JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 595–600

Electrochemical cycling of pasted antimonial lead electrodes (positives)

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Received 6 November 1980

The behaviour of Pb–5% Sb positives during electrochemical cycling experiments is followed using a combination of linear sweep voltammetry and potentiostatic pulse experiments. The poor charge acceptance of antimonial lead is discussed in terms of the morphology of the lead sulphate crystals. A comparison is made between unpasted and pasted Pb–Sb electrodes.

1. Introduction

The use of antimony as the grid alloying ingredient for the lead–acid positive plate and the reason for this choice has been discussed by us for flat, unpasted electrodes [1, 2]; we have also looked at possible replacements for antimony in the positive grid [3, 4]. Our studies have now been extended to the porous electrode since positive grid corrosion is one of the principal reasons for the failure of lead–acid batteries during service life. Cyclic studies of lead–acid battery plates (positives) (charge/discharge reactions) have been exhaustively carried out by many workers (see, for example [5–7]). It was considered that the techniques most likely to produce the sought-for data here would be electrochemical cycling using a combination of linear sweep voltammetry and potentiostatic pulse experiments. This, it was hoped, would lead to an insight into the charge acceptance behaviour of the porous antimonial lead electrode.

The charge acceptance of a lead–acid cell can be considered as the capability of the cell to store charge so that it can be re-discharged [8]. This depends on many factors some of which are temperature, construction, age and condition of the cell and the charging conditions. Particular attention must be paid to the latter, namely the actual experimental conditions of the charging operation. Bode [8] has reported that fast, uncontrolled charging can lead to copious gassing and high temperatures; gas evolution can tear small particles from the positive plates resulting in premature capacity reduction. Another consequence of gas evolution usually observed is an increase in sludge formation. Some dislodged material can be carried either electrophoretically or by convection as a positively-charged colloid to the negative electrode where it is reduced to lead. This 'spongy' form of lead grows on the peripheries of the plates and in the extreme can lead to short-circuiting. On the other hand, if charging is stopped before the onset of gas evolution, the result can be equally disturbing: the active mass will not be fully charged which produces a loss in the overall capacity of the cell.

In the experiments reported here, the charging operation is performed with the electrode in an upward-facing position to prevent oxygen bubbles saturating the porous matrix. Oxidation is carried out galvanostatically (25 mA cm^{-2}) until oxygen is freely evolved from the working electrode and a steady potential of 1.250 V (0.3 M H_2SO_4) is attained (versus the Hg/Hg_2SO_4 reference in 0.3 M H_2SO_4).

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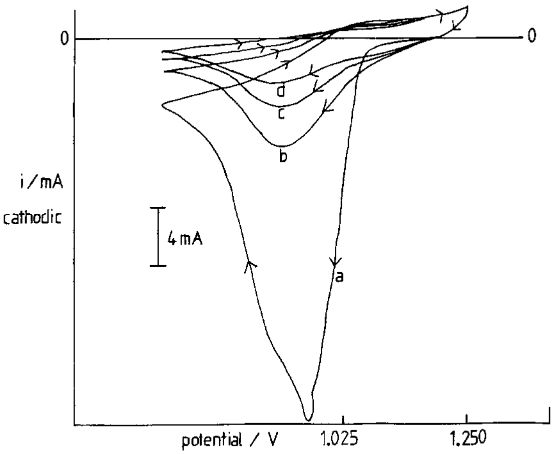

Fig. 1. Potential sweep experiments between 1250 mV and 700 mV for a pasted Pb–Sb positive ($v = 1$ mV s^{-1}, nominal surface area = 0.07 cm^2). a, First cycle; b, second cycle; c, third cycle; d, fourth cycle.

Table 1. Variation of reduction peak current with linear sweep cycling of a porous Pb–Sb electrode (700–1250 mV, 1 mV s^{-1})

Cycle number	*Reduction peak current* i_p (mA)	*Position of* i_p (E_p) (mV)
1	17.3	970
2	7.2	935
3	3.9	925
4	2.9	910
5	1.9	895
6	1.5	885
7	1.0	875
8	0.55	872
9	0.35	870
10	0.28	870
11	0.28	870
12	0.28	870

2. Experimental

The construction of the working electrode, the experimental set-up and electrical circuitry have all been described in a previous publication [9]. An Hg/Hg_2SO_4 reference electrode was used throughout and all potentials are quoted on this scale (23 ± 1° C). Experiments were performed in 5 M H_2SO_4 (deoxygenated, AnalaR) made from tri-distilled water except in the case of galvanostatic oxidation where a less concentrated electrolyte was employed (0.3 M H_2SO_4). All experiments were performed on a Pb–Sb porous positive electrode with analysis of the base metal showing 5.15 wt% Sb. The density of the standard automotive positive paste used was 4.10 g cm^{-3}.

3. Results and discussion

3.1. *Linear sweep cycling*

Potentiodynamic cycling experiments were performed between the limits 700 mV ($PbSO_4$) and 1250 mV (PbO_2/O_2) always at a sweep-speed of 1 mV s^{-1}. Fig. 1 shows a series of voltammograms for the early cycle history of the electrode. There are several interesting features of these data; the first of these is the general decrease in peak current ($PbO_2 \rightarrow PbSO_4$ reduction peak) values (i_p) with cycling, the difference between i_p values for the first and second cycles being much greater than during subsequent cycling operations. Table 1 summarizes these changes in i_p with cycle number and gives the potential at which they occur. The seemingly excessive initial reduction current can be explained in terms of the formation of a passivated form of lead sulphate which resists oxidation back to PbO_2 during the anodic potential sweep. It is impractical to raise the upper sweep limit above 1250 mV since this results in the formation of oxygen bubbles in the electrode matrix.

We have already observed this 'passivated sulphate' phenomenon on pure lead electrodes [9] and have suggested that the morphology of the lead sulphate crystals is such that a considerable overpotential is required to effect the reconversion to lead dioxide. This 'reconversion' could be achieved by galvanostatic oxidation (25 mA cm^{-2}) in an upward-facing position (cell electrolyte 0.3 M H_2SO_4).

A further interesting feature of the early cycle pattern is the rate of attainment of a constant response after approximately 10 cycles, the i_p and E_p values remaining constant regardless of any subsequent cycling operations. This suggests that the morphology of lead sulphate reaches an equilibrium form with just a small residual amount of 'unpassivated' $PbSO_4$ present in the matrix which can be oxidized to PbO_2 and reduced back again to $PbSO_4$ by linear sweep experiments.

It is interesting to compare the data reported here with that from our previous work on un-

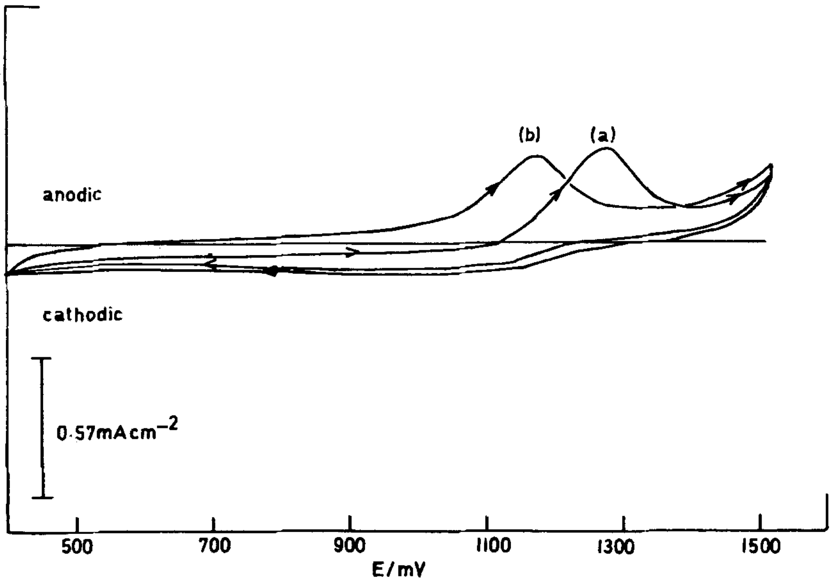

Fig. 2. Constant response linear sweep voltammetry curves for (a) Pb and (b) Pb–Sb (400–1520 mV, 40 mV s^{-1}) after cycling for 1.5 h [1].

pasted Pb–Sb electrodes [7]. The major difference can be seen in the much larger currents (and capacities) obtained with the porous electrode. This is to be expected because of the much larger surface area available for reaction in the porous matrix. A second comparison lies with the protuberance of the PbO_2 formation peak: with the flat, unpasted electrode this peak is quite prominent (Fig. 2), with the data obtained [1] being typical of that for the development of a single, passivated layer on an electrode surface with no thickening of the deposit occurring. In the case of the porous electrode, however, the absence of a pronounced PbO_2 formation peak can be explained in terms of the layered growth of the lead dioxide produced [10]. This type of oxidation produces many different oxidation peaks which overlap with each other to form a broad band coupled with the oxygen evolution reaction.

A further difference between the flat and the pasted electrodes can be seen in the form of the reduction ($PbO_2 \rightarrow PbSO_4$) peak. In the case of the pasted electrode a long 'reduction tail' is observed. This is characteristic of newly formed porous lead dioxide and shows that the discharge is being driven deep into the porous mass. With the flat electrode, the reduction 'peak' is barely distinguishable. The lack of dependence on rotation speed throughout these experiments suggests that the conversion here ($PbSO_4 \rightleftharpoons PbO_2$) proceeds via a solid-state process.

3.2. *Potentiostatic pulse experiments*

3.2.1. Uncycled electrode. Fig. 3 shows the current–time response of a porous Pb–Sb electrode as the potential is instantaneously stepped from the lead dioxide region (1250 mV) to the lead sulphate region (700 mV). An initial current spike, which can be attributed mainly to the charging of the double layer at the electrode–electrolyte

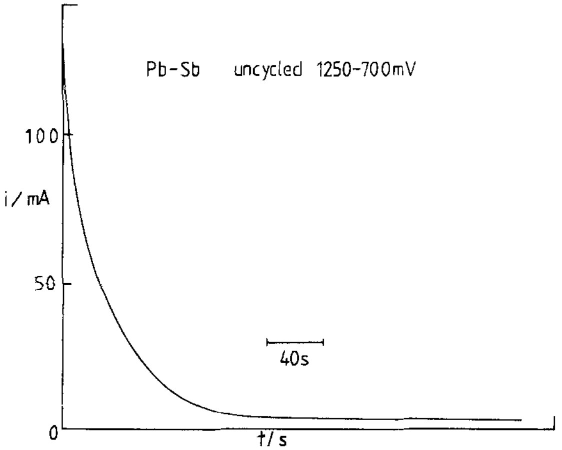

Fig. 3. Potentiostatic pulse experiment from 1250 mV to 700 mV on a porous, uncycled Pb–Sb electrode (positive).

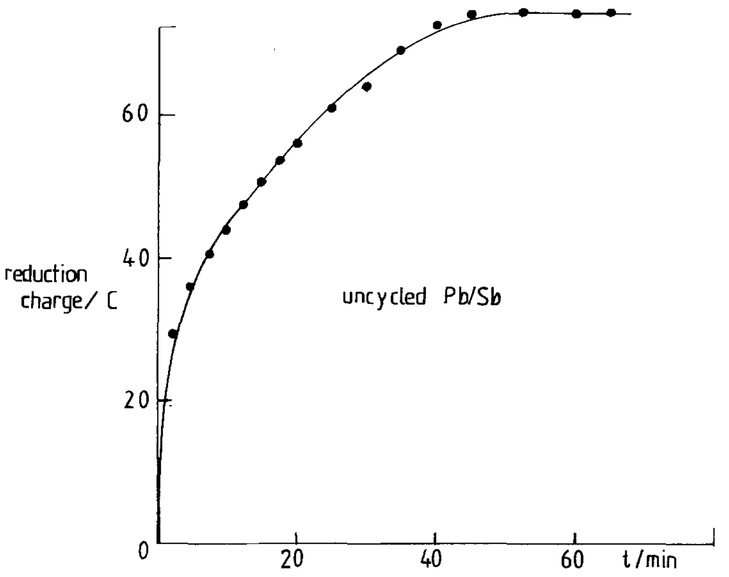

Fig. 4. Changes in reduction capacity with time for uncycled porous Pb–Sb positive electrode following potentiostatic reduction pulse (details as for Fig. 3).

interface, is followed by a simple fall in the current flow. The absence of a current peak indicates that sufficient nuclei are present in the lead dioxide matrix to initiate the electrocrystallization of lead sulphate crystals. The corresponding changes in capacity with time are shown in Fig. 4: from the graph it can be seen that the electrode is fully discharged, having passed 74 C, after a reduction period of 45 minutes. The percentage change in capacity ($C/C_{\max} \times 100\%$) as a function of time is shown in Fig. 5 from which we see that 50% of the discharge capacity (36 C) is reached after only 11% of the total discharge time (5 min). This very sudden attainment of the discharged state can once again be explained in terms of rapid formation of 'passivated' lead sulphate crystals.

The electrode was considered to be in a fully discharged condition when no further changes in capacity were observed; the electrode was then stepped back into the lead dioxide region (1250 mV). Fig. 6 shows the current–time response as the electrode was subjected to this potentiostatic oxidation. The initial double-layer charging spike is followed by an increase in the current due to the formation and growth of nucleation centres for PbO_2 production. Subsequent overlap of these growth centres causes a decrease in current flow with the resultant pattern obtained being that of the current peak shown in Fig. 6.

The changes in capacity with time for the potentiostatic oxidation are shown in Fig. 7. From this curve we can see that after an oxidation time of over 4 hours, the total charge put back into the porous matrix was only 50 C (i.e. only 68% of the total discharge capacity). This very slow charge acceptance shown by the antimonial lead electrode can be explained by the resistance of

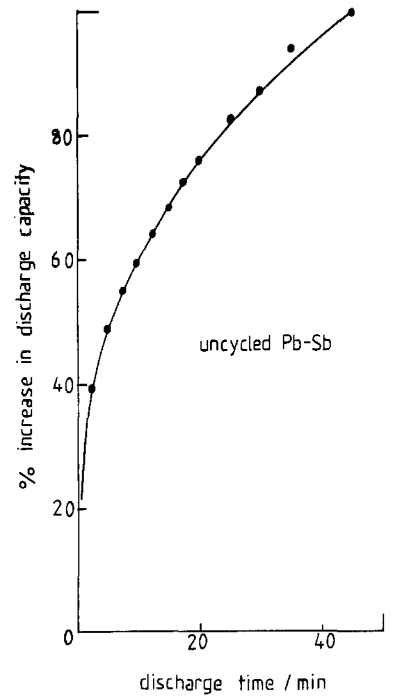

Fig. 5. Percentage change in capacity as a function of time. Details as for Fig. 4.

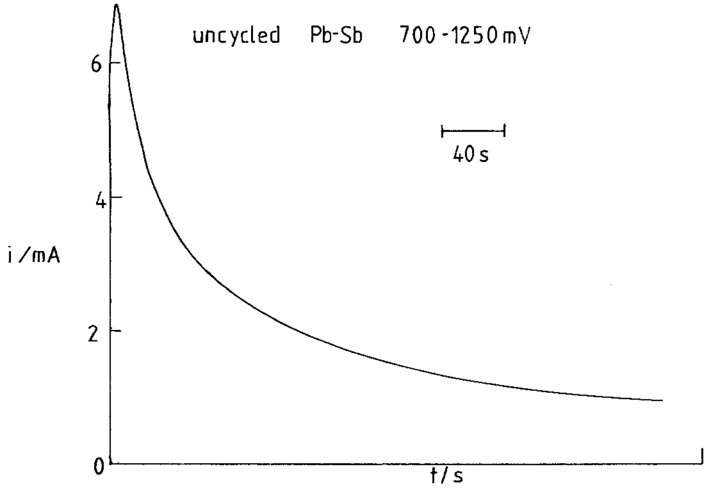

Fig. 6. Potentiostatic pulse experiment from 700 mV to 1250 m V on a porous, uncycled Pb–Sb electrode following full discharge.

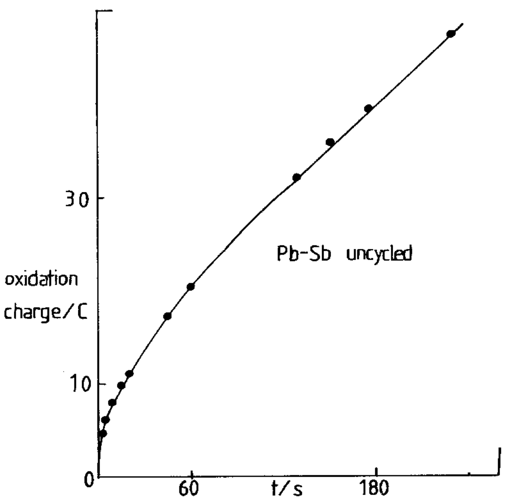

Fig. 7. Changes in recharge capacity with time during oxidation pulse (details as for Fig. 6).

'passivated' lead sulphate to oxidize back to lead dioxide. Eventually, the formation of oxygen bubbles occurs in the porous matrix causing the disruption of the lattice and ensuring the electrode is never fully charged. To ensure that the electrode was fully charged prior to each experiment it was removed from the cell and oxidized galvanostatically (25 mA cm^{-2}) in an upward-facing position until a steady potential (1.250 V) was reached (0.3 M H_2SO_4).

3.2.2. Cycled electrodes. Prior to potentiostatic pulse experiments, the electrodes were subjected to a varying number of cycles using linear sweep voltammetry between the limits 700 mV and 1250 mV. One cycle consisted of a single potential scan between these two extremes and back again with a constant sweep speed of 1 mV s^{-1} throughout. A potentiostatic reduction pulse (1250 → 700 mV) was then performed and the resulting changes in capacity followed. The variation of discharge capacity with cycling is shown in Table 2 together with the time taken to reach the fully discharged state. To ensure that the electrode was fully recharged prior to each new experiment, galvanostatic oxidation was carried out under the same conditions as before. The decrease

Table 2. Discharge capacities for electrodes subjected to potentiostatic reduction following various cycling conditions (Pb–Sb, porous)

Number of cycles	*Discharge capacity* (C)	*Time to reach full discharge capacity* (min)
0	73.9	45
4	42.3	139
6	13.9	56
11	2.2	12
15	1.8	5
20	1.5	5

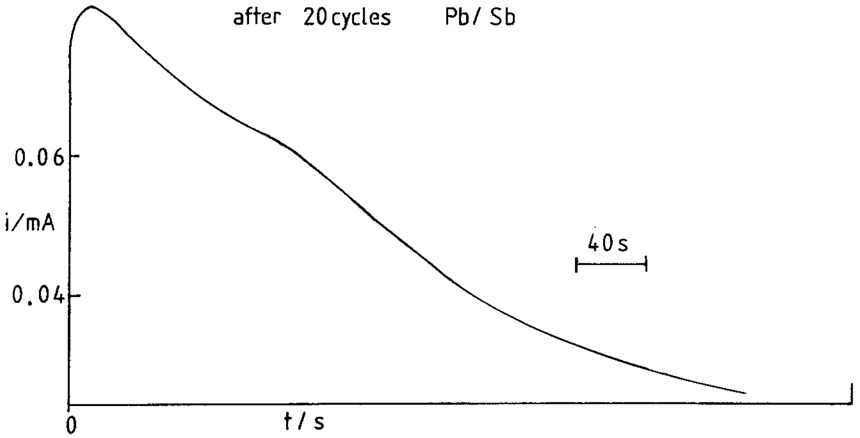

Fig. 8. Current–time transient for a potentiostatic pulse experiment (700 mV–1250 mV) on cycled (20 cycles) porous Pb–Sb electrode, following a full discharge.

in discharge capacity with cycling can once again be explained in terms of the formation of passivated sulphate during the preparatory linear sweep cycling experiments. These relatively inert sulphate crystals remain unoxidized during the anodic section of the sweep gradually leaving less PbO_2 to be reduced during subsequent potentiostatic pulse reductions.

Fig. 8 shows the current–time response of a porous Pb–Sb electrode subjected to 20 cycles of linear sweep voltammetry, fully discharged by a potentiostatic reduction pulse and finally stepped from the lead sulphate region to the lead dioxide region. It is interesting to compare the pattern obtained with that for an uncycled electrode (Fig. 6): the main difference lies in the much larger currents observed with an uncycled matrix. In the case of the well-cycled electrode, we have already shown that the passivated sulphate will have reached an equilibrium morphology so that the only lead sulphate present in the matrix which can be re-oxidized is the small amount of residual sulphate which never seems to take the passivated form. The fact that we see two rising and falling current transients for the cycled electrode brings in the penetration depth concept [10] and indicates that this residual sulphate is not conglomerated into a specific area of the electrode but rather is dispersed throughout the porous mass. The appearance of two distinct current peaks suggest the nucleation and subsequent growth of two fairly distinct layers of lead dioxide.

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