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EFFECT OF AC SUPERPOSITION ON ELECTRODEPOSITION OF LEAD DIOXIDE: THE DIFFERENCE OF SINGLE PHASE AND THREE PHASE RECTIFIERS

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ABSTRACT

The influence of different proportions of AC superposition on DC during the electrodeposition of lead dioxide on graphite substrate was studied under both stationary and rotating conditions. The measurement of stress was also carried out. X-ray analysis showed the deposit to be only the ß-variety.

Key Words: PbO_2, A C Super position, Electrodeposition stress measurement

INTRODUCTION

Electrodeposited lead dioxide finds extensive applications as an anode in the production of electrochemicals [1-4] especially in the form of graphite substrate lead dioxide (GSLD) anodes [1,5-7] for applications in halates [1,2], perhalates [1,3] and ozone [8]. During such studies, it was observed that most of the GSLD anodes obtained from using single-phase rectifier gave better adherent and crack-free deposits as compared with the deposits got from the three-phase rectifier. Since single-phase rectifiers are known to have more of AC component (ripples) as against three-phase rectifiers, this led to the study of the influence of AC superposition on DC during the electrodeposition of lead dioxide on graphite substrate.

Not much information is available on the superposition of AC for electrodeposition of lead dioxide, although a few references [9-11] are available on the influence of AC superposition on the formation of lead dioxide on lead from sulphuric acid electrolyte. The present paper deals with the influence of AC superposition on DC during electrodeposition of lead dioxide on graphite substrate from lead nitrate-copper nitrate bath, keeping the anode under either stationary or rotating conditions. The stress measurement was also carried out.

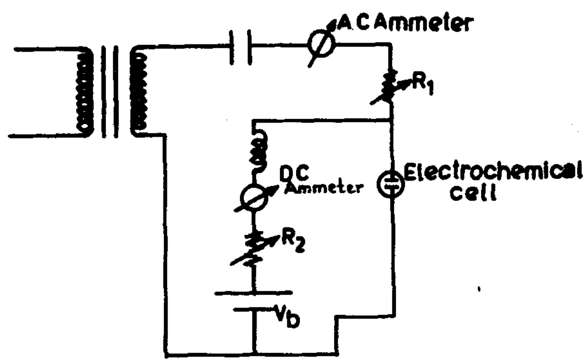
EXPERIMENTAL

Cell assembly

A 500 ml tall form beaker fitted with a PVC cover having three holes for introducing the electrodes and the thermometer acted as cell. A graphite rod (1 cm dia × 15 cm height) was employed as anode which was surrounded by a perforated cylindrical stainless steel cathode. The interelectrode distance of 2 cm was maintained for all the experiments. For experiments with rotation, the anode was connected to the bottom of a rotating shaft assembly having a mercury cup on the top for electrical connection through mercury. A FHP motor was used to drive the shaft and the RPM of rotation (1500-2000) was measured by a tachometer. The electrolyte employed for lead dioxide deposition was lead nitrate (280-300 g/l) and copper nitrate (26-28 g/l). For higher temperatures, a water bath was employed with heating facility.

Electrolysis

After subjecting the graphite anode to the usual pretreatment [5], electrolysis was carried out by passing DC from 6 V battery. For superposition of different proportions of AC over DC, a set-up shown in figure 1 was fabricated and employed. All the experiments were carried out at an anode current density of 4 A dm^{-2}; the quantity of current passed being 2.6Ahrs. Neutralisation of the acid produced during the electrolysis was done by adding the required quantities of lead carbonate (total 10g) and copper carbonate (5g) and thereby the pH was maintained at 2-3 during electrolysis.



v_b D C Source
R_1 Resistance to vary AC current
R_2 ————,,———— DC ————,,————

Block diagram of the set up for AC superposition on DC

Analysis

Samples for analysis of purity of lead dioxide were collected by depositing lead dioxide under identical conditions over a platinum tube fitted tightly into aluminium rod (1 cm dia × 10 cm ht), serving as anode. Iodometric titration procedure [12] was followed for the analysis.

Stress measurement was carried out by following the procedure described earlier [13, 14].

RESULTS AND DISCUSSION

The results on the influence of different percentage of AC superposition on DC during the electrodeposition of lead dioxide under stationary and rotating conditions are given in Table I.

Table I: Results of different percentages of AC on DC for electrodeposition of lead dioxide
Electrolyte: 280-300 g/l $Pb(NO_3)_2$ and 26-28 g/l $Cu(NO_3)_2$
Anode current density: 4 $A.dm^{-2}$
Quantity of electricity: 2.6 A.hrs

No.	AC (%)	DC (%)	Temp. (°C)	Yield efficiency(%) Stationary	Yield efficiency(%) Rotation	Purity (%) Stationary	Purity (%) Rotation
1	0	100	60	100	100	98	89
2	0	100	30	98	96	88	88
3	5	95	60	83	88	95	93
4	10	90	60	84	86	98	92
5	15	85	60	85	79	95	90
6	20	80	60	95	86	93	89
7	25	75	30	91	89	90	87
8	25	75	60	90	82	92	91
9	30	70	30	77	71	94	92
10	30	70	60	73	68	96	92
11	40	60	30	66	57	95	93
12	40	60	60	61	54	95	93
13	50	50	30	60	61	98	93
14	50	50	60	56	61	95	93

It can be seen from the results that the yield of lead dioxide with rotation is, in general, lower than that at stationary condition. The yield is lower at higher temperatures than at room temperature under the same conditions of deposition. Although there is a marked decreasing trend in the yield with increase in the AC component from 25% and above, the yield is not very much altered when the AC component is 20% and less. The purity of lead dioxide is always better with stationary anode than with rotation. The analytical results of the purity which can be computed for lead-to-oxygen content in most of the samples gave almost the same values as reported earlier [15] for β - lead dioxide.

Figure 2 shows that the mean stress of lead dioxide deposit is only tensile even with the superposition of AC (10% or 20%). When the measurements were continued after stopping the current, the mean stress changed from tensile to compressive; this tendency was prevalent in all cases, unlike metal deposition and has been reported earlier [13]. However, no conclusion could be got on the superposition of AC on DC from these stress measurements. Studies on x-ray analysis show that the samples of lead dioxide are mainly β - variety up to 25% of AC superposition on DC.

Acknowledgement

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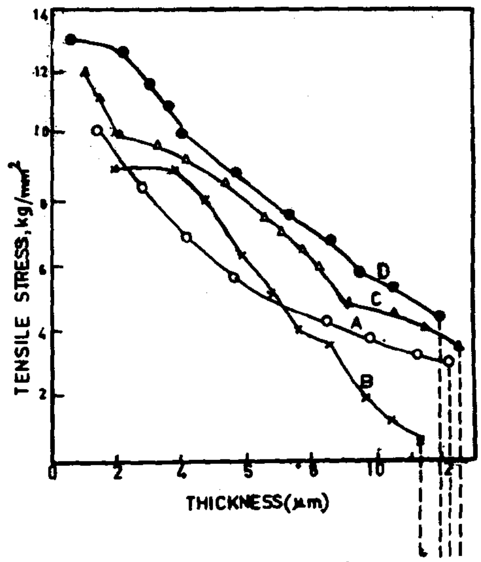

Fig. 2: Variation of stress with thickness of lead dioxide deposit
A: Pure DC at at 30°C; B = Pure DC at 60°C,
C: 10% AC at 30°C; D = 20% AC at 30°C

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