ON THE CYCLING OF POSITIVE PLANTÉ ELECTRODES

C. LAZARIDES and N. A. HAMPSON

Chemistry Dept., Loughborough University, Leicestershire LE11 3TU (U.K.)

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Summary

The development, in cell cycling tests, of $PbSO_4$ crystals in Planté electrodes has been investigated by S.E.M. Electrodes were examined electrometrically at various states-of-charge in the uncycled condition. They were then electrometrically and microscopically examined after 80 cycles of 10% rated capacity at the 10 h rate (in, respectively, the 90, 75, 50 and 25% nominal charged condition). A final examination was carried out after a constant voltage float recharge at 2.25 V per cell (140 h). The crucial point in determining the amount of capacity available from the float-recharged cell is the size of $PbSO_4$ crystallites. This is influenced by the extent of the mean state-of-charge of the electrodes.

Introduction

Planté cells were the first secondary cells and are still the preferred cell type where weight is not of paramount importance but reliability and low loss are. The Planté cell is now produced differently from the method described by Planté's original process [1] in that forming agents are used to develop the PbO_2 content of the positive electrode and pasted negatives are employed instead of being produced by repetitive cycling. The Planté criterion of a positive electrode produced from pure lead from which no low hydrogen overvoltage impurity (*e.g.*, Sb) can be removed to deposit on the negative electrode still applies, therefore, to the modern cell.

A tentative application for Planté cells is that of forming a buffer battery for the new solar technology. In operation it is conceivable that cycling of cells occurs according to the exigencies of supply (from solar cells) and demand (from the grid) at any state-of-charge of the cells. This imposes a new set of operating conditions upon the electrodes for, whereas standby duty implied an initially fully charged (constant potential floated, *e.g.*, 2.25 V) cell, the buffer battery must be capable of operating in a charge/discharge mode at all states of charge. It is axiomatic in the lead battery industry that cells should not be allowed to stand in the discharged condition and that

frequent stabilising charges are required if efficient use is to be made of, for example, traction cells. It is important to know whether or not these limitations would apply to Planté cells on the solar regime which may involve these conditions. Preliminary tests had shown that under restricted cycling there was a pronounced lack of chargeability at constant potential.

This communication records the results of some tests made to investigate this type of duty.

TABLE 1

Initial cell capacities at 10 A

A	15 h	8 min
B	14 h	4 min
C	14 h	7 min
D	13 h	10 min

Experimental

The experiments were carried out using Planté cells of 100 A h nominal capacity. After an initial discharge at the 10 A rate (to 1.6 volts per cell (V.P.C.))each cell was cycled for 80 cycles of charge and discharge in the following four states-of-charge.

90% — 80%, 75% — 65%, 50% — 40%, 25% — 15%.

Based on the recoverable capacity on the 1st rating discharge of the cells these are equivalent to the following (cf. Table 1):

93% — 87%, 82% — 75%, 65% — 58%, 43% — 35%,

i.e., for 75/65: 2.5 h discharge at 10 A from the fully charged condition followed by 10 h discharge at 1 A and 10 h at 1 A recharge. After cycling the cells were recharged at a constant potential of 2.25 V.P.C. for 140 h and capacities were determined at 10 A to 1.6 V.P.C. A final capacity test was made after the cells were fully charged galvanostatically at 7 A to a cell voltage constant over 2 h. In this connection it is recognised that the low capacity cells may have received some overcharge. At this point, however, it was thought unwise to try to adjust this slight asymmetry. The cycles of operation are shown in Fig. 1.

Cycle 80× ——→ Float ——→ Discharge 1 ——→ Recharge ——→ Discharge 2

| Recharge
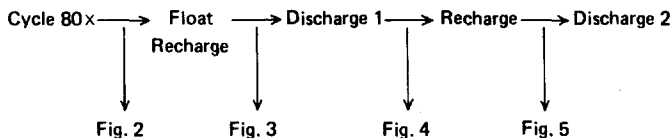
↓ ↓ ↓ ↓
Fig. 2   Fig. 3   Fig. 4   Fig. 5

Fig. 1. Key to operations and micrographs.

The positive electrodes were sampled for S.E.M. examination at various points in the cycles of electrochemical operation. This was done by cutting sections from electrolyte-soaked electrodes from the centre of the bottom of

the plate, and washing them free from sulphuric acid solution with acetone. In this way the worst conditions for the development of sulphate phases were imposed. It was important not to wash the sulphuric acid out with water because the establishment of a $PbO_2/PbSO_4$ system at two different H_2SO_4 concentrations would provide sufficient driving potential (in the Nernstian sense) to alter the $PbO_2/PbSO_4$ ratio at different areas on the electrode. When free from aqueous solution the specimens were dried and appropriate samples examined in the S.E.M. (Cambridge Stereoscan, model 2A).

TABLE 2

Cell capacities (% of initial capacities) after 80 cycles and ac.p. charge

A	11 h 31 min/15 h 8 min	=	76.1%
B	11 h 52 min/14 h 4 min	=	84.4%
C	9 h 31 min/14 h 7 min	=	67.4%
D	6 h 36 min/13 h 10 min	=	50.1%

TABLE 3

Capacities after galvanostatic recharge (% of initial capacity)

A	13 h 20 min/15 h 8 min	=	88.1%
B	12 h 45 min/14 h 4 min	=	90.6%
C	12 h 7 min/14 h 7 min	=	85.8%
D	11 h 47 min/13 h 10 min	=	89.5%

Results and discussion

The cells are most readily classified according to their cycling regimes as follows:

Group A	90/80
Group B	75/65
Group C	50/40
Group D	25/15

Table 1 shows the initial capacity at the nominal 10 h rate and these data show that all cells are satisfactory.

Table 2 shows the capacity available after the 80 cycles and after a constant potential charge. There is a serious reduction in electrochemical storage capacity for all groups with a marked deterioration of the groups C and D cells.

Following this discharge the cells were given a galvanostatic charge and the data of Table 3 show that much more capacity was obtained on the subsequent discharge after recharge.
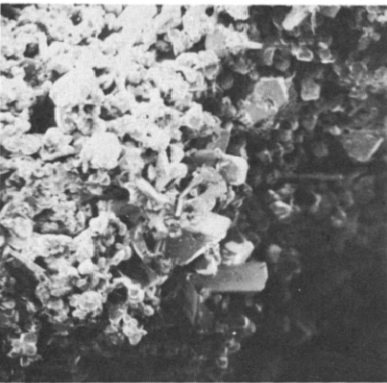
We can conclude from these electrometric results that cycling in a restricted state-of-charge range below 100% results in a loss in immediately re-

(A)

(B)

(C)

(D)

Fig. 2. Photomicrographs of electrode surface at completion of 80 cycles of charge/discharge. (A), 90% - 80% (× 300); (B), 75% - 65% (× 300); (C), 50% - 40% (× 260); (D), 25% - 15% (× 260). (Note for Figs. 2 - 5 the original magnifications have been quoted. The micrographs have been reduced × 1/2 in reproduction.)

coverable storage capacity. This loss is greater after a constant potential (potentiostatic) recharge for times approaching one week than after a galvanostatic recharge.

A possible explanation for this behaviour can be given in terms of the development of large crystals of lead sulphate in the electrode as a result of the cycling tests. Earlier work in this laboratory [2] has once more proved that such large crystals are more difficult to oxidise, and, indeed, the electro oxidation of reduced lead dioxide in 5M H_2SO_4 yields response curves which may be deconvoluted such that the component curves may be identified with crystals of different sizes. In the present case it appears that cycling in the restricted ranges has produced crystals of $PbSO_4$ which are difficultly oxidised to PbO_2 and that the deterioration is aggravated at low levels of charge.

(A)
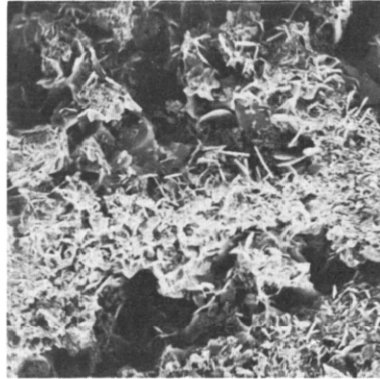
(B)

(C)

(D)

Fig. 3. Photomicrographs of electrode surface at completion of float charge at 2.25 VPC. Magnification: (A), × 280; (B), × 300; (C), × 260; (D), × 280. Other details as Fig. 2 and Fig. 1.

The examination of the electrodes using the S.E.M. technique confirmed this conclusion. Figure 2 (A) - (D) shows the condition of the electrode immediately after cycling for 80 complete cycles and finishing in the highest level of charge (*i.e.*, (A) 90%; (B) 75%; (C) 50%; (D) 25%).

It is clear from these pictures that in all cases the electrodes appear to be completely choked with $PbSO_4$, with not very much evidence for the small, prismatic PbO_2 particles. Even for the case of (A) the surface quite evidently contains considerably more $PbSO_4$ than the 10% which might be expected from energetic considerations. It is quite possible that this conclusion applies only to the surface of the electrode and that the cycling process has resulted in a redistribution of $PbSO_4$ so that the surface of the electrode is very heavily sulphated. The appearance of the electrodes is towards the development of a surface consisting of large $PbSO_4$ particles almost submerged with fine material (Fig. 2 (D)). The maximum sizes of the visible $PbSO_4$ crystals do not seem
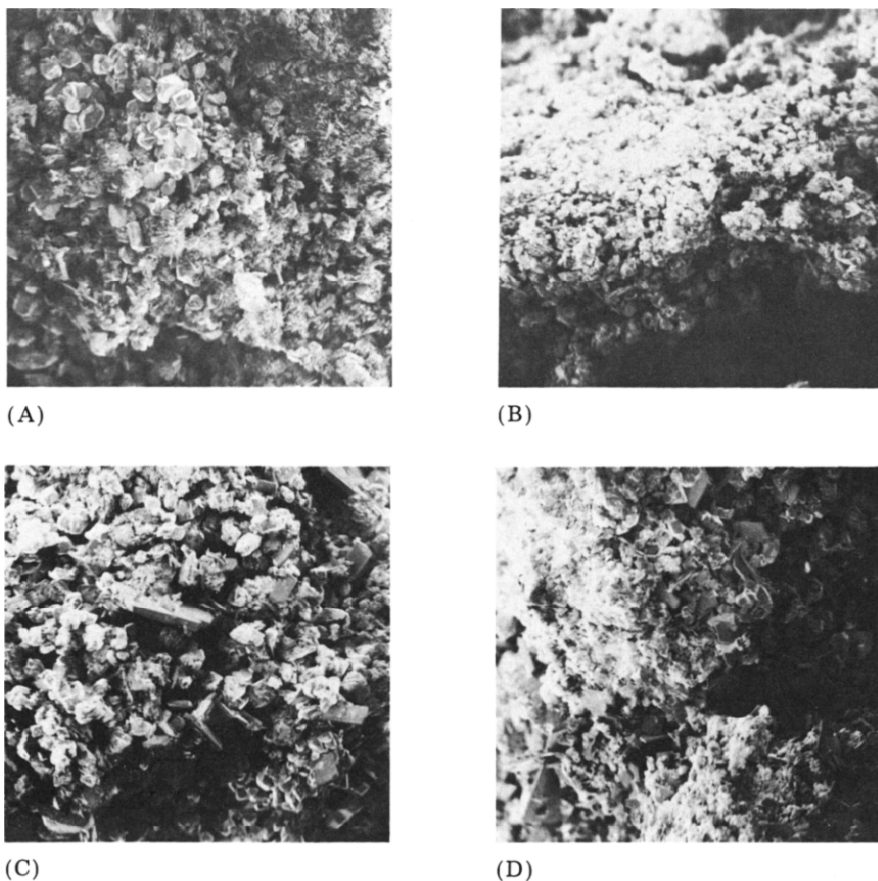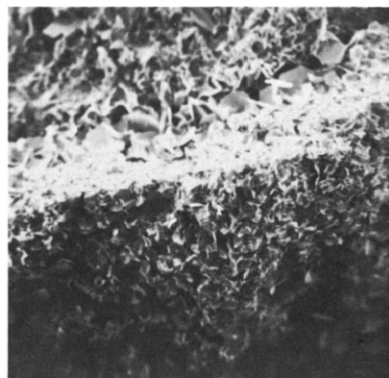
(A)

(B)

(C)

(D)

Fig. 4. Photomicrographs of electrode surface at completion of discharge after recharge. Magnification: (A), × 260; (B), × 320; (C), × 260; (D), × 260. Other details as Fig. 2 and Fig. 1.

to be related to the state of charge. This seems to be in contradiction to current ideas. However, the appearance of the electrodes after a subsequent constant potential recharge considerably clarifies the position. The photomicrographs corresponding to the completion of the constant potential charge are shown in Fig. 3 (A) - (D). Whereas the cell cycled in the highest state of charge (Fig. 3 (A)) shows some evidence of the presence of PbSO$_4$ crystals, at lower states of charge an increasing amount of PbSO$_4$ material of increasing crystal size is clearly evident. We can conclude from this that the prolonged constant potential charge (140 h) at 2.25 V is ineffective in converting the large crystals of PbSO$_4$ to PbO$_2$. We propose that for each size of crystal there exists a critical potential below which the conversion to PbO$_2$ is difficult, probably kinetically hindered. Figure 3 (D) supports this view, for the field shows that all the small PbSO$_4$ crystals have been converted and that only very large crystals remain.
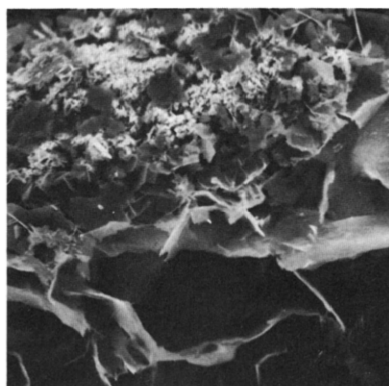
Fig. 5. Photomicrographs of electrode surface at completion of galvanostatic recharge. Magnification: (A), × 260; (B), × 270; (C), × 280; (D), × 270. Other details as Fig. 2 and Fig. 1.

That the surface under normal discharge conditions returns to a fine-grained (small crystal) texture is shown in Fig. 4. These were obtained at the termination of a 10 h rate discharge to a final cell voltage of 1.6 V.P.C. Here we see that the whole of the surface is covered by small $PbSO_4$ crystals with an occasional large crystal visible (Fig. 4 (C)).

Following a galvanostatic charge the electrodes in the higher states -of-charge return to the condition expected of cycled electrodes. Relatively small PbO_2 particles of fairly uniform shape can be readily seen in the micrographs of Fig. 5 (A) - (C). However, those electrodes from the lowest (25%) state of charge were rather untypical. Apparently the large $PbSO_4$ crystals had been oxidised to PbO_2, but with considerable damage to the structure and disruption of the electrode. This is shown, typically, in Fig. 5 (D). Areas of quite satisfactory PbO_2 structure are visible but there are also disrupted areas of PbO_2 and even some residual $PbSO_4$. It was considered unlikely that

this effect was due to the disruption of one or two crystals as it was not observed generally. This condition of the surface again emphasises the difficulty in converting $PbSO_4$ from prolonged cycling at a low state-of-charge to something approaching a fully charged condition. This can only be accomplished with difficulty and results in damage to the surface structure.

We finally conclude that restricted cycling of Planté positives in a low state-of-charge (especially $\sim 25\%$ and below) is to be avoided, for it makes complete recharging difficult and results in deterioration of electrode structure.

A final comment arises from this investigation. For solar applications, and other duties of this type where limited cycling around the 50% discharge level may occur, a float voltage of approximately 2.25 is perhaps on the low side [3]. A more realistic value of 2.3 V per cell would clearly be better. However, the optimum would be to recharge galvanostatically from time to time [3]. There is no doubt that whatever battery is used for solar purposes, considerable thought will have to be given to the operational scheme of usage.

Acknowledgements

References

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2 P. Casson, N. A. Hampson, K. Peters and P. Whyatt, *J. Electroanal. Chem., 93* (1978) 1.
3 D. Collins, personal communication.