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The failure of porous lead dioxide electrodes (positives) to accept recharge during potential step experiments

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The electrochemistry of porous lead dioxide electrodes has been followed during short cycling experiments at high discharge rates using the potential step technique. The inability of the electrode to accept recharge is explained in terms of the formation of a passivating form of lead sulphate.

1. Introduction

We have already studied the electrochemistry of flat lead electrodes [1, 2] and the effect of various alloy additions to the base metal [3–5]. In order to extend our studies to the porous lead dioxide electrode, which is more indicative of the industrial lead–acid battery situation, it was considered worthwhile to begin by examining the effect of very high discharge rates on a porous, pure, lead dioxide electrode. The technique most likely to provide the sought-for data is the potential step method on a small geometric electrode area. This paper records the early cycle history for both charge and discharge reactions.

2. Experimental

Experiments were performed on a porous lead dioxide working electrode which was shrouded in Teflon and placed in the centre compartment of a three-limbed cell containing deoxygenated sulphuric acid (5 M, Analar grade) made from tri-distilled water. The Hg/Hg_2SO_4 reference electrode was connected to the working electrode via a Luggin capillary system and all potentials are quoted on this scale at 23 ± 1° C. The electrical circuitry has been described in previous publications [1, 2].

The working electrode was constructed from a pure lead disc (C-Metals, 4 mm diameter) lying 0.7 mm beneath the flat surface of the Teflon holder such that pasting of the lead surface with a conventional lead–acid battery positive paste produced a porous layer of lead oxide flush with the Teflon surface. The electrode was humidified and oven-dried prior to PbO_2 formation; conversion of the porous matrix to PbO_2 was effected by galvanostatic polarization ($25\ mA\ cm^{-2}$, 0.3 M H_2SO_4) in an upward facing position (to prevent oxygen bubbles from saturating the porous matrix) until a steady potential was attained and oxygen was freely evolved from the matrix. The electrode was then washed with tri-distilled water and then by the cell electrolyte (5 M H_2SO_4), placed in the cell and rotated to ensure uniform electrolyte concentration throughout the pores prior to electrochemical experiments.

3. Results and discussion

Electrochemical cycling was performed by a series of potential step experiments from 1240 mV (PbO_2) to 700 mV ($PbSO_4$) for a short reductive period followed by a recharge pulse back into the PbO_2/O_2 region. This was repeated several times and the resulting changes in capacity during cycling are summarized in Table 1. There are three interesting features in this data; the first of these is the inability of the electrode to accept recharge: the charge put into the system during the oxidation pulse never matched the charge given out

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Table 1. Charge obtained in early cycling experiments

Cycle number	*Discharge capacity* (C)	*Recharge capacity* (C)
1	73.0	13.1
2	25.3	12.1
3	26.8	10.8
4	21.8	10.2
5	20.0	9.0
6	18.5	8.0
7	15.7	5.3

Table 3. Charge/discharge capacities following galvanostatic oxidation

Cycle number	*Discharge capacity* (C)	*Recharge capacity* (C)
13	58.8	8.4
14	24.2	6.0
15	18.0	4.8
16	6.5	3.7
17	6.3	3.3

during the corresponding reduction reaction. Secondly, the discharge capacity in the first cycle is much greater (3–5 orders of magnitude) than during subsequent cycling experiments. Finally, the data shown in Table 1 exhibit a general trend of decrease in capacity with cycle number.

This latter observation is at first sight rather alarming since previous work on porous lead dioxide electrodes [6] has shown an initial increase in capacity with cycling until a plateau is obtained. A close examination of the experimental conditions, however, soon leads to an explanation for these results. In the experiments reported here, the electrode was subjected to much more severe conditions (with higher discharge rates) than before [6], the potential being instantaneously (~ 10 μs) stepped through 540 mV. We can explain the decrease in capacity with cycle number in terms of the formation of 'passivated' lead sulphate crystals whose morphology is such that, as a consequence of the severe reduction treatment, they resist oxidation when the electrode is stepped back into the PbO_2 region. As cycling continues, more of the electrode is converted to this 'passive' form of $PbSO_4$ leaving less of the matrix available for reoxidation to lead dioxide. This also explains the inability of the positive electrode to accept recharge and also the very large initial reduction charge as the product lead sulphate is formed.

Table 2. Charge/discharge capacities following prolonged reduction

Cycle number	*Discharge capacity* (C)	*Recharge capacity* (C)
8	39.3†	0.1
9	12.4	0.1
10	7.9	0.1
11	6.7	0.1
12	5.7	0.1

† Prolonged reduction.

To confirm these findings, the electrode was then subjected to prolonged reduction in the lead sulphate region (700 mV) and cycling experiments were continued as before. The results, summarized in Table 2, show the almost total inability of the electrode to accept charge during potentiostatic oxidation following a prolonged reduction period. This in good agreement with our 'passivated sulphate' theory; prolonged reduction results in almost complete formation of lead sulphate which cannot be oxidized to lead dioxide by the potential step technique.

The electrode was removed from the electrolytic cell and oxidized galvanostatically for several hours in an upward-facing position (25 mA cm^{-2}, 0.3 M H_2SO_4) with oxygen being freely evolved from the matrix. The final steady-state potential under these conditions was 1.250 V (versus Hg/Hg_2SO_4). Following equilibration with the cell electrolyte, the electrode was then subjected to the same cycling conditions as before; the results are shown in Table 3. Once again, the same trends are observed as in Table 1, with the reduction charge being very much larger in the first reaction than during subsequent cycles. This shows that the galvanostatic oxidation enables the conversion of 'passivated' $PbSO_4$ to PbO_2 which cannot be effected by the potential step technique.

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References

[1] N. A. Hampson, S. Kelly and K. Peters, *J. Appl. Electrochem.* **10** (1980) 91.
[2] *Idem, ibid* **10** (1980) 261.
[3] N. A. Hampson, S. Kelly, K. Peters and P. Whyatt, *ibid* **10** (1980) 597.
[4] *Idem, J. Electrochem. Soc.* **127** (1980) 1456.
[5] S. Kelly and N. A. Hampson, 'Power Sources 8', (edited by J. Thompson).
[6] G. Smith, 'Storage Batteries', Pitman Publishing, London (1971) p. 40.