IMPROVEMENT OF LEAD/ACID BATTERY PERFORMANCE BY ADDITION OF PHOSPHORIC ACID IN ELECTROLYTE

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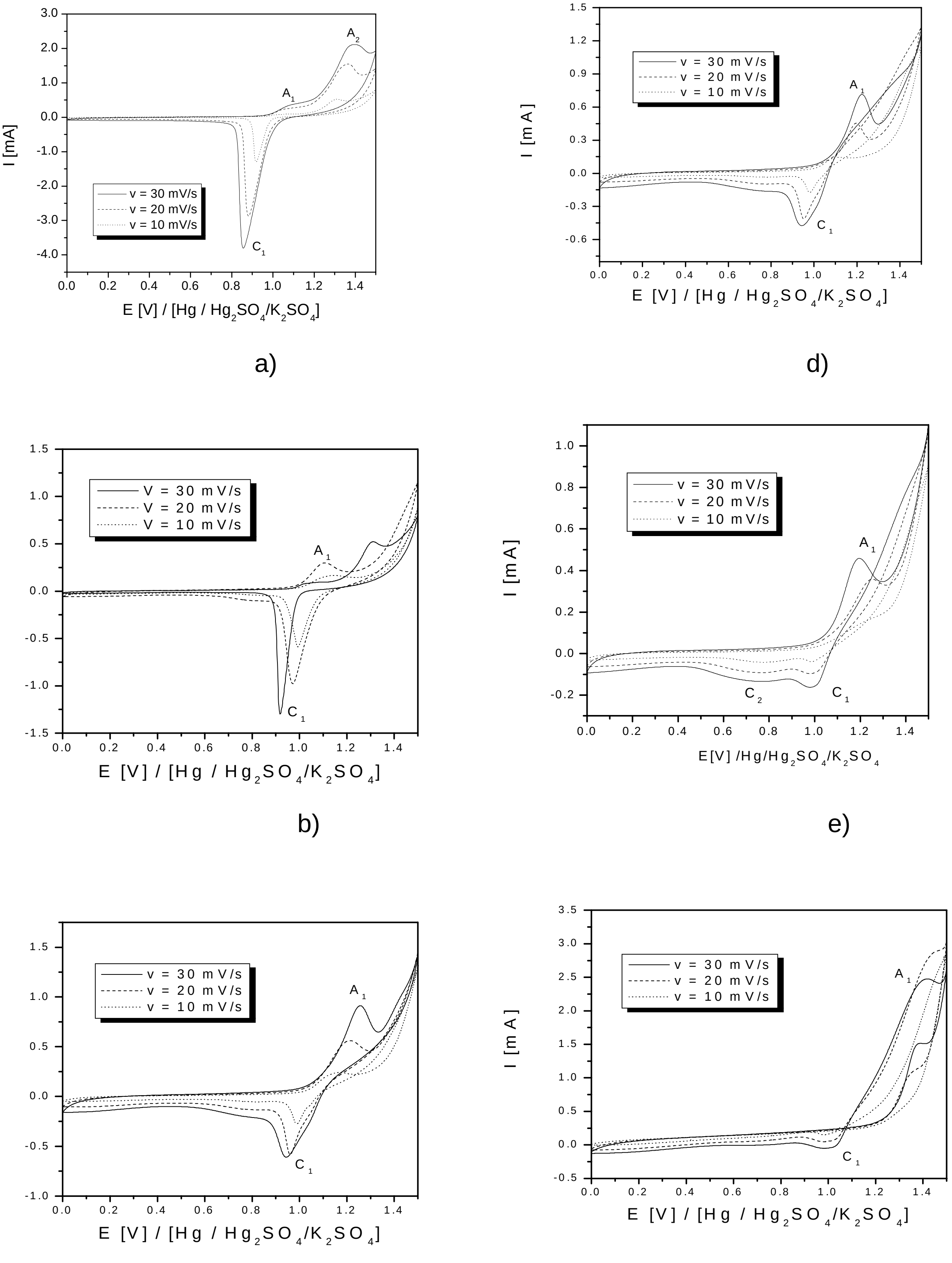
Introduction

To increase the cycle life and to decrease the rate of the self-discharge reaction of a lead-acid battery, at low temperature, some additives in electrolyte have been proposed [1-3]. Kathryn R. Bullock has been proved that in lead oxidation in sulfuric acid solution, in the presence of H_3PO_4, an intermediate lead phosphate [$Pb_3(PO_4)_2$] is formed which influences the sulphation rate of PbO_2 [4-5]. Several investigators have found that phosphoric acid reduces the amount of sulfate on the grid of the positive electrode during float charging and cycling, and that phosphate enters in the positive plate during charge and lives during discharge [6].

Experimental

The study of the H_3PO_4 effects on the electrochemical behaviour of PbO_2 has been made by using the cyclic voltammetry. Pure lead electrodes have been used (99.99%). The electrolyte consisted of a solution of 4.3 m H_2SO_4 with different contents of H_3PO_4 additives. A $Hg/Hg_2SO_4/K_2SO_4$/(sat) electrode served as the reference electrode. The counter electrode was made of pure lead.



a)

d)

b)

e)

c)

f)

Fig.1. Cyclic voltammograms of lead in 4.3 m H_2SO_4 :
a) without H_3PO_4.
Containing H_3PO_4 :
b) 0.3%; c) 0.6%; d)) 0.9%; e)) 1.2%; f)) 1.5%;

Results and discussion

Some typical voltammograms recorded on a disk shaped lead electrode in 4.3m H_2SO_4 solution by sweeping the potential between 0 to +2 V, at different scan rate, are shown in figure 1(a). In the positive going potential scan two peaks corresponding to α-PbO_2 (A_1) and β-PbO_2 (A_2) formation progressively developed with increasing cycle number.

The addition of phosphoric acid in electrolyte shifts the anodic peaks of phase formation α and β PbO_2 towards more positive potential values concomitently with the decrease of their area, figure 1, (b-f). With the gradual increase of H_3PO_4 concentration added to H_2SO_4 solution, peak A_2 corresponding to phase β-PbO_2 disappeared. Like the oxidation peaks, the reduction peaks of PbO_2 to $PbSO_4$ (C_1) moved in anodic direction, a decrease of their area taking place. This result would suggest that H_3PO_4 decreases the rate of sulfation. The greater the cathodic peak shift the greater the anode peak A_1 is and the more it moves towards more positive potentials (towards the range of oxygen evolution).

Conclusion

In the presence of H_3PO_4, the formation of soluble phosphate species causes the decrease of corrosion layer thicknes (but this corrosion layers can not stopped to form). Higher that 0,9% concentrations of H_3PO_4 negatively affect the behaviour of the electrodes, higher potentials being required for the oxidation of $PbSO_4$ to PbO_2 , when the rate of oxygen evolution is also higher. As a result the charging efficiency of electrode is consequently lower. It is to remark that with high concentration of H_3PO_4 the electrolyte became opaque. This fact can be explained by the increase of solubility of lead phosphate species formed. Based on these experimental observations , formation of $Pb_3(PO_4)_2$ as an intermediate in the corrosion of Pb to PbO_2 seems reasonable.

References

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