

New operational strategies for gelled-electrolyte lead/acid batteries

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Abstract

Gelled-electrolyte and flooded-electrolyte lead/acid batteries are cycled according to a new schedule that is based on partial-state-of-charge operation. With this strategy, the energy delivery of gelled-electrolyte batteries increases threefold, compared with that expected under traditional cycling procedures. In addition, overcharge is reduced by an order of magnitude. This provides charging efficiencies of up to 99.5%. Under the same duty, flooded-electrolyte batteries fail prematurely due to degradation of active-material at the bottom of the positive plates. This limitation is induced by increased active-material utilization as a result of acid stratification. The phenomenon is termed 'localized PCL', and is explained in terms of the uniform theory of PCL that has been developed by CSIRO.

Keywords: Lead/acid batteries; Gelled-electrolyte; Acid stratification; Partial-state-of-charge; Cycle life; Premature capacity loss

1. Introduction

The lead/acid battery was the first rechargeable battery to be commercialized and is still the most commonly used. Present applications include: starting, lighting and ignition (SLI) of automobiles; telecommunications; stationary back-up power; motive power; remote area power supply (RAPS) systems; portable power. The batteries are generally purpose-built for each duty in order to satisfy specific performance requirements.

The first lead/acid batteries employed a flooded-electrolyte design. This technology remained the only one available until the early 1960s, when the German battery company, Sonnenschein AG, placed valve-regulated lead/acid (VRLA) technology on the market. The Sonnenschein battery accommodates the acid in a gel that is formed by mixing the electrolyte solution with fine particles of silicon dioxide (gelled-electrolyte design). In 1972, the Gates Rubber Company commercialized a second type of VRLA battery, i.e., one that contains the electrolyte in absorptive glass-microfibre separators (AGM design).

VRLA batteries are variously referred to as 'maintenance-free', 'sealed', 'recombinant-electrolyte', 'starved-electrolyte', or 'immobilized-electrolyte' systems. They have certain advantages and disadvantages relative to their flooded-electrolyte counterparts [1]. For example, VRLA batteries do not require water maintenance or special ventilation, are easily transported, emit negligible acid fumes, can be operated horizontally, and require less space due to multi-

stacking. On the other hand, VRLA batteries require very careful charging and their performance at elevated temperatures is questionable.

Both flooded-electrolyte [2-6] and AGM batteries [7,8] can suffer from acid stratification. In simple terms, this phenomenon can be defined as 'a build-up of higher strength acid at the bottom of the battery'. Stratification occurs because sulfuric acid has a high density and, when formed during the charging process, can sink to the bottom of the battery container. This behaviour results in a decrease in battery capacity due to uneven utilization of the active material [2-5]. Moreover, if the resulting concentration gradient is allowed to remain for extended periods, premature failure of the battery can occur [2-7].

Acid stratification in AGM batteries can be minimized through proper cell design [9]. For instance, the use of high quality glass mat and short plate heights can each provide a significant reduction in stratification. It is also important to achieve the correct level of acid fill within the glass mat. Oversaturation of the AGM separators can render the battery more susceptible to acid stratification, and once stratification has occurred, it is very difficult to remove.

The problem of acid stratification in flooded-electrolyte batteries can be ameliorated by providing sufficient overcharge during the charging procedure. Indeed, this technique is usually performed on a regular basis through a so-called 'equalization charge'. The gas produced during this period mixes the electrolyte and equalizes the acid concentration within each cell. Unfortunately, the additional overcharge can

increase the corrosion of the positive grids and, thereby, can shorten significantly the life of the battery.

As part of a continuing research programme into advanced VRLA technology, CSIRO has been seeking means to improve the manufacture and operation of gelled-electrolyte batteries. This paper describes preliminary results from a new operating strategy for gelled-electrolyte batteries. The strategy capitalizes on the main advantage of the battery technology, i.e., its resistance to acid stratification.

2. Experimental

Batteries of both flooded- and gelled-electrolyte design are cycled under a partial-state-of-charge profile (Fig. 1). The schedule is comprised of three regimes. Regime 1 consists of an initial discharge at the $C_3/5$ rate for 3 h to a nominal 40% state-of-charge (SOC).

Regime 2 involves recharging at the $0.6 C_3/5$ rate for 2.5 h to 70% SOC, then discharging at the $C_3/5$ rate for 1.5 h to 40% SOC (note, from this point onwards, a 'cycle' is defined as a discharge to 40% SOC followed by a charge to 70%). The sequence is continued for 2 weeks (i.e., 84 cycles), or until the battery voltage drops to 1.75 V/cell. The battery is then subjected to regime 3 (note, regime 2 terminates with the battery at a nominal SOC of 40%).

Regime 3 comprises the following: (i) a $C_3/5$ rate discharge to 1.75 V/cell; (ii) a restoration charge at the $C_3/5$ rate until a pre-set voltage is reached (2.4 V/cell for gelled-electrolyte batteries; 2.55 V/cell for flooded-electrolyte units), then constant-voltage charging for 9 h; (iii) a $C_3/5$ rate discharge to 1.75 V/cell, and (iv) repeat of step (ii). If the capacity recorded during the second discharge is lower than 75% of the initial value, the battery is considered to have failed and is removed from the test. If the capacity of the battery is above 75%, it is returned to the start of the test sequence.

Equipment designed and manufactured in the CSIRO laboratories was used for battery cycling. The batteries were tested in an air-conditioned room maintained at $20^\circ\text{C} \pm 2$. Capacities are quoted at the $C_3/5$ rate, unless stated otherwise.

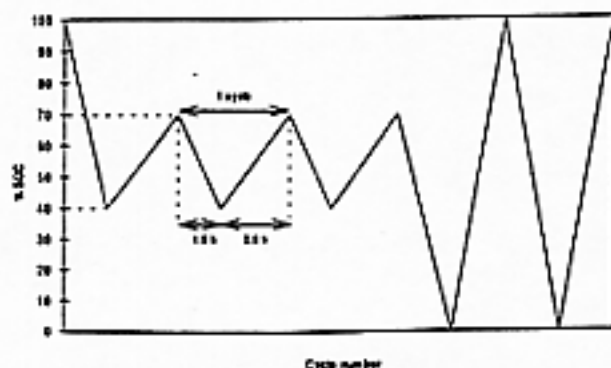


Fig. 1. Partial-state-of-charge schedule.

3. Results and discussion

3.1. Electrolyte stratification under partial-state-of-charge operation

Gelled-electrolyte (6 V, 143 Ah) and flooded-electrolyte batteries (6 V, 115 Ah) were cycled under the partial-state-of-charge profile. The specific gravity (sp. gr.) of the acid in the flooded-electrolyte batteries was measured at two-day intervals during regime 2. Results for a typical two-week period are presented in Fig. 2. The data are expressed as the difference (ΔSG) between the density (in points) of the electrolyte at the bottom and the top of the battery at 70% SOC (note, the ΔSG values at 40% SOC followed a similar trend to those obtained at 70% SOC).

During the cycling period, the ΔSG of the flooded-electrolyte battery increased from 60 to 130 points. This demonstrates that significant stratification of the electrolyte solution occurs during the two-weekly cycling period. (Note, the ΔSG value of 60 points at the commencement of the given two-weekly cycling period indicates that stratification was not entirely removed by the previous equalization charge.)

The gelled-electrolyte and flooded-electrolyte batteries lost 5 and 15%, respectively, of their initial capacities during regime 2 of the partial-state-of-charge schedule. This decline in performance can be attributed to self-discharge, charging inefficiencies, acid stratification, or to a combination of all three.

Self-discharge processes are expected to decrease the capacity of the gelled-electrolyte battery by approximately 1 to 2% during regime 2, i.e., by 2 to 4% per month [10]. The corresponding decrease for the flooded-electrolyte battery would be 3 to 5%, or 6 to 10% per month [11]. The latter battery contains antimony that is known to increase the rate of self-discharge.

Losses due to charging inefficiencies are also possible. Nevertheless, these are considered to be negligible as the conversion of lead sulfate to lead dioxide at SOC's < 80% has an efficiency very close to 100%. Therefore, the additional loss of capacity that occurred in the batteries during regime 2, i.e., the difference between the total capacity loss

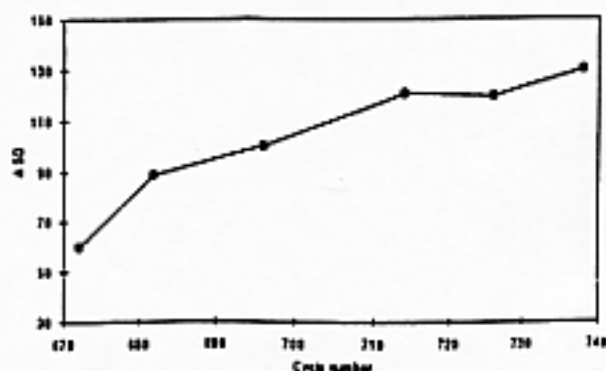


Fig. 2. Difference in electrolyte sp. gr. (ΔSG) between bottom and top of flooded-electrolyte battery cycled under partial-state-of-charge conditions.

and the capacity loss due to self-discharge, can be attributed to acid stratification. In the above tests, a ΔSG value of 130 points in the flooded-electrolyte battery resulted in a 10 to 12% capacity loss. Similar results have been obtained by other authors. For example, Sunu and Burrows [2] showed that a ΔSG of 100 points reduced the capacity of a flooded-electrolyte battery by about 10%, while Shimpo et al. [4] found that a ΔSG of 180 points yielded a 10% loss. The decrease in capacity with increasing electrolyte stratification has been attributed [2-5] to non-uniform utilization of the active material. That is, active material in contact with the stronger acid at the bottom of the battery is discharged preferentially.

The voltage at the end of both the charge period (TOCV) and the discharge period (EODV) during regime 2 of the partial-state-of-charge schedule was recorded. Data for a typical two-week period are presented in Figs. 3 and 4 for flooded-electrolyte and gelled-electrolyte batteries, respectively.

The TOCV of the flooded-electrolyte battery increased by ~500 mV during the 84 cycles of regime 2. Concomitantly, the EODV decreased by ~200 mV. Shimpo et al. [4] have performed similar experiments and observed equivalent changes in TOCV and EODV. The variations were related directly to the degree of acid stratification that developed in the battery.

Changes in TOCV and EODV were also observed for the gelled-electrolyte battery during partial-state-of-charge operation. The variations were minimal, however, compared with those recorded for the flooded-electrolyte unit, i.e., 150 and

40 mV for TOCV and EODV, respectively (see Fig. 4). The small variations are consistent with negligible acid stratification and support previous claims [10] that the technology is quite immune to this problem.

In conclusion, gelled-electrolyte batteries are shown to be resistant to electrolyte stratification. By contrast, electrolyte stratification in flooded-electrolyte units causes capacity loss and greater rises in voltage during charging. The latter effect on voltage results in poor charge efficiency. Finally, electrolyte stratification can be quantified in terms of shifts in both TOCV and EODV during partial-state-of-charge operation. In particular, measurements of EODV and TOCV obtained under partial-state-of-charge conditions may provide a useful 'non-destructive' technique to assess the resistance of VRLA batteries to stratification. This is especially relevant to AGM units, as they are known to be susceptible to this problem.

3.2. Cycle life under partial-state-of-charge operation

An evaluation was made of the performance of two types of battery that differed in design and intended application. One battery contained gelled-electrolyte, used 2.5 mm thick positive plates, and was designed for general-purpose duty. The other battery was a flooded-electrolyte unit, had thick positive plates (5.5 mm), and was built specifically for deep-cycle use.

The endurance of both batteries under the partial-state-of-charge schedule is summarized in Fig. 5. The gelled-electrolyte battery has completed 5500 cycles and is still operating at 98% of its original capacity. This corresponds to a total energy delivery of 235 950 Ah. (Note, the decrease in capacity between cycles 2500 and 4000 was related to a problem with the cycling equipment. After the fault was rectified, the capacity of the battery increased to ~100% of the original value.) By contrast, the flooded-electrolyte battery failed after only 1796 cycles, or 61 962 Ah.

3.3. Gelled-electrolyte battery

The cycle life and associated delivery of energy claimed by manufacturers of gelled-electrolyte batteries under traditional cycling conditions, i.e., a full recharge after each dis-

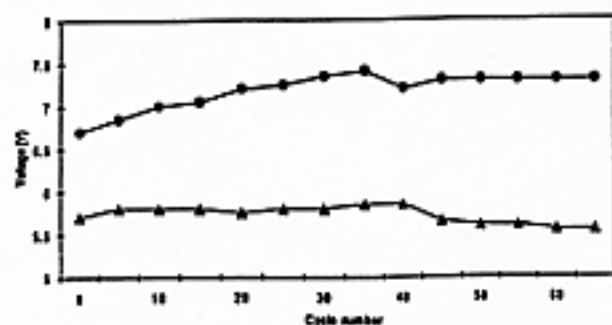


Fig. 3. Typical voltage data for flooded-electrolyte battery during two-week cycle: (●) TOCV, and (▲) EODV.

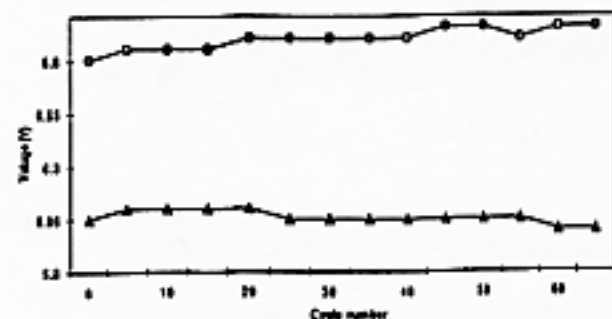


Fig. 4. Typical voltage data for gelled-electrolyte battery during two-week cycle: (●) TOCV, and (▲) EODV.

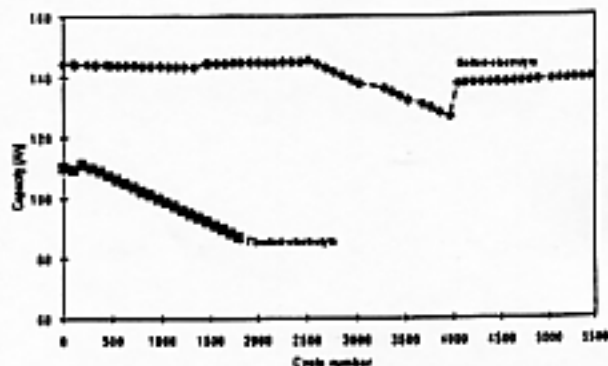


Fig. 5. Cycle life of batteries operated under partial-state-of-charge duty.

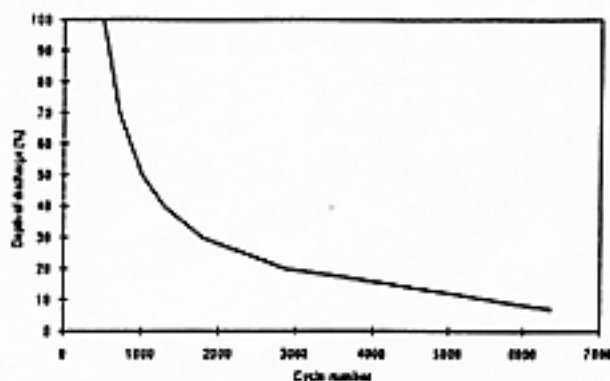


Fig. 6. Relationship between cycle life and depth-of-discharge for general-purpose, gelled-electrolyte battery (manufacturer's data).

Table 1

Total energy available from gelled-electrolyte battery at different depths-of-discharge

Depth-of-discharge (%)	Number of cycles	Total available energy (Ah)
10	6000	86000
20	3200	91500
40	1250	71500
60	900	77000
80	700	80000
100	500	71000

charge, at varying depths-of-discharge are given in Fig. 6 and Table 1, respectively. The energy delivery under partial-state-of-charge duty (235 950 Ah) is approximately three times that obtained under traditional cycling conditions to 60% depth-of-discharge, i.e., 40% SOC viz. 77 000 Ah. This marked increase in energy is not attributable to the moderate depth-of-discharge of the partial-state-of-charge profile, i.e., 60%, as decreasing the depth-of-discharge from 100 to 20% under traditional operating conditions will offer only a small increase in energy delivery, i.e., 20 500 Ah or 30% (Table 1).

Under normal charging schedules, a valve-regulated battery receives approximately 105% of the energy delivered during discharge, i.e., the charging efficiency is ~95%. By contrast, a battery operated under partial-state-charge conditions is subjected to two full recharges every 84 cycles, i.e., every two weeks). Each recharge delivers 105% of the rated capacity of the battery, or 7 Ah of overcharge. Hence, for every 84 cycles or 3604 Ah of energy delivered, the battery receives only 14 Ah of overcharge. This corresponds to a charge efficiency of 99.5%. (Note, a battery that has delivered 3604 Ah under traditional control strategies will receive ~105% of 3604 Ah in overcharge, i.e., ~180 Ah.) In other words, partial-state-of-charge operation can reduce overcharge and related oxygen production by more than an order of magnitude, compared with traditional operating algorithms. Clearly, therefore, reduced overcharge is responsible for the greater delivery of energy under partial-state-of-charge duty.

Positive-grid corrosion is a common failure mode in designs of lead/acid battery [11,12]. Although several factors, e.g. temperature and acid strength, enhance corrosion, the activity of oxygen near the grid is considered to exert significant influence. Hence, any decrease in gassing during charging will reduce the corrosive attack.

Gassing during charging has also been noted [11,12] to affect the performance of the positive plate. The vigorous evolution and movement of gas through the positive active material can disrupt and degrade the integral structure of the positive plate, and thus accelerate failure. Such degradation of the positive active-material during charging can now be explained in terms of the 'uniform theory' of premature capacity loss (PCL) developed recently by CSIRO [13,14]. This concept describes PCL as: 'a loss of electrical conductivity in the active mass that is caused by the progressive expansion of the positive active-mass during cycling'. Hence, excessive gassing during charging could weaken the mechanical integrity of the backbone lead dioxide structure, and lead to isolation of active material, loss of electrical contact, and decrease in capacity.

3.4. Flooded-electrolyte battery

The flooded-electrolyte battery provided 1796 cycles under partial-state-of-charge conditions (Fig. 5). This corresponded to a total energy delivery of 61 962 Ah. Under traditional operating conditions, the battery is expected to deliver ~1200 cycles to 100% depth-of-discharge, or 138 000 Ah. This two-fold decrease in performance is attributed to acid stratification (see Section 3.1, above).

Traditionally, battery failure from acid stratification has been attributed to sulfation of the negative plates [2,4,7]. A full tear-down and analysis of the above battery revealed, however, that the negative plates were in good condition and that failure was related to the positive plates. The active material at the bottom of the positive plates was in a poor condition: it had undergone significant expansion, was very soft, lacked cohesion, and was poorly bonded to the grid. Total loss of the material from the plate was only prevented by the presence of separator envelopes.

The degradation of the positive active-material and related battery failure can be explained in terms of the uniform theory of PCL [13,14]. As described above, PCL occurs when the positive active-material undergoes a progressive increase in volume. This increase results in a loss of contact and, hence, electrical conductivity within the active mass. Further, PCL is exacerbated by increases in active-material utilization. Stratified batteries are known to experience higher active-material utilization at the bottom of the plates than at the top, due to the accumulation of strong acid in the lower regions as a result of inadequate charging. For the flooded-electrolyte battery, it is therefore suggested that the deterioration of the positive active-material at the bottom of the plates, and subsequent failure, is a consequence of increased active-material

utilization and the occurrence of PCL. We call this type of capacity loss: 'localized PCL'.

The relationship between electrolyte stratification and PCL has been examined previously in our laboratories [6]. It was observed that batteries operated under incomplete charging conditions failed prematurely, but neither the positive nor the negative plates contained appreciable levels of sulfate. In the absence of any obvious mode of failure (even though severe degradation of the active material at the bottom of plates was noted), the capacity loss was attributed to PCL in general. While the diagnosis was indeed appropriate, it was not recognized that the PCL had occurred at the bottom of the positive plates in a localized manner, rather than in a homogeneous fashion throughout the plates.

4. Conclusions

It has been shown that the energy available over the lifetime of gelled-electrolyte batteries can be increased by a factor of at least three through the use of advanced charging algorithms. Such strategies can also provide charging efficiencies as high as 99.5%. The method involves operating batteries under partial-state-of-charge conditions. This procedure acts to reduce capacity losses that are associated with corrosion and overcharge processes. Long-term operation under partial-state-of-charge conditions is possible with gelled-electrolyte technology because the batteries are not susceptible to acid stratification.

Flooded-electrolyte batteries have been shown to fail prematurely under partial-state-of-charge conditions. The poor performance has been attributed to acid stratification that results in increased acid concentration and, correspondingly, greater active-material utilization in the lower regions of the positive plates.

The losses in capacity that occur in lead/acid batteries due to both acid stratification and excessive overcharge can now be explained in terms of PCL. In particular, it has been concluded that PCL can occur in localized regions within the positive active-material: it does not necessarily occur uni-

formly throughout the plate. This phenomenon has been termed 'localized PCL'.

Finally, the partial-state-of-charge algorithm is being developed further to increase the energy available during each discharge. At present, the operational strategy offers only 30% of the available capacity of the battery before a recharge is required. Accordingly, SOC operating windows of 80 to 20% and 90 to 20% are being investigated. With such developments, up to 70% of the capacity would be available during a single discharge. This level of capacity delivery would meet most operating requirements. The affect of partial-state-of-charge cycling on long strings of gelled-electrolyte batteries is also being examined.

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