

DEGRADATION OF THE POSITIVE PLATE OF THE LEAD/ACID BATTERY DURING CYCLING

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Introduction

In the pasted (flat plate) electrode, the active mass is contained in an open lead grid. The coherence of the mass and the contact to the grid are created through the curing and the formation processes. During charge and discharge, the volume of the solid material in the electrode undergoes large changes (*i.e.*, $\text{PbO}_2 \rightarrow \text{PbSO}_4$; $24.6 \rightarrow 48.2 \text{ cm}^3 \text{ mol}^{-1}$), but as the porosity of the electrode is large (*i.e.*, 55 - 60%) and the depth of discharge is less than 60%, these volume changes can be accommodated in the porous structure.

From experience, it is known that unintended addition of BaSO_4 to the positive mass accelerates the capacity decline. It appears, however, that no systematic investigation of this effect has been published. To elucidate the mechanism, therefore, a comparison has been made of the effects of three levels of BaSO_4 addition to the positive mass, *viz.*, 0, 0.3 and 3%. The physical loss of active material can be prevented by using a plane — not corrugated — separator and compressing the separator/plate assembly. This is known to increase the cycle life considerably. For this reason, cells with such a design ('pressurized cells') have been used in the BaSO_4 experiments reported here.

Experimental

Cell design and test procedure

Commercial plates were used in all experiments. The grid dimensions were $76 \times 79 \text{ mm}$, and the cured and formed positive plates contained $\sim 76 \text{ g}$ active mass and were 4.2 - 4.5 mm thick. The grid was cast from an alloy containing 0.06 wt.% Ca and 1.5 wt.% Sn. The plates were very uniform and free from cracks.

In all cells, two negative plates were used for each positive in order to make the positive the limiting electrode. An excess of 5 mol dm^{-3} of

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sulphuric acid was used. Cells with free-standing electrodes were mounted in acrylic vessels with an electrode distance of 7 mm. A single sheet of 'Amersil' separator was sometimes inserted against the negatives to prevent short circuits.

For the pressurized cells, four sheets of ribbed 'Amersil' separators were employed, giving an electrode distance of ~ 6 mm. The plane side of the separator was placed adjacent to the plate surface. The cells were assembled in poly(ethylene) bags and compressed with coil springs between steel plates. The pressure used was 13.75 kPa (0.14 kg cm^{-2}), which is known to be 1.5 times the lower limit for a significant compression effect. Acid stratification was prevented by air bubbling every 2 h.

The discharge/charge regime consisted of a constant-current discharge at 25 A kg^{-1} positive mass to 1.7 V/cell, followed by an 'IUI' charge profile. The latter consisted of, first, a constant-current charge (I) to a preset voltage limit (25 A kg^{-1} to 2.40 V), then a constant-voltage charge (U) until the current dropped to a preset minimum (5 A kg^{-1}) and, finally, a second constant-current charge (I) at the minimum current until a preset fraction (charge factor > 1) of the previously delivered capacity was reached. In the present experiments, the charge factor was 1.05. The low charge factor restricts the overcharge gassing to a minimum. The current used corresponds roughly to a $C/5$ discharge.

Chemical analysis of sludge

The sludge from cells using free-standing electrodes was collected during the cycling tests, washed with water, and air dried. The purpose of the chemical analysis was to determine the molar ratio of PbO_2 to total lead. PbO_2 could be determined iodometrically according to standard procedures. A new method had to be developed to determine the total amount of Pb. This was based on dissolution of PbO_2 and Pb in HNO_3 and H_2O_2 and dissolution and complexing PbSO_4 in EDTA. Surplus EDTA was then back-titrated potentiometrically with Cu^{2+} using a Cu-Se ion-selective electrode.

Expansion of positive plate

The intention was to follow the changes in the plate thickness during a single cycle as well as during the entire cycle life. The changes were, however, too small for this to be done mechanically. The apparatus eventually used for expansion studies is shown in Fig. 1. The methodology is based on continuously recording the thickness variations using an LVDT transducer (linear variable differential transformer) that, in connection with a conditioning module, provides a d.c. output proportional to the displacement of the central core. The positive plate under investigation is placed between two circular glass frits (5 mm thick) that serve as non-compressible separators. Negatives are placed on both sides. The lower glass frit is fixed to the electrode vessel, but the upper is free to follow the thickness variations of the plate. An acrylic rod cemented into the upper frit transfers the movements to the LVDT core. Lead weights are used to control the compression of the electrode.

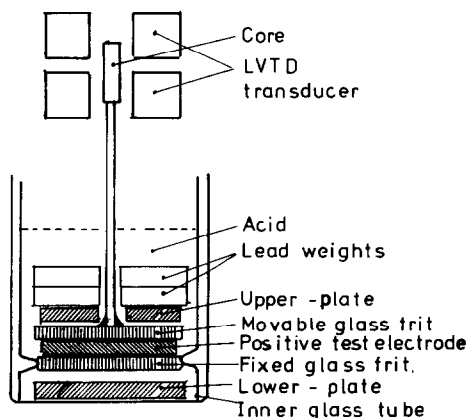


Fig. 1. Expansion test cell.

Electrodes of 16 cm^2 area were cut from positive plates. Cycling was done in 5 mol dm^{-3} acid, according to an *IUI* scheme, against an Hg_2SO_4 reference electrode. The discharge end-point was 0.7 V . The charge factor was 1.05 and both a $C/5$ and a $C/10$ load was used. The pressure was either 1 or 0.5 kPa (10 or 5 g cm^{-2}).

Results

Cycling of free-standing positive plates

The development of the capacity of plates with 0 , 0.3 and $3 \text{ wt.}\%$ BaSO_4 during cycling is shown in Fig. 2. The results are somewhat erratic, in some cases due to computer failures. Three cells of each type were cycled. The points indicate results from each cell. The curves drawn are not averages, but estimates of the general trend.

The performance of one of the cells, that without BaSO_4 , was significantly inferior to the other two. A separate curve is drawn for this cell. The arrows indicate where the first sample of sludge was collected (sludge amount: $7 - 15 \text{ g}$). The cell life to 60 A h kg^{-1} is estimated to be $60 - 80$, 18 and 8 cycles, respectively, for cells with 0 , 0.3 and $3 \text{ wt.}\%$ BaSO_4 .

Cycling of pressurized positive plates

The capacity development during cycling is shown in Fig. 3. In this case, the results are much more uniform and the curves represent averages of the three cells in each category. The cell life to 60 A h kg^{-1} is estimated to be 320 , 80 and 35 cycles, respectively, for cells containing 0 , 0.3 and $3 \text{ wt.}\%$ BaSO_4 . The ratio between the numbers of cycles obtained is about the same as for free-standing plates, *viz.*, $10:2:1$.

On disassembling the cells after failure, it was observed that for cells with BaSO_4 addition, the positive mass had the consistency of soft mud, even

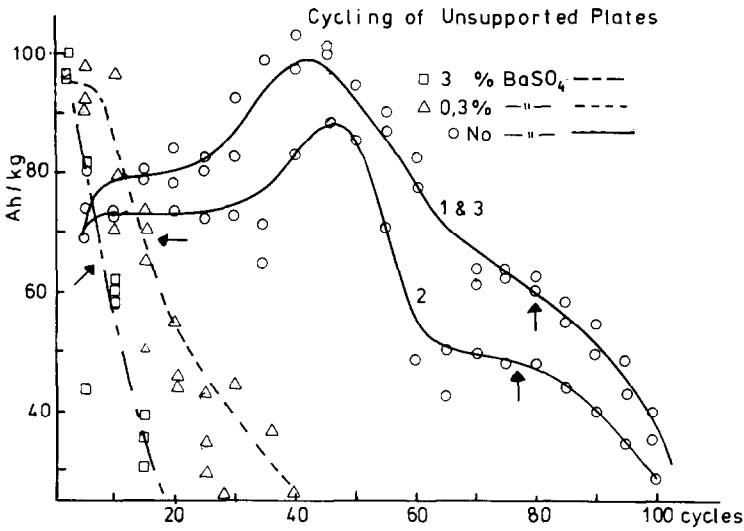


Fig. 2. Cycling behaviour of free-standing plates with 0, 0.3 and 3 wt.% BaSO_4 .

if, in some cases, a thin, hard layer remained at the centre. By contrast, the cells without BaSO_4 had a layer of 'mud' at the surface only, together with a hard core, even if the cells had expanded considerably (up to 1.5 mm).

Amount and composition of sludge

The weight of the sludge was determined and samples analysed for PbO_2 and total lead. Typical results are given in Table 1. It is obvious that, in relation to the initial capacity, $\sim 100 \text{ Ah kg}^{-1}$, and the plate weight, the amount of sludge cannot account for the decline in capacity. Consequently, a considerable amount of the material remaining on the plate is inactive during discharge.

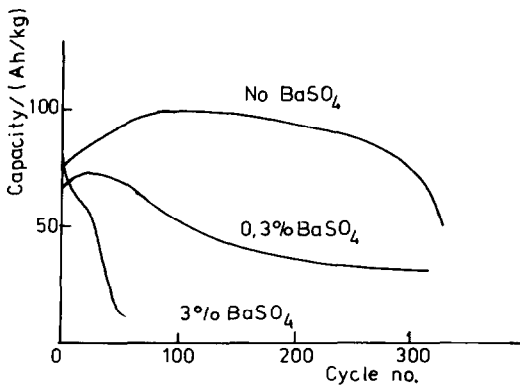


Fig. 3. Cycling behaviour of pressurized plates with 0, 0.3 and 3 wt.% BaSO_4 .

TABLE 1

Sludge collected from shedding experiments

Electrode no.	Cycle no.	Capacity (A h kg ⁻¹)	Total sludge (g)	PbO ₂ /Pb molar ratio
Electrodes before cycling		—	—	0.81
Electrodes with no addition				
14	79	64	8.4	0.87
14	242	1	30.7	0.96
15	76	50	8.0	0.80
15	252	1	35.1	0.96
17	80	63	7.5	0.85
17	168	1	24.1	0.96
Electrodes with addition of 0.3 wt.% BaSO ₄				
14A	17	56	21.6	0.90
14A	33	10	57.9	0.90
14A	60	2	72.1	0.92
15A	17	66	16.2	0.97
15A	31	19	50.7	0.91
15A	42	7	59.0	0.92
15A	56	3	72.2	0.93
Electrodes with addition of 3 wt.% BaSO ₄				
14B	10	60	7.6	0.90
14B	22	15	41.6	0.92
14B	49	4	56.9	0.95
14B	69	3	60.9	0.98
15B	11	51	8.4	0.87
15B	24	15	38.6	0.91
15B	43	11	52.1	0.97
16B	11	54	10.3	0.92
16B	23	18	40.3	0.91
16B	50	2	61.2	0.93
16B	72	2	64.4	0.93

The precision of the PbO₂/Pb molar ratio determination of the sludge composition is estimated to be $\pm 2\%$. After formation, this ratio is 0.80 - 0.82. For most of the sludge samples, however, the ratio is above 0.90. Thus, the sludge consists mainly of fully charged material. This shows that the *shedding* does not take place as a consequence of the volume increase during discharge. Analysis of the mass remaining in the grid at the end of cycling shows a PbO₂/Pb ratio of 0.88 - 0.92; this is not significantly different from the ratio in the sludge. There is no clear difference in ratio between the different additions of BaSO₄, when a comparison is made of plates in the same capacity range.

In cases where the shedding was excessive, it was observed that the 'sludge' could take a 'dendritic' form and grow away from the electrode, as illustrated in Fig. 4. This shows a cell with a free-standing electrode with

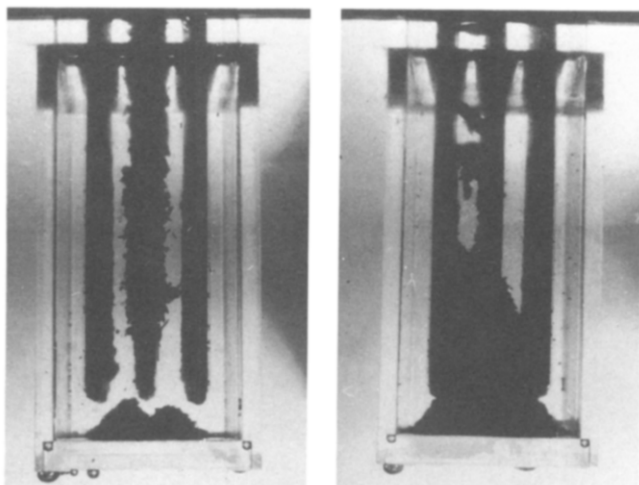


Fig. 4. Shedding from free-standing plates with 3 wt.% BaSO_4 after 10 (left) and 15 (right) cycles.

3 wt.% BaSO_4 after 10 and 15 cycles. It is noteworthy that the PbO_2 sludge bridging to the negative electrode did not short the cell, showing that the sludge had no appreciable electronic conductivity.

Expansion of positive plate

Typical results for the expansion of an electrode with 3 wt.% BaSO_4 during one cycle are given in Fig. 5. The discharge/charge regime was $C/5$, IUI , and the pressure 0.7 kPa (7 g cm^{-2}). The discharge voltage is also shown in Fig. 5. The cell had been cycled 12 times and had a capacity of 60 A h kg^{-1} . Cells without BaSO_4 showed a much smaller expansion and the measurements were not precise, but were in qualitative agreement with those presented in Fig. 5.

Expansion measurements at higher cycle numbers, where the capacity had dropped to $20 - 30 \text{ A h kg}^{-1}$, gave a very different picture. Then, a signifi-

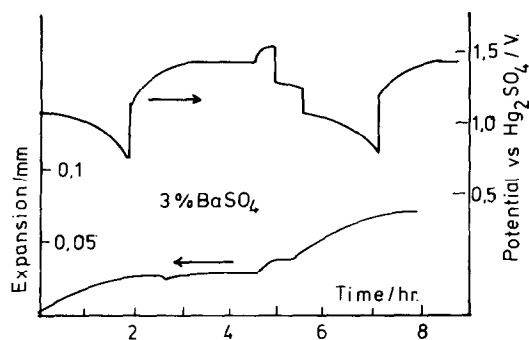


Fig. 5. Expansion and voltage during one cycle. Plate with 3 wt.% BaSO_4 after 12 cycles.

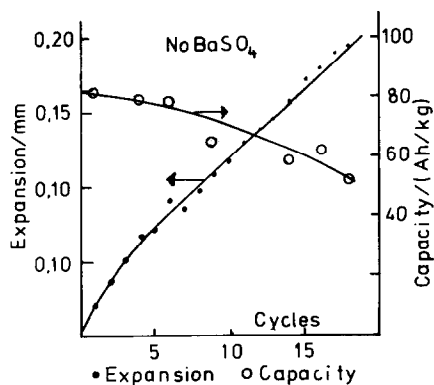


Fig. 6. Expansion and capacity of test electrode (no BaSO_4) during the first 20 cycles.

cant contraction was observed during discharge followed by slight expansion during charge. This behaviour was quite erratic. It coincides, however, with the transformation of the mass into 'mud' that is squeezed out of the grid due to the applied pressure.

As shown in Fig. 5, the expansion during one cycle is not reversible; the increase in thickness accumulates from cycle to cycle. This is illustrated in Figs. 6 and 7. The former shows the accumulated expansion and the corresponding capacity for the first 20 cycles. The electrode contained no BaSO_4 , the pressure was 1 kPa (10 g cm^{-2}), and the cycling regime $C/10, IUI$. In this case, the expansion starts immediately and is proportional to the cycle number until the capacity drops to $50\text{--}60 \text{ A h kg}^{-1}$. A comparison between

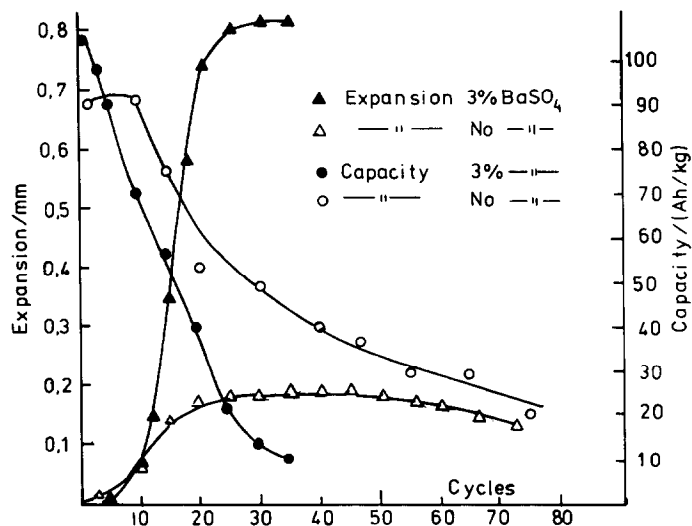


Fig. 7. Expansion and capacity of test electrodes with 0 and 3 wt.% BaSO_4 during cycling.

electrodes with and without BaSO_4 is shown in Fig. 7. Here, the expansion is followed during prolonged cycling and related to the capacity. The overall picture is one where the expansion levels off after about 25 cycles, but the capacity continues to decline. BaSO_4 (3 wt.%) increases the final extent of expansion and the expansion rate by a factor near 4.

From Fig. 5 it can be seen that there is a small but significant expansion during the rest period after charge. The most important change in this period is a decline in the acid concentration. This initiated an investigation of the change in thickness of the charged electrode with change in acid concentration. An electrode without BaSO_4 , cycled 20 times in $5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ and compressed at 1 kPa (10 g cm^{-2}), was equilibrated in the charged state in $10 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ whereby a small contraction (0.03 mm) took place. Changing the acid concentration in steps down to 2 mol dm^{-3} caused a considerable expansion, in total 0.18 mm. Changing the acid concentration back to 5 mol dm^{-3} caused a contraction to the original thickness. The effect was, however, not very reproducible, and often the thickness varied erratically for a long time before constant values were obtained.

Discussion

The results reported above all relate to continuous deep cycling at a medium load, as is typical in traction applications. It is believed, however, that the conclusions that may be drawn from these results, with minor modifications, can be applied to other load conditions.

In summary, the following information has been obtained.

(i) During the first 25 cycles, a normal electrode expands by 5 - 10% in thickness, even when it is compressed slightly ($0.5 - 1 \text{ kPa} = 5 - 10 \text{ g cm}^{-2}$).

(ii) When the normal, positive, free-standing electrode is cycled to 50 - 60% of its initial capacity, ~10% of the active mass is lost by shedding. With further cycling, 30 - 40% of the material is lost.

(iii) On the addition of BaSO_4 to the positive mass, all the degrading factors are dramatically enhanced. For example, an addition of 3 wt.% BaSO_4 decreases the cycle life by a factor of 10, increases the expansion by a factor of 4, and increases the loss by shedding by a factor of 8. The addition of 0.3 wt.% BaSO_4 has an effect half-way between 0 and 3 wt.% BaSO_4 .

(iv) Material resulting from shedding has a PbO_2/Pb ratio of ~0.9.

(v) By compressing the positive electrode between plane, rigid, separator sheets at a pressure of ~14 kPa (0.14 kg cm^{-2}), the cycle life is increased by a factor of 3 - 4. This is also the case for BaSO_4 -containing plates.

Qualitatively, these results are more or less known. The important aspect is how these observations can lead to an understanding of the processes in the pasted positive electrode that are responsible for the degradation during cycling. For this purpose, it is necessary to consider some basic factors in the spatial distribution of the charge/discharge processes that are important for the operation of the porous electrode.

Consider first, the charging of a PbSO_4 particle. The initial step is the dissolution of PbSO_4 :



This reaction can take place anywhere in the electrode. It is followed by diffusion to a site where the electrochemical anodic reaction occurs:



As H_2O is always present, this reaction can occur at any site that has an electronic connection to the grid — eventually at the grid itself. The overall reaction rate may be diffusion controlled and will be slow when the PbSO_4 particle is positioned well away from an electronically conductive site. All PbSO_4 particles can be converted to PbO_2 , however, when the charge is continued for a sufficient length of time.

The possibility for the discharge of a PbO_2 particle is much more restricted:



For this reaction to occur, the particle must have, and maintain, electronic contact with the grid. Thus, a PbO_2 particle that has become completely surrounded by either a water film or PbSO_4 particles can never be discharged. The situation is irreparable by chemical or electronic means. The capacity loss during cycling may therefore be identical with the rate of formation of isolated PbO_2 particles.

Initially, the structure of the positive electrode is a rigid matrix of inter-connected PbO_2 aggregates. They are all in electronic contact both with each other and with the grid because this is the only way that the aggregates can be created during the formation process (which can be considered as a special sort of charging). The porosity is created partly by the initial porosity of the cured electrode and partly by the difference in molar volume between PbO_2 and the different basic Pb^{2+} sulphates created during curing. Even in the case of deep discharges, it is therefore obvious that the PbSO_4 formed *can* be accommodated in the pores without disturbing the structure. This requires, however, a spatially uniform precipitation of PbSO_4 during discharge.

The spatial distribution of the precipitate is controlled by nucleation processes. It is known (*e.g.*, from investigations of the initial part of the discharge) that the super-saturation of PbSO_4 may be quite high. Thus the activation energy for nucleation at the PbO_2 surface is high. If for one reason or another a region exists where nucleation is facilitated, then the precipitation of PbSO_4 will take place preferentially in this region. A large amount of PbSO_4 deposited there may eventually deform the PbO_2 structure. This is typically manifested as electrode expansion. When the process takes place at the surface of the electrode, PbO_2 particles may be surrounded by PbSO_4 and isolated from the main structure. During charge, the PbSO_4 disappears and is substituted by a water film. These PbO_2 particles form the soft mud that is observed on the surface of cycled electrodes. Upon further cycling, only the

remaining rigid structure is active and the formation of the PbO_2 mud continues at the interface with the previously formed mud layer.

With free-standing plates, part of the mud sheds away from the electrode and is deposited as sludge, but a large part remains at the electrode. In the case of supported (or pressurized) electrodes, the mud remains between the separator and the rigid part of the electrode. Nevertheless, the mud cannot be discharged because the PbO_2 particles are electronically insulated from each other and from the active part of the electrode.

The above mechanisms explain all of the experimental observations. The very significant effect of BaSO_4 is due to the BaSO_4 particles acting as permanent nuclei for PbSO_4 . This prevents supersaturation and the formation of PbSO_4 nuclei elsewhere. The result is a non-uniform precipitation of PbSO_4 and, therefore, a large expansion, and mud formation. The high PbO_2/Pb ratio of the sludge is caused by the fact that the PbO_2 in the mud cannot be discharged.

The observation that the expansion is dependent upon changes in the acid concentration is consistent with the existence of a dispersion of insulated conductive particles. The electrochemical double layer around these particles depends upon the ionic strength of the solution. A change in the latter will alter the repulsive forces between the particles which, in turn, will result in a change in the apparent thickness of the mud layer.

The observations illustrated in Fig. 4 can be explained by the individual particles in the mud being conductive and thus aligning themselves in the direction of the current. The fact that the sludge formed under these conditions does not short circuit the battery shows that these PbO_2 particles are insulated from the plate.

The effect of compressing the electrode is important because it is the only method to improve cycle life that emerges directly from the experiments reported here. It is not likely that the pressure can prevent the PbO_2 particles from being displaced from their position in the rigid PbO_2 network by large PbSO_4 crystals during discharge, but the beneficial effect of pressure may act in two ways. During discharge, the pressure on the surface may cause the displacement to proceed into the electrode, where the electronic contact can be restored. This requires a pressure high enough to compress the electrode structure. The second possibility is that the PbO_2 particles are squeezed away from the surface against the applied pressure, but are then pushed back again when the cause of the displacement (the PbSO_4) is dissolved during charge. This necessitates that the compression be achieved by elastic means, not by direct force to a fixed thickness. Independent experiments have demonstrated that considerably improved results are obtained with spring-controlled, rather than with fixed, compression.

Conclusions

The following are the main conclusions reached from this investigation.

(i) Prolonged deep cycling of pasted positive plates transforms the initially rigid electrode structure into a structureless 'mud' consisting of

PbO_2 dispersed in acid. The PbO_2 particles are electronically insulated and cannot be discharged. The discharge capacity declines accordingly.

(ii) The formation of the mud takes place at the surface of the rigid parts of the electrode, and is accompanied by shedding and precipitation of sludge.

(iii) The formation of the inactive mud is caused by uneven precipitation of PbSO_4 in the pores during discharge. In the first stage, this is signalled by a slight expansion of the initially rigid structure.

(iv) Material such as BaSO_4 that can act as discrete, permanent nucleation centres for PbSO_4 greatly accelerates the mud formation and electrode expansion.

(v) Compression of the electrode delays mud formation and increases cycle life. A sustained pressure above 14 kPa causes a four-fold increase in cycle life.

From the above, it appears that the best way to improve cycle life when a pressurized design is not possible, is to aim for a uniform, mechanically strong electrode structure.

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