THE INFLUENCE OF THE SOLID/POROUS ELECTRODE INTERPHASE ON THE BEHAVIOUR OF POROUS LEAD DIOXIDE ELECTRODES

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Summary

A method is described by which the ease of reduction and reoxidation of porous lead dioxide electrodes may be assessed in the short time. Fourteen alloy porous electrode supports are compared with pure lead with special reference to the charge output on reduction, ease of reoxidation, and electrode support/porous phase adhesion.

Antimony at 6% is far superior to the other electrodes investigated. Bismuth appears to be an enhancing ingredient and it is suggested that evidence from battery scale tests would be interesting. Barium is also a moderately useful ingredient. Lithium additions accelerate porous electrode failure to a marked degree.

Introduction

We have shown in previous communications [1, 2] how the reduction of porous lead dioxide electrodes in 5M H_2SO_4 using a potential sweep from 1250 mV *vs* $Hg/Hg_2SO_4/5M\ H_2SO_4$ to 700 mV at 0 1 mV s^{-1} gives a curve which indicates that the porous inner structure contributes significantly to the overall charge output on reduction. This experiment can readily be extended to provide a method of obtaining a measure of the ease of reoxidation of the electrode by potentiostatically stepping the electrode, swept to a series of potentials in the lead sulphate region, back to the PbO_2 region.

Specifically, on stepping back a reduced electrode to the lead dioxide region, the development of an initially rising transient in the current–time

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response indicates a slow process in the crystallisation of lead dioxide on sulphate. In practice this is observed as a *coup de fouet* in the recharge The limiting potential to which the electrode may be driven before a step back generates a rising transient is a measure of the rechargeability. The number of cycles taken without deterioration in the magnitude of the area under the reductive sweep curve is a measure of the cycle life of the electrode. The magnitude of the peak and the area under the curve of the reductive sweep are measures of the electrode output. A technique has been devised in which all these criteria are incorporated in a single repetitive experiment

The development of low loss batteries and the alternator for recharging has made the use of antimony free grids (electrode supports) desirable. Over the last few years alloys of lead with calcium, tin, and aluminium have been used to replace antimonial lead alloys. However, it has been reported that low cycle lives result when the alloy contains less than 3% antimony and, moreover, the lead, calcium, tin, aluminium alloys show unsatisfactory recharging characteristics. Experiments using the above technique have been made on a number of alloys selected in order to identify and evaluate likely enhancing ingredients for lead|calcium|tin|aluminium alloys. This paper records the results.

Experimental

The apparatus and cells have already been described [3] Porous electrodes were constructed as described previously [1], however, the solid supports for the porous electrode material were either pure lead or various lead, calcium, tin, aluminium-based alloys.

Experiments were made by sweeping the electrode potential negatively to 700 mV, followed by a potential step back to 1300 mV. The electrode was completely reconverted to PbO_2 by a galvanostatic charge (25 mA cm^{-2}) and the cycle of operations repeated. These cycles were repeated until a constant response was obtained.

On a stabilised electrode the terminal potential to which the reductive sweep could be driven without the development of an initial rising transient on stepping back to 1300 mV was determined. If the electrode failed prior to stabilisation, the number of cycles prior to failure was recorded.

Results

Figure 1 shows the reduction by a potential sweep of porous lead dioxide with an antimonial alloy solid support. The long tail is characteristic of all newly produced porous lead dioxide electrodes and indicates that the discharge is being driven into the porous matrix.
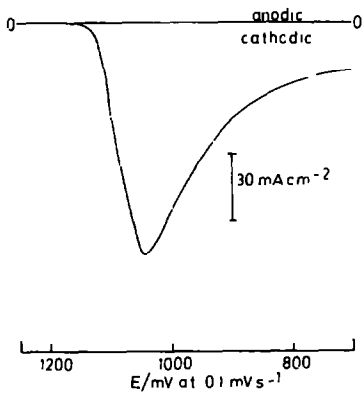
Fig 1 Stabilised negative going sweep at 0 1 mV s^{-1} Porous lead dioxide electrode (57% porous) on 6%Sb/94%Pb support 5M H_2SO_4 at 22 °C

Figure 2 shows the reduction curve for the lithium alloy after a few cycles. The long tail has disappeared, indicating that the inner structure of the electrode contributes but little to the reduction. This appears to be a prelude to the complete collapse of the electrode. In later stages adhesion between the porous matrix and electrode support is lost The co-ordinates of the maxima in Figs 1 and 2 reflect the initial potential of discharge of a battery. The appearance of a shoulder in this curve indicates the operation of a new passivating process, in this case the isolation of the active material due to a complete layer of $PbSO_4$ around the active material support.

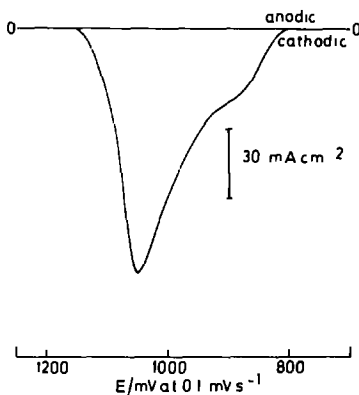Fig 2 Negative going sweep at 0 1 mV s^{-1} Porous lead dioxide electrode (57% porous) on 0 74%Sn/0 051%Ca/0 004%Al/0 003% Li/Pb support 5M H_2SO_4 at 22 °C

Figure 3 shows two curves for the reoxidation (step back) of reduced porous lead dioxide electrodes. The potential step is initiated from different final sweep potentials. In one, the final potential is insufficient to cause the rising transient observed in the other. The terminating potential prior to the occurrence of a rising transient is a measure of the ease of recharge.
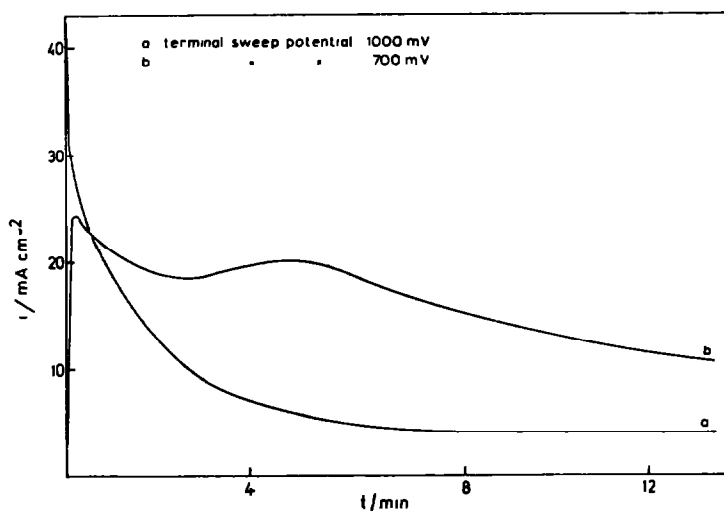
Fig 3 Current responses to a step back to the lead dioxide region following a negative going sweep at 0 1 mV s^{-1} Porous lead dioxide (57% porous) on pure lead 5M H_2SO_4 at 22 °C Curve A - terminal potential of reduction 1000 mV, curve B - terminal potential of reduction 700 mV

Table 1 shows the constitution of the alloys and Table 2 shows the results of the experiments.

TABLE 1

ALLOY	X (%)	Sb (%)	Ca (%)	Sn (%)	Al (%)	As (%)
1	0 01 (Se)	2 5	—	0 12	—	0 3
2	0 02 (Se)	6	—	0 13	—	0 14
3	—	6	—	—	—	—
4	—	—	0 070	0 7	0 05	—
5	0 003 (Li)	—	0 051	0 74	0 004	—
6	0 165 (Mg)	—	0 058	0 64	—	—
7	0 113 (Sr)	—	0 056	0 64	0 005	—
8	0 025 (Ba)	—	0 056	0 64	0 004	—
9	0 229 (Bi)	—	0 054	0 81	0 004	—
10	0 174 (Ag)	—	0 054	0 7	0 002	—
11	0 165 (Zn)	—	0 056	0 64	—	—
12	0 248 (Cd)	—	0 057	0 79	0 004	—
13	0 22 (In)	—	0 064	0 74	0 005	—
14	0 2 (In)	—	—	—	—	—

Discussion

The antimony alloys occupy a position of their own vis-à-vis the other alloys. Cycling could be carried out extensively (20 cycles) with no disastrous

TABLE 2

ALLOY	E_{MI} (mV)	E_{MS} (mV)	CL	i_{MS} (mA cm^{-2})	CRT	E_T (mV)
1	1065	1040	—	99 0	4	—
2	1050	1025	—	113 17	7	795
3	1030	1030	—	110 3	4	810
4	1065	1045	6	113 17	4	925
5	1065	1050	2	116 0	1	—
6	1075	1045	2	101 8	2	—
7	1080	1045	3	103 3	2	—
8	1070	1045	6	102 0	3	950
9	1060	1045	7	134 4	5	900
10	1075	1055	2	110 3	2	—
11	1080	1055	2	106 1	2	—
12	1070	1070	2	96 2	2	—
13	1075	1055	5	93 4	1	—
14	1070	1040	4	109 0	4	—
Pb	1070	1050	—	48 0	6	800

CL, Life in cycle number, CRT, number of cycles before the development of a rising transient on stepping back from 700 mV, E_{MI}, potential coordinate of maximum in the first negative going sweep, E_{MS}, potential coordinate of maximum in the "stabilised" negative going sweep, E_T, minimum potential of sweep for the development of a rising transient on step back to lead dioxide region, i_{MS}, current coordinate of maximum in the "stabilised" negative going sweep

loss in charge output in the reduction. It has been reported [4, 5] that the small particle size, large specific surface area, and prismatic morphology of the lead dioxide crystals were preserved when antimony was present in the plates During the course of charge and discharge cycles [4], the particle size of the lead dioxide increased, and the end of life was associated with this increase, as well as the anhedralization of the grains. Freshly prepared active material had about the same morphology and particle size characteristics, whether formed on pure lead or antimonial lead [4, 6]. Kordes [4] found that, in active materials on pure lead grids, the increase in particle size with cycling was more rapid than on antimonial grids, reaching a maximum after only 8 - 10 cycles The same paste on antimonial grids increased in particle size at a markedly slower rate and reached a maximum after twenty cycles. It has been reported [5] that the presence of antimony in the grid metal gives rise to an increased content of α-PbO_2 in the formed active material.

    Of the other alloys, bismuth is observed to give the best performance Comparison with the basic lead, calcium, tin, aluminium alloy (alloy 4) shows that bismuth is the only additive to enhance the electrode behaviour It appears that barium addition is not particularly detrimental, but it should be noted that in this experiment the amount of barium present in the alloy is much lower than the additives to all the other alloys except for lithium (due to difficulties encountered when making the alloys). The remaining additives all have marked detrimental effects on the electrode behaviour

It was evident, following the alloy preparation, that the (non-antimonial) alloys containing magnesium, strontium, and lithium became covered by a thick oxide film when left exposed to the atmosphere. This aerial oxidation phenomenon would greatly affect the subsequent alloy/porous interphase of the pasted and formed electrode in terms of adhesion of the two phases This arises from the presence of a passivating oxide film (ultimately transformed to $PbSO_4$) which would increase the rate of the self-discharge reaction. The increased rate of self discharge in alloys lacking the beneficial effects of antimony would give the dramatically short cycle lives observed for the majority of the alloys. Thus, it is proposed that bismuth acts in a similar way to antimony, which is not unexpected due to the close proximity of the two metals in the Periodic Table.

The theoretical background of these results is not understood and an exhaustive study of the literature has not revealed any satisfactory theory on which to base any satisfactory argument. The most attractive idea appeared to be invoking semiconductor behaviour which might give enhanced electrochemical responses due to band bending and electron tunnelling This does not appear to be a factor in the present studies since metals expected to show this effect are valueless as doping agents.

It is emphasised that the results in this paper are characteristic of these particular experiments and ought to be followed up closely by battery scale trials.

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