)_2$ solutions containing 0–1000 ppm of arsenic either in the trivalent or pentavalent state. A scan rate of $50\,mV\,s^{-1}$ was used in all the experiments. The potential was scanned from 400 to 2000 mV in the case of anodic polarization studies and from 400 to −500 mV in the case of cathodic polarization studies.

Anodic polarization studies were carried out with a $0.3\,mol\,dm^{-3}$ $Pb(BF_4)_2$ solution containing 0–$4\,g\,dm^{-3}$ of H_3PO_4. Galvanostatic studies with Pt electrodes in $0.3\,mol\,dm^{-3}$ $Pb(BF_4)_2$ solution containing 0–1000 ppm of As(III) at an anodic current density of $250\,A\,m^{-2}$ for 1 h duration were carried out and current efficiencies for PbO_2 deposition were determined. The corresponding potential–time curves were also plotted.

A saturated calomel electrode was used as the reference electrode. All potentials are quoted

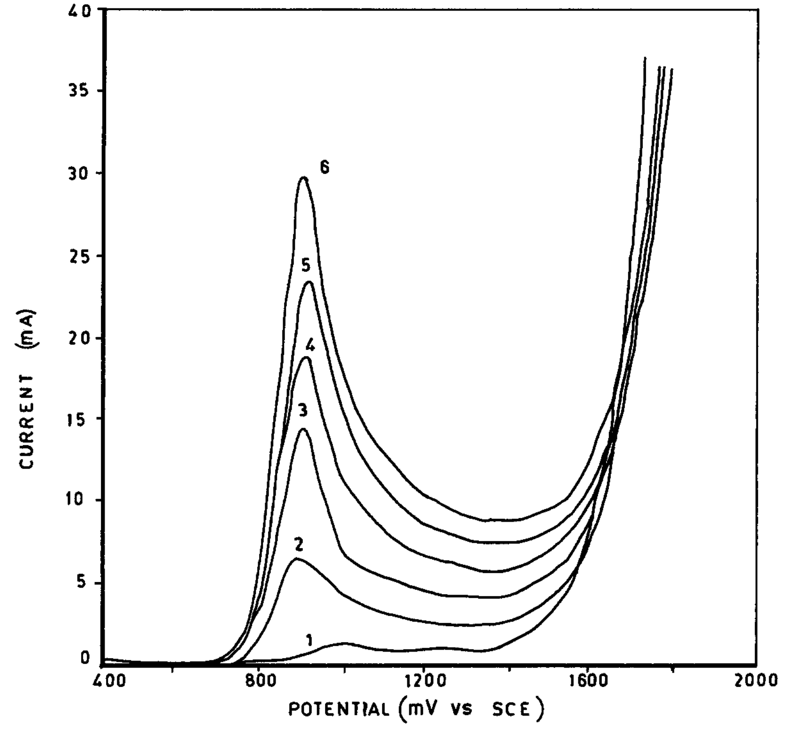

Fig. 1. Potentiodynamic curves of Pt in 0.5 mol dm^{-3} HBF_4 with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; 5, 800 ppm; and 6, 1000 ppm of As(III) at 50 mV s^{-1}.

with respect to this reference unless otherwise stated.

3. Results and discussion

The electrowinning of lead from aqueous solutions of soluble salts such as fluoborate is always accompanied by a simultaneous deposition of PbO_2 on the anode. The anodic reaction is

$$Pb(BF_4)_2 + 2H_2O \longrightarrow PbO_2 + 2H^+ + 2HBF_4 + 2e \quad (1)$$

The cathodic reaction is

$$Pb(BF_4)_2 + 2H^+ + 2e \longrightarrow Pb + 2HBF_4 \quad (2)$$

The overall reaction is

$$2Pb(BF_4)_2 + 2H_2O \longrightarrow PbO_2 + Pb + 4HBF_4 \quad (3)$$

In essence, one mole of PbO_2 is produced for each mole of lead deposited.

Fig. 1 shows potentiodynamic curves for Pt in fluoboric acid containing different amounts of arsenic added in the form of sodium *m*-arsenite. An anodic peak formed at 950 mV (SCE) is due to oxidation of arsenite to arsenate. The peak current increases proportionately with addition of arsenic (III) after which the current begins to drop. E^0 for the reaction

$$AsO_4^{3-} + 4H^+ + 4e \rightleftharpoons AsO_2^- + 2H_2O \quad (4)$$

is 0.977 V (NHE) [2].

Fig. 2 shows the potentiodynamic curves of Pt in lead fluoborate solution with addition of As(III). In the absence of arsenic ions, the anodic reaction is the formation of PbO_2 as indicated by the current rise at the lower potential, namely 1450 mV (SCE). E^0 for

$$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O \quad (5)$$

is 1.456 V (NHE). The tendency towards O_2 evolution replacing PbO_2 formation increases with addition of arsenic compound.

Fig. 3 shows the potentiodynamic curves for the electrolyte of lower concentration of lead, viz., 0.03 mol dm^{-3} $Pb(BF_4)_2$ containing varying amounts of arsenic compound, where the PbO_2 formation and O_2 evolution regions are seen distinctly. The peak at 1450 mV (SCE) is due to PbO_2 formation. The addition of arsenic com-

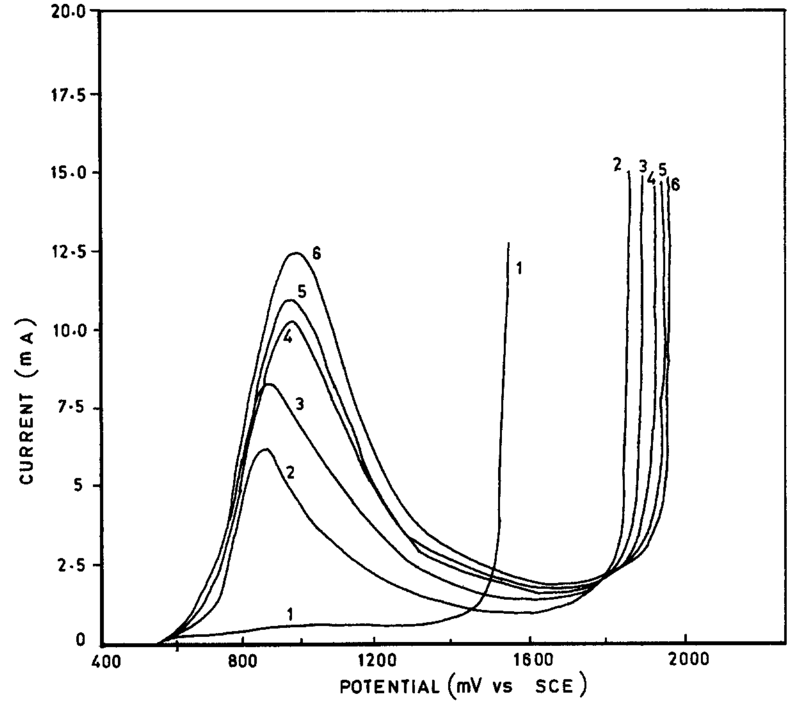

Fig. 2. Potentiodynamic curves of Pt in 0.3 mol dm^{-3} Pb(BF$_4$)$_2$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; 5, 800 ppm; and 6, 1000 ppm of As(III) at 50 mV s^{-1}.

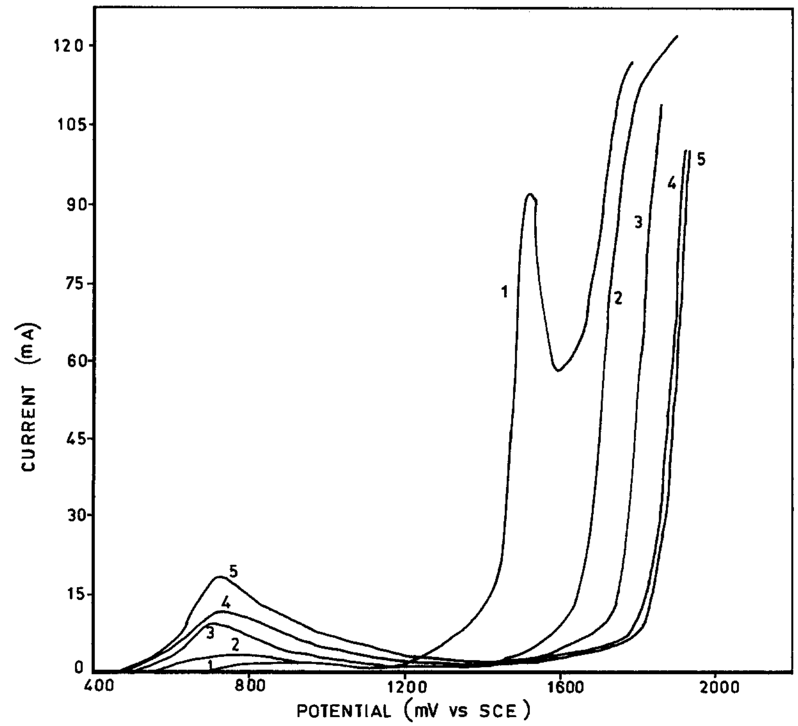

Fig. 3. Potentiodynamic curves of Pt in 0.03 mol dm^{-3} Pb(BF$_4$)$_2$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; and 5, 800 ppm of As(III) at 50 m V s^{-1}.

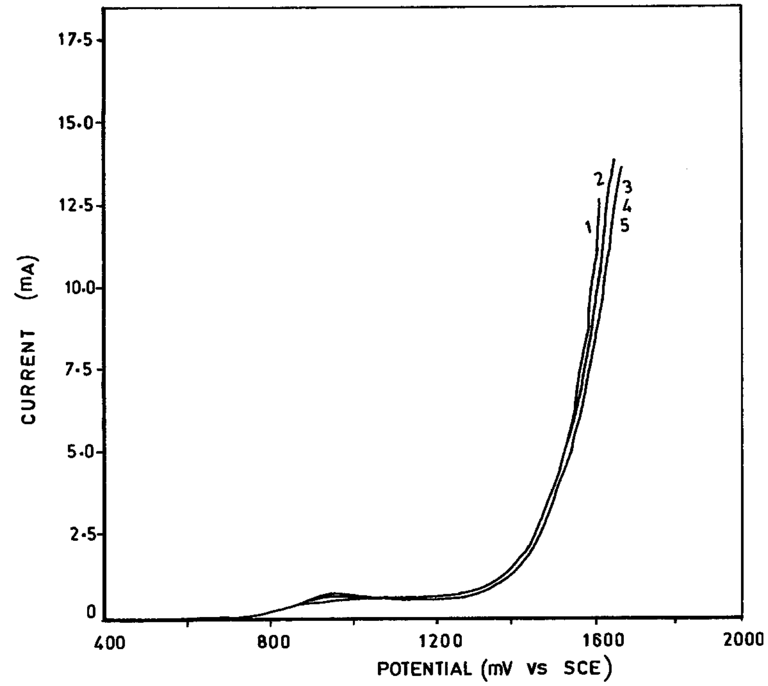

Fig. 4. Potentiodynamic curves of Pt in 0.5 mol dm^{-3} HBF_4 with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; and 5, 800 ppm of As (V) at 50 mV s^{-1}.

pound inhibits the formation of PbO_2 and the peak due to PbO_2 is eliminated. The current rise at more positive potential is due to oxygen evolution (visibly seen) along with the formation of a thin layer of PbO_2 in the case of lower amounts of arsenic ion, namely in the range of 200–600 ppm. With the addition of 800 ppm of arsenic ion, oxygen evolution takes place at 2.0 V and further addition alters the oxygen overvoltage very little.

The effect of addition of arsenic (V) compound has also been studied. Figs 4 and 5 are the potentiodynamic curves of Pt in HBF_4 and $Pb(BF_4)_2$ respectively with addition of arsenic (V) compound. The elimination of the PbO_2 formation peak and the shifting of the oxygen evolution potential to more positive values in the presence of arsenic (V) are clearly seen in Fig. 6.

Galvanostatic studies of Pb electrowinning from $Pb(BF_4)_2$ using a current density of 250 A m^{-2} indicate that in the absence of arsenic ions the anodic reaction is almost 100% the formation of PbO_2. Additions of arsenic compound reduce PbO_2 formation significantly promoting instead the evolution of O_2. With addition of arsenic ion above 600 ppm the anodic current efficiency of PbO_2 formation is reduced to less than 1% (Fig. 7). Potential–time curves as shown in Fig. 8 indicate lower anode potentials in the absence of arsenic ion. With increased addition of arsenic compound the anode potential becomes increasingly more positive indicating the O_2 evolution reaction is proceeding. The potentiodynamic curves 1–6 in Fig. 9 show the influence of arsenic(III) on the oxygen evolution potential in HBF_4 solutions and this effect is more pronounced in the presence of Pb^{2+} in solution as indicated by curve 7 in Fig. 9.

3.1. *Possible redox reactions*

It is necessary to consider some alternative reactions at the anode in the absence of PbO_2 formation. The presence of oxidizable species such as Fe^{2+}, Co^{2+} and No_2^- affects the lead dioxide deposition process due to their involvement in the electrode reaction [3, 4]. Similar redox reactions involving arsenic at the electrodes can be envisaged:

$$AsO_4^{3-} + 2H^+ + 2e \rightleftharpoons AsO_3^{3-} + H_2O \quad (6)$$

This possibility can be ruled out on the basis of the cathodic polarization studies with Pt in $Pb(BF_4)_2$ containing arsenic (V) as given in Fig. 10. There is no reduction peak for arsenic (V) to

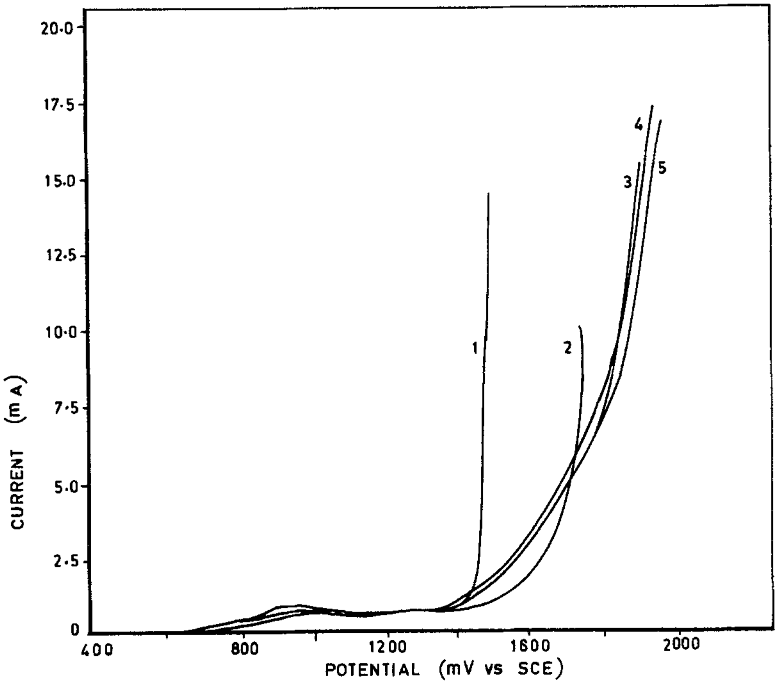

Fig. 5. Potentiodynamic curves of Pt in 0.3 mol dm^{-3} Pb(BF$_4$)$_2$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; and 5, 800 ppm of As(V) at 50 mV s^{-1}.

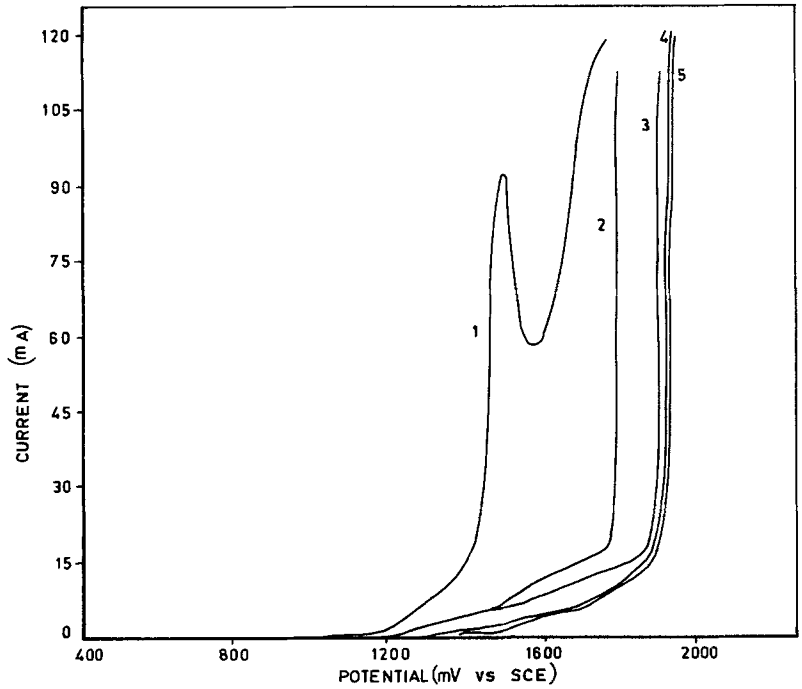

Fig. 6. Potentiodynamic curves of Pt in 0.03 mol dm^{-3} Pb(BF$_4$)$_2$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; and 5, 800 ppm of As(V) at 50 mV s^{-1}.

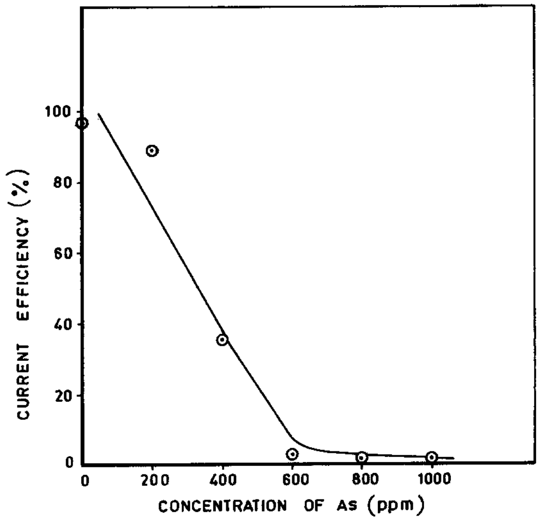

Fig. 7. Current efficiency for PbO_2 deposition with As(III) addition in 0.3 mol dm^{-3} $Pb(BF_4)_2$ solution.

arsenic (III). The fact that current efficiency for lead deposition is not lowered by addition of arsenic compound should also be taken into account in this context.

A further factor requiring consideration is the influence of certain elements such as Ag and Co in reducing the corrosion of lead anodes in H_2SO_4 solution [5]. These elements are present either as soluble species in the electrolyte or as alloying elements of lead anodes which decrease the O_2 overpotential. The result is O_2 evolution in preference to PbO_2 formation. Co^{2+} probably acts as a redox catalyst to provide an alternative path for oxygen evolution [6].

$$Co^{2+} \rightleftharpoons Co^{3+} + e \qquad (7)$$

$$Co^{3+} + OH^- \rightleftharpoons CoOH^{2+} \qquad (8)$$

$$2CoOH^{2+} \rightleftharpoons Co^{2+} + H_2O + (O) \qquad (9)$$

$$(O) + (O) \rightleftharpoons O_2 \qquad (10)$$

Such a redox couple mechanism will not explain the absence of PbO_2 formation with the arsenite–arsenate couple since O_2 overpotential values are higher as opposed to the situation with the Co^{2+}–Co^{3+} couple. Moreover, it is to be noted that PbO_2 formation associated with less polarization does not take place in the presence of arsenate.

3.2. *Inhibition through peroxy compound formation*

The presence of hydrogen peroxide can be a deterrent to the PbO_2 build-up due to the reaction

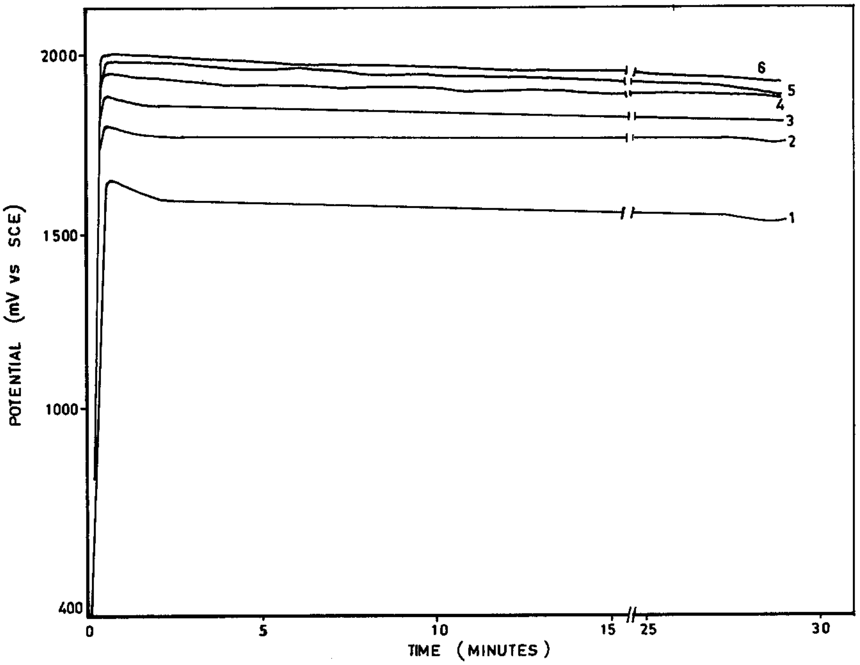

Fig. 8. Anode potential–time curves of Pt in 0.3 mol dm^{-3} $Pb(BF_4)_2$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; 5, 800 ppm; and 6, 1000 ppm of As(III).

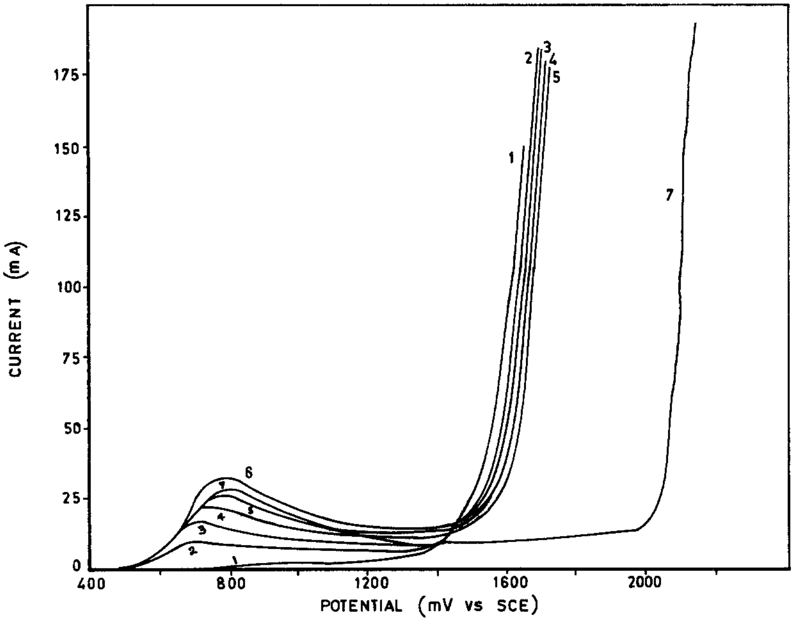

Fig. 9. Potentiodynamic curves of Pt in 1 mol dm^{-3} HBF$_4$ with: 1, 0 ppm; 2, 200 ppm; 3, 400 ppm; 4, 600 ppm; 5, 800 ppm; and 6, 1000 ppm of As(III); 7, in 1 mol dm^{-3} HBF$_4$ + 0.3 mol dm^{-3} Pb (BF$_4$)$_2$ with 1000 ppm of As(III) at 50 mV s^{-1}.

$$PbO_2 + H_2O_2 + 2H^+ \longrightarrow Pb^{2+} + O_2 + 2H_2O \quad (11)$$

H_2O_2 can be formed electrochemically or through a peroxy salt. The fact that anodic formation of H_2O_2 in acid medium is not possible [7] and that the peroxy compound of arsenate could not be produced anodically [8] rules out the role of H_2O_2 in the prevention of build-up of PbO$_2$.

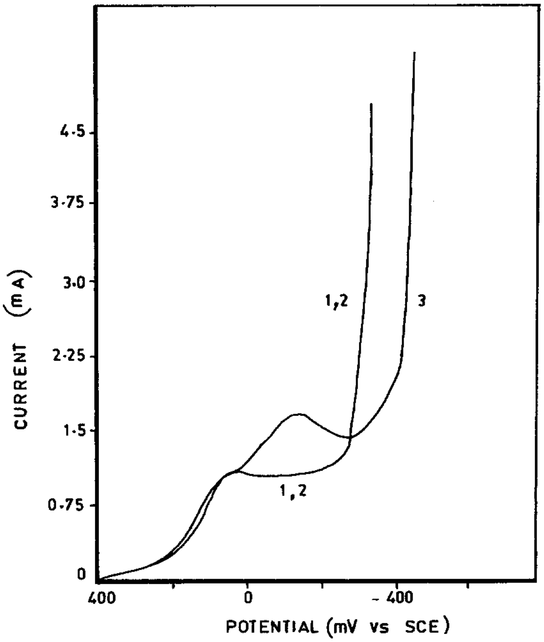

Fig. 10. Cathodic polarization curves of Pt: 1, in 0.5 mol dm^{-3} HBF$_4$; 2, in 0.5 mol dm^{-3} HBF$_4$ with 800 ppm of As(V); 3, in 0.5 mol dm^{-3} HBF$_4$ + 0.3 mol dm^{-3} Pb(BF$_4$)$_2$ with 800 ppm of As(V) at 50 mV s^{-1}.

3.3. *Adsorption of arsenic compounds on the electrode surface*

The influence of arsenate ion in inhibition of the formation of PbO$_2$ can be explained on the basis of preferential adsorption on the electrode surface. It is known that surface active substances inhibit electrode reactions.

A probable mechanism for PbO$_2$ formation suggested by Fleischmann and Liler [9] is

$$OH^- - e \rightleftharpoons OH_{ads} \quad (12)$$

$$Pb^{2+} + OH_{ads} + OH^- - e \longrightarrow Pb(OH)_2^{2+} \rightleftharpoons PbO_2 + 2H^+ \quad (13)$$

Hampson *et al.* [10] suggested the following mechanism:

$$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2 + 2H^+ \quad (14)$$

$$Pb(OH)_2 \longrightarrow (HO\cdot Pb\cdot OH)^+ + e \quad (15)$$

$$(HO\cdot Pb\cdot OH)^+ \longrightarrow PbO_2(H^+)_{2ads} + e \quad (16)$$

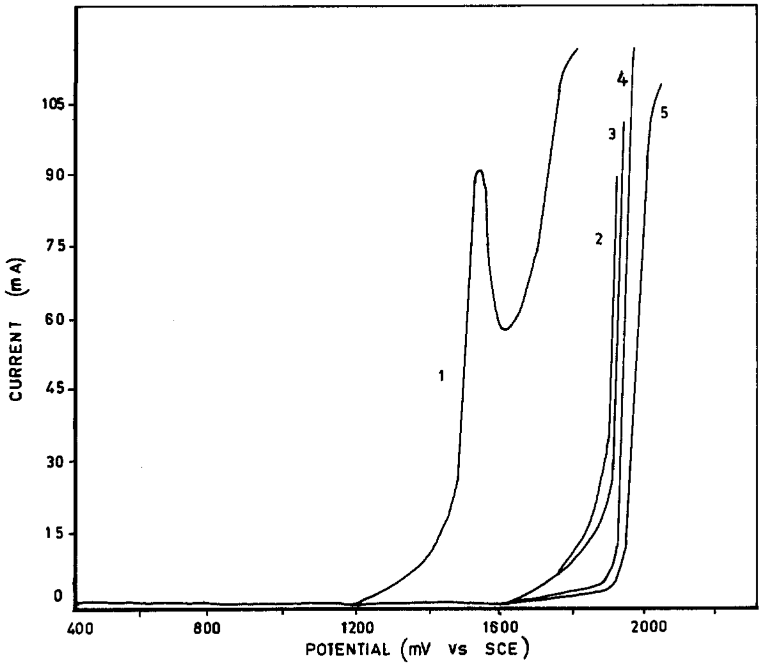

Fig. 11. Potentiodynamic curves of Pt in 0.03 mol dm^{-3} $Pb(BF_4)_2$ with: 1, 0 g dm^{-3}; 2, 1 g dm^{-3}; 3, 2 g dm^{-3}; 4, 3 g dm^{-3}; and 5, 4 g dm^{-3} H_3PO_4 at 50 mV s^{-1}.

$$PbO_2(H^+)_{2ads} \longrightarrow PbO_2 + 2H^+ \tag{17}$$

The overall reaction involves a Pb^{4+} species, namely $PbO_2(H^+)_2$, adsorbed at the electrode surface. This reaction is inhibited in the presence of arsenate ions which have a tendency to occupy the active centres of the Pt surface.

Similar inhibition of electrode reactions by the readily adsorbed extraneous species such as chloride and thiocyanate has been reported for the anodic oxidation of oxalic acid on a platinum surface [11]. Moreover, it is observed that addition of arsenic compound increases the anode potential, resulting in oxygen evolution in place of PbO_2 formation, and that the anode potential increases proportionately with the amount of arsenic compound added. It is known that in the formation of peroxy compounds a higher anode potential is essential, and surface active substances such as fluoride, thiocyanate compounds or urea are used to achieve this. The size of the ion is also a factor to be considered. Anions such as arsenate and phosphate, having higher ionic radii, tend to give higher surface coverage.

Hence the role of arsenic compounds in inhibiting PbO_2 formation can be explained in the following manner. Trivalent arsenic compounds oxidize to the pentavalent state on the electrode surface:

$$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e \tag{18}$$

The adsorption of arsenate ion on the electrode surface leads to a shift of the anode potential to a more positive value resulting in the oxygen evolution reaction,

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e \tag{19}$$

The effect of addition of arsenic compound on the increase of anode potential is more pronounced in the presence of Pb^{2+} ion in the electrolyte as indicated by Fig. 9. This may be due to the increased tendency of arsenic compound adsorption on the PbO_2 film as compared to a platinum surface.

The presence of phosphorus compounds such as phosphoric acid and organic phosphates prevent anodic formation of PbO_2 [12]. Polarization studies with addition of H_3PO_4 in small amounts give rise to similar types of potentiodynamic curves as those given in Fig. 11, where the absence of a PbO_2 peak and the shift of O_2 evolution to more positive potential values has been indicated. Capacitance measurements reported earlier for phosphoric acid indicates a surface activity of phosphate ions on platinum

[13]. Similar adsorption phenomenon can be a possible reason for the inhibition of PbO_2 formation in the presence of arsenate ions. It is proposed to carry out capacitance mesurements with arsenate ions to confirm the adsorption phenomenon.

4. Conclusion

In electrowinning of lead, the addition of arsenic either in the trivalent or pentavalent state effectively controls PbO_2 formation on the anode and promotes O_2 evolution. The effective range of arsenic addition is from 600–800 ppm. Arsenic addition increases the anode potential and inhibits lead dioxide formation which is associated with lower polarization. The inhibition is due to the preferential adsorption of arsenic compounds on the electrode surface.

Acknowledgement

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