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Anodic polarisation of lead in H_2SO_4 solution – Effect of cobalt (II) as solution species

P Ramachandran and K Balakrishnan

Central Electrochemical Research Institute, Karaikudi - 263 006, INDIA

The dramatic effect of Co^{2+}, in reducing the corrosion of lead anode and facilitating oxygen evolution, has been made clear through cyclic voltammetry.

Key words: Corrosion of lead, cobalt (II) addition, cyclic voltammetry

INTRODUCTION

Impurities or additives commonly present in electrowinning electrolytes affect both oxygen evolution characteristics and corrosion of lead anodes. The effect of cobalt addition as solution species is reported in this paper. An attempt is made to characterize the anode dissolution by cyclic voltammetry.

EXPERIMENTAL

Electrolytic lead, cast in the form of rod, cut into discs and embedded in teflon rod, was used. Cyclic voltammetric study was carried out in 1M H_2SO_4 with additions of Co^{2+}. A saturated calomel electrode was used as reference electrode and the potentials were quoted with respect to it.

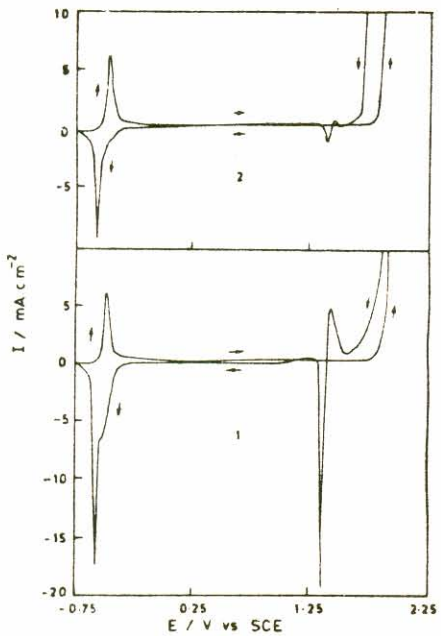

Fig. 1: Cyclic voltammograms of Pb (1) in 1M H_2SO_4 and (2) in 1M H_2SO_4, with 2000 mg.l^{-1} Co(II) at 5 mV.s^{-1}

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of Pb in 1M H_2SO_4 with and without the addition of Co^{+2}. A peak at –0.50V in the anodic sweep is due to oxidation of Pb to $PbSO_4$, which is not influenced by Co^{2+}. The current rise corresponding to oxygen evolution is shifted to the less positive potential with the addition of Co^{2+}. A reduction peak seen at 1.40 V in the cathodic sweep is due to reduction of PbO_2 to $PbSO_4$ and the peak height is very much reduced in presence of added Co^{2+} indicating that the corrosion in the form of PbO_2 formation is reduced. Figure 2 illustrates the progressive diminution in peak height for the electrode process $PbO_2 \longrightarrow PbSO_4$ with an increase in the addition of Co^{2+}.

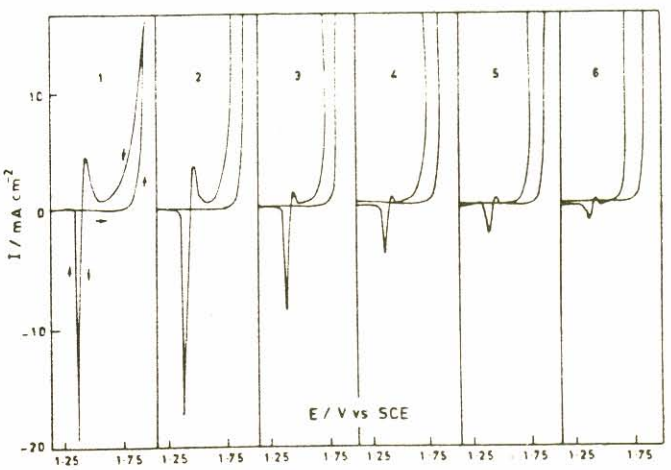

Fig. 2: Variation of peak current for PbO_2 reduction in the cyclic voltammetry of Pb in 1M H_2SO_4 with (1) 0 mg.l^{-1} (2) 100 mg.l^{-1} (3) 200 mg.l^{-1} (4) 500 mg.l^{-1} (5) 1000 mg.l^{-1} and (6) 2000 mg.l^{-1} Co(II) at 5 mV.s^{-1}

The addition of Co^{2+} gives rise to the Tafel plots as shown in Fig. 3 with the slope of 62-68 mV instead of the normal value of 120 mV, which indicates a catalytic effect on oxygen evolution. Koch [1] has suggested a redox

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couple mechanism.

$$CO^{2+} \rightleftharpoons Co^{3+} + e$$
$$Co^{3+} + OH^- \rightleftharpoons CoOH^{2+}$$
$$2CoOH^{2+} \rightleftharpoons 2Co^{2+} + H_2O + O$$
$$O + O \rightleftharpoons O_2$$

Theory predicts for this mechanism a slope of 0.06 V, which has been experimentally verified in the present work.

CONCLUSION

The addition of Co^{2+} retards the formation of PbO_2 as a corrosion product in the process of oxygen evolution on lead and the lower Tafel slope indicates the catalytic effect of cobalt on oxygen evolution.

REFERENCE

1. D F A Koch, *Aust J Chem*, **12** (1959) 127

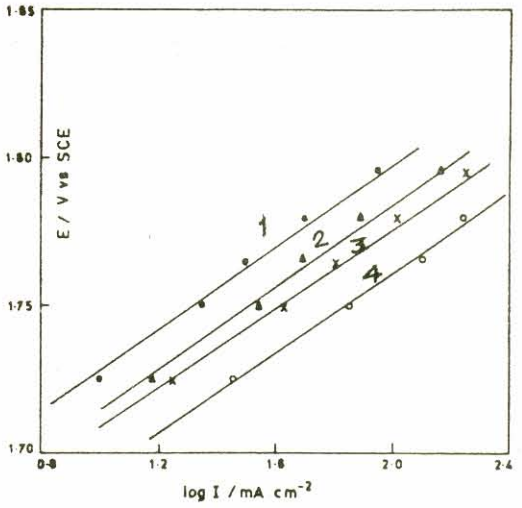

Fig. 3: Tafel plots for O_2 evolution on Pb in 1M H_2SO_4 with (1) 20 mg.l^{-1} (2) 50 mg.l^{-1} (3) 100 mg.l^{-1} and (4) 200 mg.l^{-1} Co(II)