SULPHATION IN DISCHARGED LEAD–ACID BATTERIES

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Summary

The inability of lead–acid batteries to be efficiently recharged after prolonged storage in the discharged state has been studied. Experimental (three plate) cells have been fully discharged and stored for various periods (0, 4, 8, 24 weeks) prior to being recharged by a constant voltage schedule. In addition, the electrolyte of some of the cells stored for 24 weeks was replaced by water before the cells were recharged.

Current/time profiles, ampere-hour input, and capacity after recharge data have been recorded for the recharges after each storage period. Samples of active material have also been examined by S.E.M. and chemical analysis.

The results obtained confirmed that it becomes increasingly difficult to recharge as the period in store increases and that the crystal growth is greater on the positive PbO_2 electrode than on the negative electrode. The results also indicate that the increased size of the crystals may not be the complete cause of the inability to recharge.

Introduction

It is well established that the lead–acid battery cannot be efficiently recharged after prolonged storage in the discharged state. This inability to recharge by normal charging procedures has been attributed to the "irreversible sulphation" of the active material.

The formation of "hard" sulphate is said to occur when the normally rechargeable lead sulphate crystals produced during discharge undergo a prolonged and/or elevated temperature ageing process. The lead sulphate crystals apparently undergo a recrystallisation process which results in an enlargement of the sulphate crystals. Bode [1] states that the sulphate crystals formed initially on discharge are up to 1 μm in diameter. After 8 days they will have grown to $\approx$5 μm and after 5 months to 10 μm.

Since the recrystallisation process is dependent on the solubility of lead sulphate in the electrolyte, the fact that the solubility increases with temperature [2] (see Fig. 1) means that overall increases in temperature, and temperature fluctuation during storage, will increase the rate of
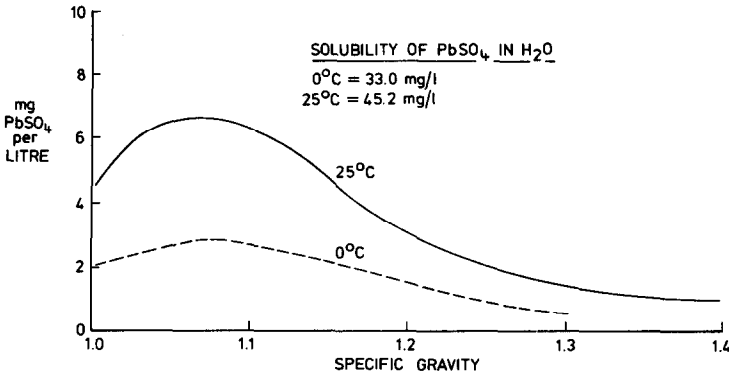
Fig. 1. Solubility of PbSO$_4$ in sulphuric acid [2].

dissolution of lead ions from lead sulphate. Thus, crystal growth is accelerated leading to increased recharge problems.

Crystal growth occurs on both positive and negative electrodes. Visual examination of sulphated electrodes show the positive electrode to have a bright colour with a rough, hard surface, the active material exhibiting a sandy or grainy texture. Sulphated negatives are also hard and sandy in texture and fail to exhibit the characteristic metallic sheen after the active material has been scratched [3].

It is evident that the dissolution of Pb^{2+} ions is an important factor in the irreversible sulphation phenomenon and it is commonly suggested that the decreased surface areas of the large crystals grown during storage do not allow sufficient Pb^{2+} ions to go into solution to permit efficient recharge. Thus, it would be expected that both positive and negative electrodes would exhibit problems on recharge. Indeed, since lead sulphate crystals are, in general, larger on the positive than on the negative electrode, [3, 4] and the efficiency of the conversion of PbSO$_4$ to lead at the negative electrode is initially greater than the oxidation of PbSO$_4$ to PbO$_2$, it may be expected that the major problems of irreversible sulphation could be attributed to the positive electrode. However, although little detailed published work exists, irreversible sulphation problems on the positive PbO$_2$ electrode are not generally accepted to be any greater than those exhibited by the negative lead electrode.

Another theory on the nature of irreversible sulphation has been proposed by Popova and Kabanov [5]. They suggest that the basic cause of the decrease in the dissolution of Pb^{2+} ions is due to the absorption of surface-active additives (*e.g.*, organic expanders) on the negative lead electrode. They indicate that 8 months storage in the discharged state of negative electrodes free from additives caused few difficulties on recharge, although recrystallisation and enlargement of the lead sulphate crystals had taken place. They suggest that the presence of additives creates an overvoltage to the charge processes in that the crystal surface is blocked by the absorbed species, reducing the dissolution of Pb^{2+} ions. They promote the

theory by suggesting that the irreversible sulphation difficulties of the positive PbO_2 electrode, even with their larger sulphate crystal size, are less than those of the lead electrode because the additives are destroyed by oxidation at the positive electrode.

Furthermore, in accordance with their theory, they suggest that an effective way of counteracting irreversible sulphation is by desorption of additives in the presence of strong cathodic polarisation, the size of the current being ≈ 100 mA/cm^2, *i.e.*, much larger than normal charge currents.

Another proposed method of alleviating the sulphation problem is based on the vastly increased solubility of $PbSO_4$ in water [2] (see Fig. 1). Replacement of the acid electrolyte in the stored batteries by water is reported [3] to facilitate an efficient recharge of the sulphated plates.

Thus, the inability of the lead–acid couple to recharge efficiently after prolonged storage in the discharged state is well known, and although it is accepted that the dissolution of Pb^{2+} ions from lead sulphate is important in explaining the phenomenon, the process of irreversible sulphation is not fully understood. This work attempts to obtain additional information and data to gain further insight into the phenomenon of irreversible sulphation.

Experimental

Experimental three-plate cells were constructed using standard automotive size positive and negative grids cast in 6% antimonial alloy. Three types of active material were investigated:
  (i) standard positive;
  (ii) standard negative with conventional additives;
  (iii) negative without organic "expander" additive.
The pasted grids were oxidised and reduced in separate compartments until in the active state. The formed plates were then built up into the three different cell types, details of which are shown in Table 1. The electrodes

TABLE 1

Cell construction

Group code	Middle electrode	Counter electrodes
P	Positive	Standard negative grids
N+	Negative with organic additives	Standard positive grids
N—	Negative without organic additives	Standard positive grids

were separated by standard automotive materials, namely Darak AR60 with ribs facing towards the negative electrode. The acid gravity of the cells in the fully charged state was 1.275.

The experimental cells were fully discharged at the 20 h rate (final cell voltage 1.75, electrolyte s.g. ≈ 1.200) and set aside in the discharged state for various time periods (0, 4, 8, and 24 weeks). The cells were then recharged at constant voltage (2.35 V for 24 h) after which a 20 h rated capacity discharge was carried out. In addition, the electrolyte of some of the cells stored for 24 weeks was replaced by water before the constant voltage recharge was commenced. After the recharge the cells were refilled with s.g. 1.275 acid prior to the rated capacity discharge.

After each storage period samples of active material were taken for chemical analysis and examination by S.E.M. (JEOL JSM 35). The chemical analyses were carried out by the following methods:

(a) Determination of sulphate: the active material sample was dissolved in HNO_3 and sulphate precipitated as barium sulphate. The sulphate analysis was completed gravimetrically.

(b) Lead dioxide: ammonium acetate and acetic acid were used to dissolve the combined lead compounds leaving residual PbO_2. The PbO_2 was reacted with KI to produce iodine which was titrated against sodium thiosulphate to complete the analysis.

(c) "Combined" and "residual" lead (combined lead is a measure of the amount of lead combined in the active material as lead compounds. Residual lead is the amount of lead in the active material sample). The combined lead was dissolved in an ammoniacal solution of ethylenediaminetetraacetic acid (EDTA). The solution was then back titrated with $MgSO_4$ to determine the combined lead. The remaining residual lead was dissolved in HNO_3 and lead titrated with EDTA.

Results and discussion

The current–time plots for the constant voltage recharges after the various periods of storage are shown in Figs. 2 and 3. The ampere-hour input during these recharges is shown in Table 2, together with details of the discharge capacity of the cells after the recharge.

Figures 2 - 4 show that it became increasingly more difficult to recharge the cells as the storage period increased. However, for all three cell groups it was still possible to fully recharge the cells in 24 h after 4 and 8 weeks storage in the discharged state. This was not the case for the cells stored for 24 weeks.

The ampere-hour input data (Table 2) show that as the storage period increased the majority of the current input was put into the cells at a progressively later time during the recharge. The shapes of the current–time plots for the 4 and 8 week tests show a rising, then a falling response, indicating an initial inhibition of the recharge reaction. This may be indicative
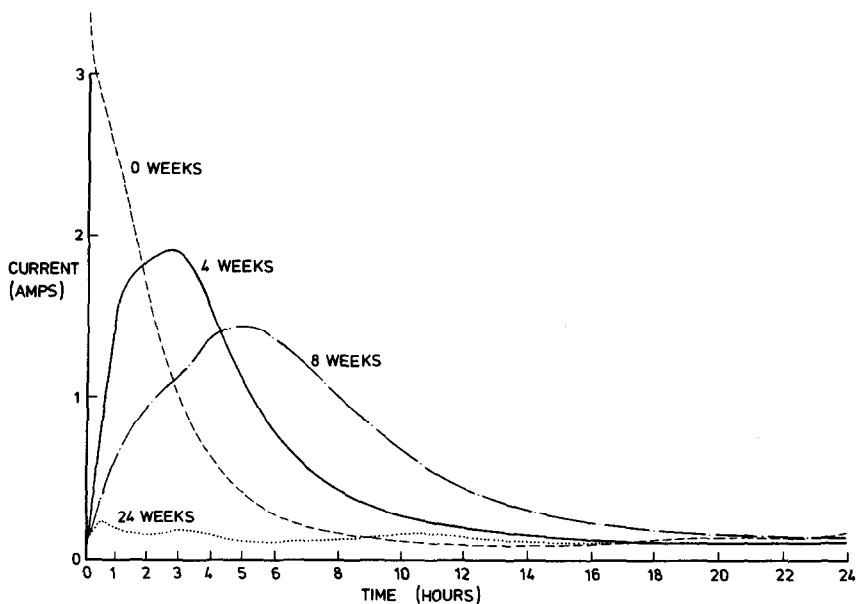
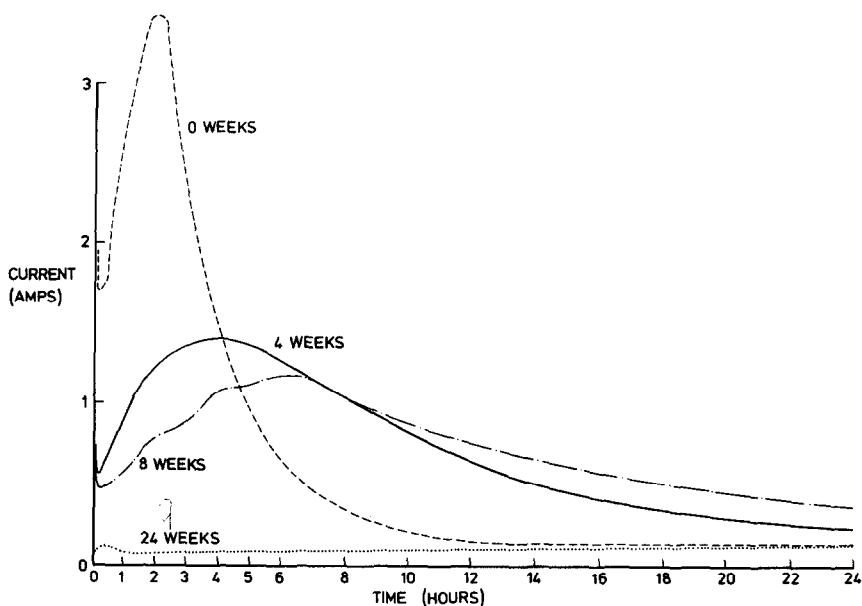Fig. 2. Recharge current profiles at 2.35V: — Positive (Group P).

Fig. 3. Recharge current profiles at 2.35V: — Negative (Group N+).

of an initial lack of suitable reactive sites and species, followed by a slow build up of centres until a maximum current is obtained when surface effects overlap and/or the majority of the active material has been converted and consequently the current falls.

TABLE 2

Ampere hour input and capacity measurements

Cell type	Storage period (wks)	20 h Rated capacity before storage (A h)	Input during recharge (2.35 V for 24 h) after storage in discharged state (A h)					20 h Rated capacity after storage and recharge (A h)	A h obtained from discharge / A h put in during recharge (%)
			0 - 2 h	2 - 6 h	6 - 16 h	16 - 24 h	Total input (A h)		
Positive (P)	0	6.9	4.93	2.82	1.17	0.84	9.76	6.8	70
	4	6.9	2.50	5.63	2.81	0.82	11.76	8.0	68
	8	7.8	1.15	4.51	6.36	1.23	13.25	9.5	72
	24	7.3	0.38*	0.54*	1.23*	0.84*	2.99*	0.6*	20
Negative (N+)	0	12.1	5.46	6.64	2.25	0.80	15.15	11.7	77
	4	11.8	2.97	5.40	7.30	2.30	17.97	12.3	68
	8	11.5	1.20	4.02	8.36	3.70	17.28	10.5	67
	24	9.9	0.16*	0.30*	0.87*	0.60*	1.93*	0.2*	10
Negative without additive (N—)	0	11.3	12.61	2.57	1.62	0.60	17.40	11.4	66
	4	10.7	3.89	6.34	5.15	1.60	16.98	8.7	51
	8	10.1	0.92	2.46	5.91	3.75	13.04	6.5	50
	24	11.1	0.28*	1.19*	3.00*	2.40*	6.87*	0.9*	13

Results mean of three.
*Single result only.
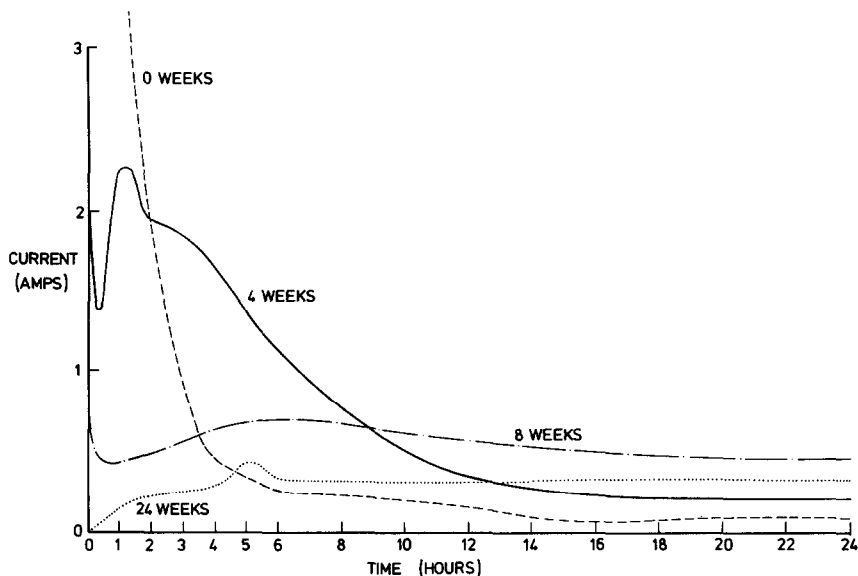
Fig. 4. Recharge current profiles at 2.35V: — Negative without additive (Group N—).

As mentioned previously, the cells stored for 24 weeks were divided into two groups: the first group was recharged in the electrolyte in which the plates had been stored, the second group was recharged in water. The results of these test are shown in Table 3.

It is seen that the replacement of the acid electrolyte by water allowed these cells to be fully recharged although at greatly reduced efficiencies. The current–time profiles and ampere-hour input data again showed an initial increase in current from zero to a maximum current after 4 - 6 h followed by a gradual fall.

Thus the results of recharge tests indicated that it became increasingly more difficult to recharge as the storage period increased, and that the water recharge was an effective method of recharging the cells stored for 24 weeks. The results also indicated that no large differences occurred between the cell types tested.

The chemical analysis results are shown in Table 4. Examination of the results after storage and prior to recharge shows that the amount of lead, lead dioxide, and lead sulphate does not markedly change as the storage period increases. The small differences which are observed do not appear significant, suggesting that the difficulties of recharge are not directly related to the amount of lead sulphate or to the lack of active material. The chemical analysis of the active material recharged after 4 weeks storage shows that there is a sizeable amount of sulphate still present after the recharge. However, after recharge in water of cells stored for 24 weeks the lead sulphate is almost completely oxidised.

TABLE 3

Water experiment for cells stored 24 wks in discharged state

Cell type	Recharge electrolyte	20 h Rated capacity before storage (A h)	Input during recharge (2.35 V for 24 h) (A h)					20 h Rated capacity after recharge (A h)	A h obtained from discharge / A h put in during recharge (%)	s.g. of electrolyte after recharge
			0 - 2 h	2 - 6 h	6 - 16 h	16 - 24 h	Total input (A h)			
Positive (P)	Acid	7.3	0.38	0.54	1.23	0.84	2.99	0.6	20	
	Water	7.8	2.17	6.13	10.26	3.55	22.11	10.5	48	1.120
Negative (N+)	Acid	11.6	0.16	0.30	0.87	0.60	1.93	0.2	10	
	Water	12.0	1.62	5.33	11.36	2.73	21.24	11.8	56	1.140
Negative without additive (N−)	Acid	11.1	0.28	1.19	3.00	2.40	6.87	0.9	13	
	Water	11.5	3.74	11.63	12.13	3.37	30.87	9.8	32	1.140

TABLE 4

Chemical analysis results

Cell type	Storage period (Wks)	State of active material	Chemical analysis (%)			
			Sulphate (SO$_4$)	PbO$_2$	Combined lead	Lead
Positive (P)	0	After formation	—	75.0		
		Discharged	21.4	14.5		
		Recharged	6.3	67.2		
	4	Discharged	25.8	9.9		
		Recharged	5.7	74.9		
	8	Discharged	25.7	13.7		
	24	Discharged	26.7	7.0		
		Recharged in water	0.7	87.2		
Negative (N)	0	After formation	—		7.6	90.6
		Discharged	21.4		49.0	30.2
		Recharged	—		17.3	84.1
	4	Discharged	25.7		61.4	11.9
		Recharged	5.7		15.7	79.3
	8	Discharged	27.4		65.9	9.0
	24	Discharged	26.5		66.3	5.7
		Recharged in water	—		17.5	78.0
Negative without additive (N—)	0	After formation	—		6.2	92.0
		Discharged	22.9		54.9	20.1
		Recharged	—		8.6	80.0
	4	Discharged	23.5		56.3	18.7
		Recharged	10.1		7.0	82.3
	8	Discharged	25.0		55.8	15.1
	24	Discharged	26.8		63.4	11.7
		Recharged in water	0.2		15.4	81.5

S.E.M. photomicrographs of samples of the active material from the three types of electrode after various storage periods are shown in Figs. 5 - 8.

Figure 5(a) - (g) illustrates the positive active material (A.M.) throughout the test programme. Figure 5(a) shows the active material immediately after formation and displays a porous structure of lead dioxide. Figure 5(b) shows A.M. after the 20 h rate discharge and shows a field of sulphate crystals of up to ≈ 10 μm in size, with evidence of residual lead dioxide. On recharge (Fig. 5(c)) most of the sulphate crystals have been converted back to lead dioxide. After 4 weeks storage (Fig. 5(d)) the sulphate crystals have grown somewhat but there is still evidence of residual lead dioxide. Figure 5(d) also illustrates that sulphate has grown from the underlying dioxide. The sulphate crystals have continued to grow at the 8 week stage (Fig. 5(f)), the size of the crystals being 15 - 20 μm. The photomicrographs after 24 weeks (Fig. 5(g)) show an extensive coverage of sulphate crystals similar in size to those seen after 8 weeks (Fig. 5(f)).

The photomicrographs of the negative A.M. group N+ (Fig. 6) follow a similar pattern to the positive samples. The open, porous lead structure of the sample after formation (Fig. 6(a)) is converted into a field of predominantly sulphate crystals of 2 - 5 μm in size after the initial discharge (Fig. 6(b)). On storage there is some evidence of crystal growth, together with some indication of a densification of the sulphate crystals (Fig. 6(b), (d), (f), (g)). However, the growth is not as extensive as that shown by the positive active material and, in general, the sulphate crystals on the negative electrode are much smaller than those shown on the positive electrode. Figure 5(e) illustrates that the negative A.M. can be reconverted into a porous lead structure after recharge following 4 weeks storage.

Figure 7 illustrates the effect of storage of the negative A.M. without the organic additive (N--). The photomicrographs show that storage creates a similar situation to that observed for the normal negative A.M. However, the size of the sulphate crystals observed (Fig. 7(b), (d), (f), (g)) are somewhat larger than those found on samples with organic additives (Fig. 6(b), (d), (f), (g)). In addition, the photomicrographs of the A.M. in the charged state (Fig. 7(a), (c), (e)) illustrate that removal of the additive has created a less porous structure of larger lead particles than that observed in samples with the additive (Fig. 6(a), (c), (e)). Thus Figs. 6 and 7 indicate that the adsorption of the organic surface-active additives alters the morphology of both the lead sulphate crystals and lead dendrites and supports the findings of previous researchers [6 - 8].

The photomicrographs of the A.M. of electrodes recharged in water after 24 weeks storage are shown in Fig. 8. Figure 8(b) and (c) illustrate that the recharge of the negative electrodes in water has efficiently converted the field of sulphate crystals (Fig. 6(g) and 7(g)) into a porous structure of lead dendrites. Figure 8(a) illustrates the positive A.M. after the recharge and shows a rather curious structure in that the lead dioxide formed with this recharge procedure appears to grow in a defined "contour" pattern from the underlying sulphate crystal. This may suggest that under these
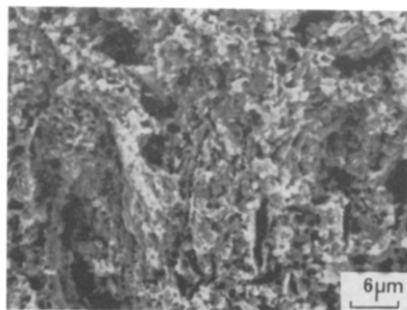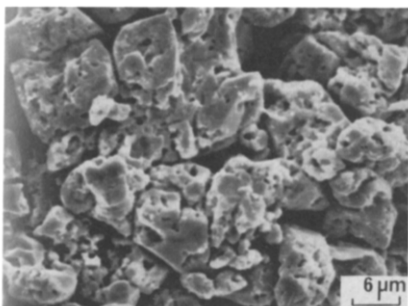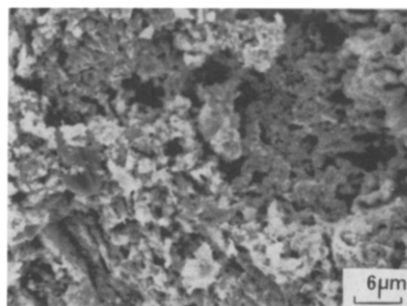
(a) After formation.
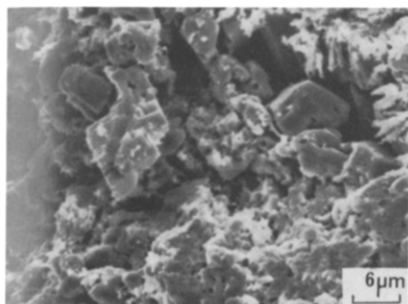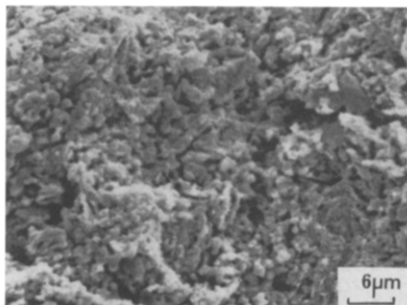
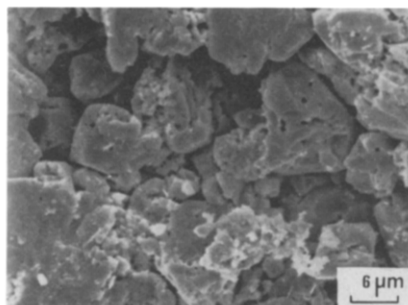(b) 0 weeks storage discharged.

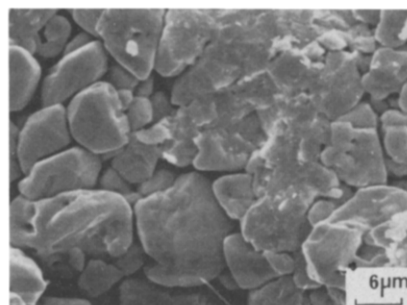(c) 0 weeks storage: — after recharge.

(d) 4 weeks storage discharged.
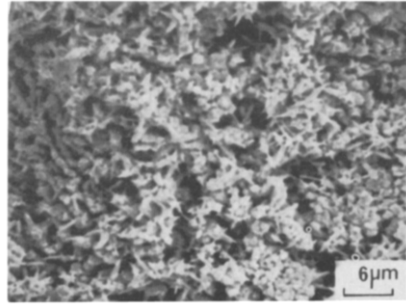

(e) 4 weeks storage: — after recharge.
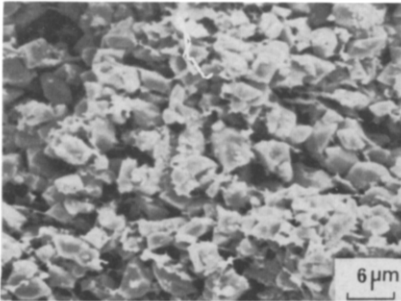

(f) 8 weeks storage discharged.

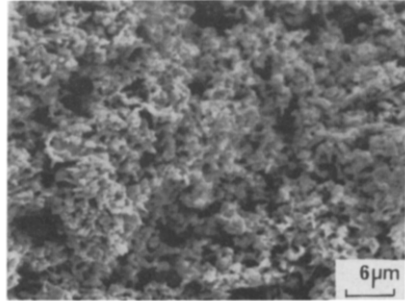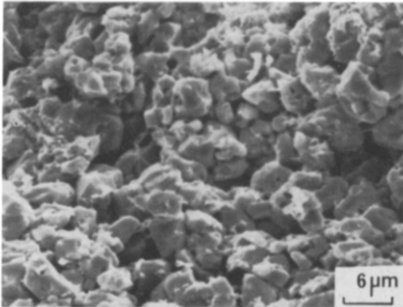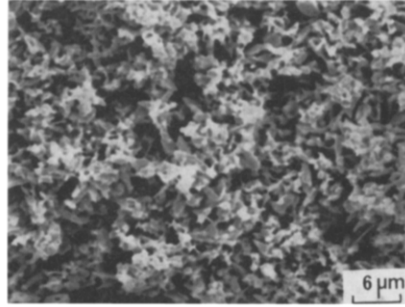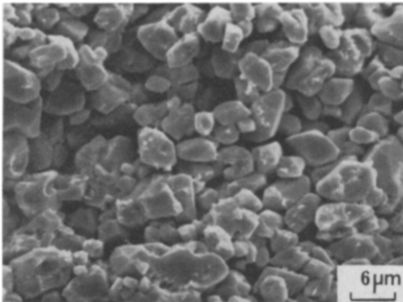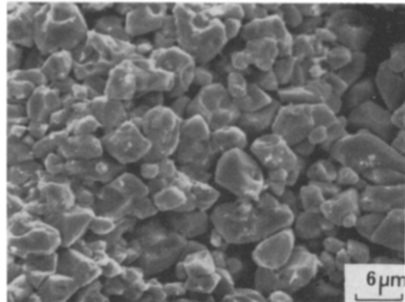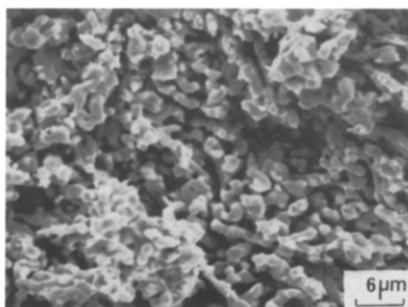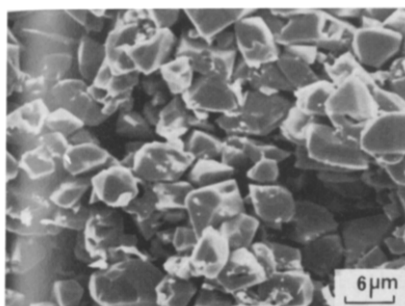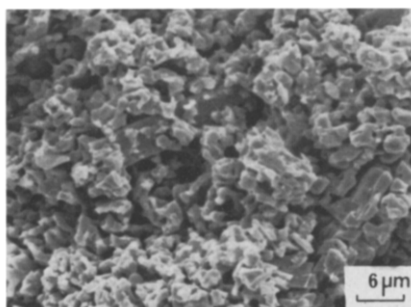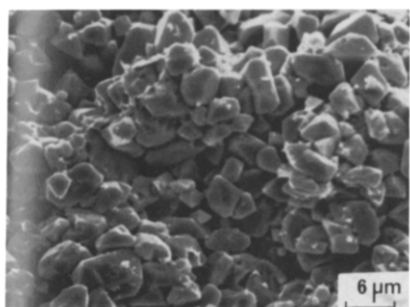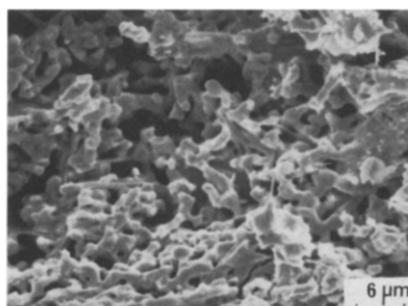(g) 24 weeks storage discharged.

Fig. 5. S.E.M. photomicrographs positive (P).

(a) After formation.

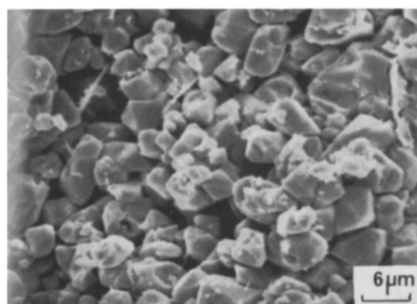(b) 0 weeks storage discharged.
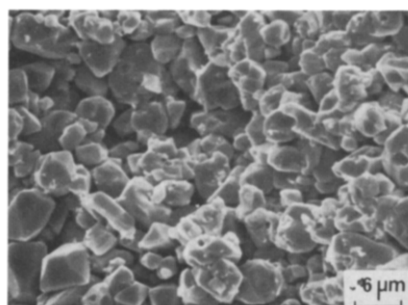

(c) 0 weeks storage: — after recharge.

(d) 4 weeks storage discharged.

(e) 4 weeks storage: — after recharge.

(f) 8 weeks storage discharged.

(g) 24 weeks storage discharged.

Fig. 6. S.E.M. photomicrographs negative (N+).

(a) After formation.

(b) 0 weeks storage discharged.

(c) 0 weeks storage: — after recharge.

(d) 4 weeks storage discharged.

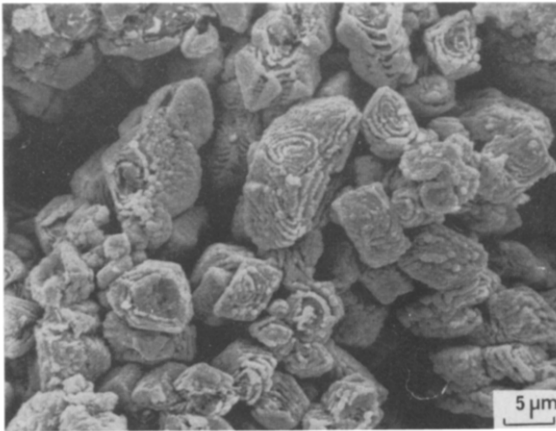(e) 4 weeks storage: — after recharge.
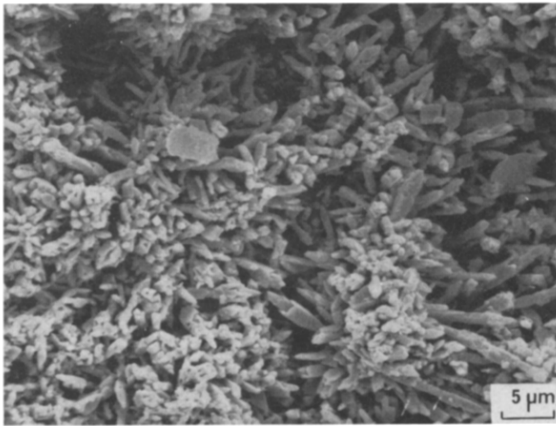

(f) 8 weeks storage discharged.

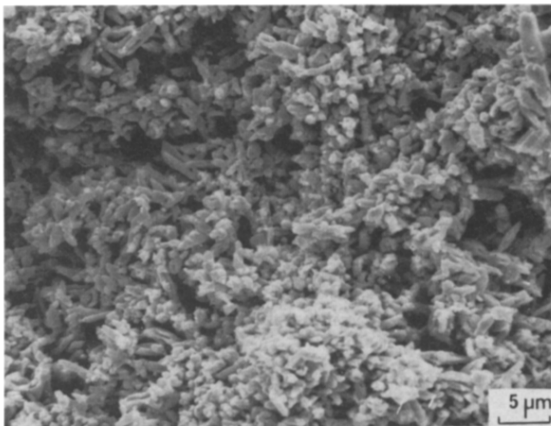(g) 24 weeks storage discharged.

Fig. 7. S.E.M. photomicrographs negative without additive (N—).

(a) Positive (P).

(b) Negative (N+).

(c) Negative without additive (N—).

Fig. 8. S.E.M. photomicrographs after 24 weeks storage in discharged state and recharge in H_2O. (a) Positive (P); (b) Negative (N+); (c) Negative without additive (N—).

conditions the growth of lead dioxide is energetically more favourable along certain lattice axes of the lead sulphate crystal.

Thus, the S.E.M. investigation has highlighted the following points.

(a) The work has confirmed that the sulphate crystals are larger on the positive PbO_2 electrode than those formed on the negative electrode.

(b) The organic additive alters the morphology of both the charged active material and the sulphate crystals formed on discharge.

(c) The photomicrographs of active material after 24 weeks storage showed insufficient differences from those obtained after 8 weeks storage to explain the large difference in the recharging ability of the electrodes.

(d) The recharge of the positive active material in water after 24 weeks storage yielded a curious "contour" pattern of lead dioxide built up from the underlying sulphate crystal structure.

It is evident that the complete processes involved in the "irreversible sulphation" phenomenon have still to be fully established. However, it is clear that the dissolution of Pb^{2+} ions is an important feature and any factor affecting the availability of such species must contribute to the sulphate problem.

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