

## A COMPARISON OF FLOODED, GELLED AND ABSORPTIVE-SEPARATOR LEAD/ACID CELLS

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### Historical perspective

A requirement for lead/acid batteries in which the electrolyte is immobilised has existed for well over fifty years, and the demand for a totally-sealed, maintenance-free product for use in a wide range of market sectors has steadily increased since the 1960s.

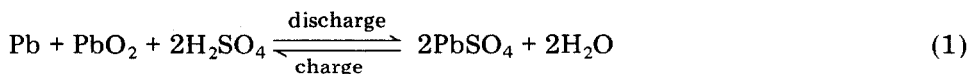
The original need to immobilize the electrolyte was purely for safety reasons, for example, in a battery to be used in an aircraft having aerobatic capabilities; this was achieved by absorbing the electrolyte in materials such as Kieselguhr. Such batteries found application in other market areas, but they, as in conventional flooded cells, required periodic maintenance in the form of water addition ('topping up').

Other developments to immobilize the electrolyte resulted in early models of the gelled-electrolyte cell. Subsequently, it was discovered that as a result of partial drying out of the gelled electrolyte, such a cell exhibited gas-recombination characteristics. This led (from the early 1960s) to the production and marketing of sealed gel lead/acid cells, predominantly with low ampere-hour capacities.

The first absorptive-separator, recombinant-electrolyte (RE) lead/acid cell was of the wound (cylindrical) form. This particular product appeared on the market during 1973. The continued search for a product having applications potential in market sectors not traditionally covered by sealed, gelled cells led to the manufacture and marketing of prismatic, absorptive-separator RE cells towards the end of the 1970s. The development of these types of sealed, maintenance-free lead/acid cells can be traced back to patents such as that held by the Gates Company under *U.S. Pat. No. 3862861* (filed 3 August, 1970). The use of unwoven, randomly orientated, short staple, micro-fibre diameter, borosilicate glass mats has made possible an almost 100% efficient gas-recombinant product. It may be of interest to note that before its value in battery engineering was discovered, microfibre glassmat material was first developed as a high efficiency filter in the World War II nuclear research program; later, it was introduced into bio-medical filter systems and found use as a lightweight and highly efficient insulator in space missions.

## Electrochemical aspects

In the lead/acid cell, the positive active material, negative active material, and the sulphuric acid electrolyte all participate in the electrochemical reactions that take place during the discharge and charge processes. The cell reaction can be expressed as:



In the traditional flooded cell, all the electrolyte (*i.e.*, that contained within plates and separators, between plates and separators, and both above and below the plate group) is utilized in the electrochemical reactions during a discharge/charge cycle. On the other hand, in both the gelled and absorptive separator cells, the only electrolyte available during a cycle is that contained within the plates themselves, plus that held in either the gell or the absorptive separator. Thus, to obtain the same capacity from cells containing equivalent weights of active material, gelled or absorptive-separator types will require an electrolyte of higher specific gravity (*s.g.*) than the flooded counterpart, in order to supply the requisite number of sulphate ions.

When considering the electrochemical efficiencies of positive and negative plates, it is found that the positive has an inferior charge acceptance (Fig. 1). Once a positive plate has attained  $\sim 70\%$  state-of-charge, oxygen will start to be evolved. By contrast, the negative plate has to be over 90% charged before hydrogen evolution commences. By taking advantage of this difference in the electrochemical efficiency of the respective positive and negative active materials during charging, cell design may be optimized so that little or no hydrogen is evolved and the recombination of oxygen with pure lead at the negative plate is close to 100%.

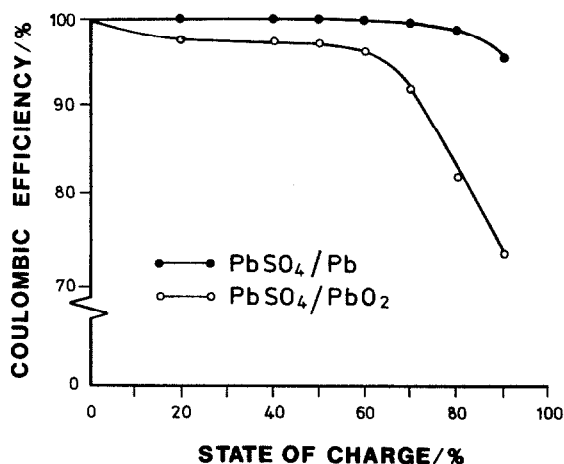
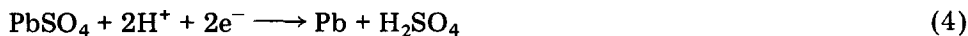


Fig. 1. Coulombic efficiency of lead and lead dioxide electrodes during charge.

Figure 2 indicates traditional distributions of active materials and electrolyte in flooded, gelled, and absorptive-separator standby-power cells. For ease of comparison, the combined active-material values have been kept to a constant amount. It can be seen that the distribution of active materials between vented flooded cells and sealed gell or absorptive-separator cells is quite different. In the traditional flooded cell, the cell capacity is negative limited, there generally being an excess of both positive active material and electrolyte. These design parameters lead to long service life and minimal voltage drop during discharge. However, such cells require regular topping-up maintenance. The sealed gelled and absorptive-separator cells have, historically, been designed with an excess of negative active material. With such a design, the negative plate never attains a fully charged state and, therefore, little if any hydrogen is produced during service life under normal conditions. Meanwhile, the oxygen released from the positive (*i.e.*, at  $\sim 70\%$  recharge) migrates to the negative, via cracks in the gelled electrolyte or voids in the absorptive separator, and there recombines with the highly active lead material.

During the charging of gelled or absorptive-separator cells, the following reactions take place at the negative plate:



Clearly, if the rate of oxygen production does not exceed the rate of reaction at the negative plate, then the oxygen will be recombined and no venting from the cell to atmosphere will occur.

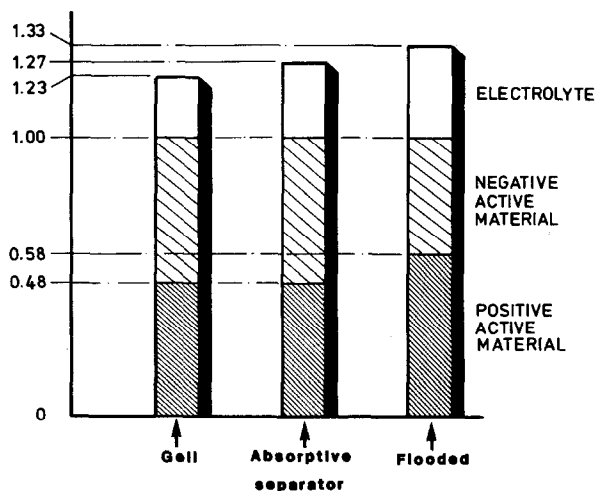


Fig. 2. Distribution of active materials and electrolyte for various types of lead/acid cells.

Continued development of RE cells has tended towards a reduction in the amount of excess negative active material, present designs generally have excess positive active material. These changes have not impaired recombination efficiency but have enhanced both cycling and life capabilities.

An important difference between the conventional flooded, and sealed maintenance-free products lies in the type of alloy used for grid manufacture. For sealed cells, the alloy must be antimony free in order to avoid the effect of antimony poisoning which causes the premature evolution of hydrogen gas from the surface of the negative plate. Thus, the grids are made from either lead-calcium or lead-calcium-tin alloys. Furthermore, because of the deleterious effects of trace metal contaminants on the performance and life of sealed, maintenance-free cells, it is considered obligatory to use oxide that has been processed from virgin pure lead.

### **Performance aspects**

Cell (battery) performance is extremely dependent on design, since applications can demand discharge periods from as little as micro-seconds to many hours. Examples at each end of the applications range are switch tripping (or closing) and 10 h uninterruptible power supplies. Further, the performance of a cell (battery) cannot be judged in total isolation. Rather, it must be taken in conjunction with the charger system, as well as with design aspects such as grid alloy composition and electrolyte s.g. Finally, and not unimportantly, the temperature at which the battery system is to operate must be taken into consideration. On the basis that equivalent comparisons are being made, the following performance generalizations are valid.

#### *Capacity*

At extended discharge rates to a given cut-off voltage, the conventional flooded cell yields the greatest capacity for a given combined weight of positive and negative active materials (on the assumption that the cell contains an excess of electrolyte). The ratios of performance at the 5 h discharge rate are 1.00, 0.77 and 0.68 for flooded, absorption separator, and gelled electrolyte cells, respectively.

In discharge situations having durations measured in minutes or seconds the order of performance is rather different. As the absorptive-separator cell has a very low internal resistance, the performance of this cell is superior to that of the flooded type and, in turn, the latter is superior to the gelled type.

#### *Service life*

The service life of flooded cells in the various market sectors is well known. In addition, the life expectancy of gelled-electrolyte products is well understood. On the other hand, since the absorptive-separator cell is a relative newcomer to the marketplace, the data base for making life expectancy predictions is naturally restricted. Nevertheless, experience is

showing a life of over three years in automotive applications, whereas ten-year lives in standby applications are now clearly attainable.

### Advantages of sealed versus flooded cells

Sealed lead/acid cells offer the following advantages over conventional, vented, flooded types:

(i) No maintenance in the form of topping up or the cleaning away of corrosion products caused by acid-spray emission is necessary.

(ii) Improved safety, as acid spills are not possible either during transit and installation or during battery life. Also, as no gases are evolved (under normal operating conditions), the risk of explosion is removed.

(iii) Sealed batteries can be installed, and operated equally well, in any position.

(iv) As a result of the above three features, sealed batteries become equipment- and office-compatible. This removes the requirement for special battery rooms.

(v) Because there is no need for either mud spaces or headroom, sealed batteries can be packaged into smaller volumes. This can increase significantly the volumetric energy density ( $\text{W h l}^{-1}$ ). For the same reasons, and also since the high-rate performance is superior due to the lower internal resistance, there is also an improvement in gravimetric energy density ( $\text{W h kg}^{-1}$ ).

(vi) In the case of absorptive-separator cells used in automotive starter applications, because of the improved high-rate performance (CCA at  $-18^\circ\text{C}$ ), it is possible to fit a smaller battery (compared with a conventional flooded battery of the same CCA ability). How far this advantage can be employed will, to some degree, be dependent upon reserve-capacity constraints.

### Disadvantages of sealed versus flooded cells

Sealed, maintenance-free cells have not yet been developed to the stage where they can be used in motive-power applications. The electrochemical and physical characteristics currently limit the use of these products to applications requiring relatively shallow discharges during their service life. The lower the depth-of-discharge, the greater the cycling ability, and *vice versa*.

### Chloride experience of absorptive-separator cells

Chloride currently produces three ranges of product using absorptive-separator technology. These are in the automotive field (*i.e.*, Torque Starter

range), in standby power applications (*i.e.*, Powersafe range), and in the specialised field of the miners' cap-lamp battery.

### Automotive

In view of field experience, the original designs of the Torque Starter automotive battery range have been modified. Present designs now have much more restricted passage in the common gas-space between cells. This latest form of battery now gives lives and warranty claims compatible with conventional, flooded, low-maintenance, automotive batteries.

Figures 3 and 4 demonstrate the superior cranking ability of absorptive-separator automotive batteries compared with conventional, flooded types. The data of Table 1 illustrate the superior charge-acceptance of absorptive-separator batteries, and Table 2 gives the recombination efficiency under both constant-potential and constant-current regimes.

### Standby power

Chloride produces a range of absorptive-separator cells specifically designed for standby power applications. These applications cover areas such as:

- (i) main, private, and mobile telephone exchanges and systems;
- (ii) uninterruptible power supplies;
- (iii) emergency lighting and alarm systems;
- (iv) engine starting for standby-power sets.

These products are currently made in monoblocs of 2, 4 and 6 V with rated capacities of between 77 and 304 A h (10 h rate at 20 °C). This range of cells, which has British Telecommunications approval, BC91, has performed exceedingly well in the field. Life projections of over ten years are now being confirmed.

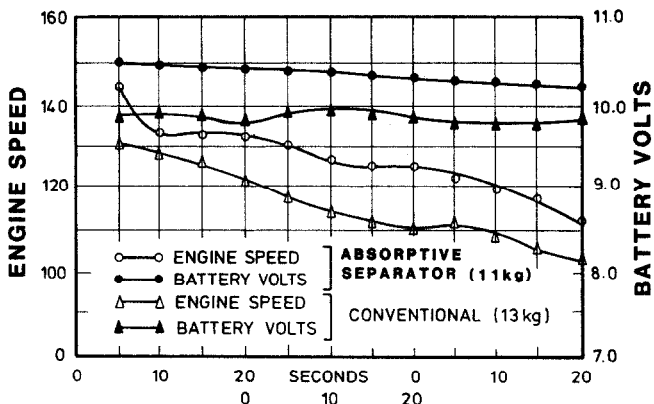


Fig. 3. Engine trials. Engine: 2 l OHC; starter: Nippon 0.9; oil: 10/20; transmission: auto; test: 3 × 20 s dead crank; temperature: -18 °C.

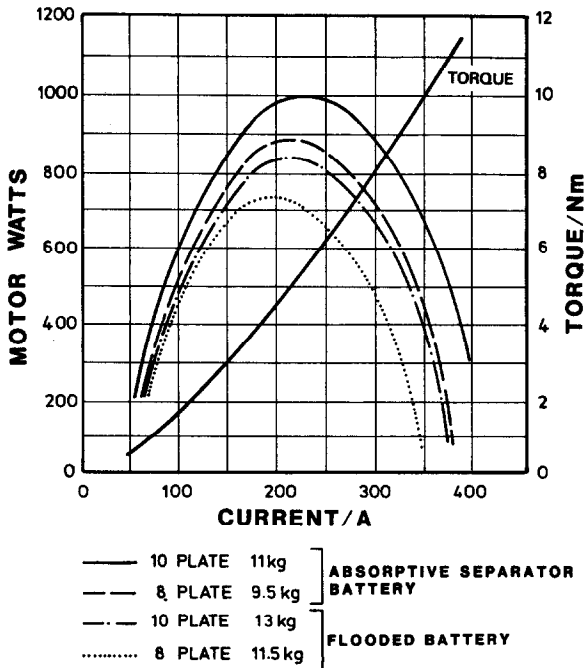


Fig. 4. Power curves.

TABLE 1

Charging currents of fully discharged RE and flooded batteries

Absorptive separator designs	Charge temp. (°C)	0	0	25	25
	Charge voltage (V)	14.2	15.4	14.2	15.4
	Charge current (A)				
	10 min	17.5	35.8	49.7	53.5
	15 min	17.5	33.3	41.0	53.5
	60 min	9.2	10.4	7.7	3.2
	5 h	1.1	0.5	0.2	0.3
Flooded designs	Charge temp. (°C)	0	0	25	25
	Charge voltage (V)	14.2	15.4	14.2	15.4
	Charge current (A)				
	10 min	11.0	20.0	31.0	50.0
	15 min	10.0	17.4	27.0	50.0
	60 min	5.8	8.2	10.0	9.7
	5 h	1.0	1.0	1.2	0.5

*Miners' cap-lamp*

The present model of this absorptive-separator cell, when operated at 60% depth-of-discharge, provides 800 cycles, *i.e.*, a three-year operating life. Although the traditional flooded product gave a service life of up to five

TABLE 2

Water losses and recombination efficiencies during continuous charge

Test schedule		Test time (h)			
		1000	3000	6000	12000
Charge at 14.5 V	Average current (A)	0.39	0.35	0.34	0.34
	Weight loss (g)	11	15	16	18
	Recombination efficiency (%)	98.6	99.3	99.6	99.8
Charge at 2 A	Weight loss (g)	120	145	150	153
	Recombination efficiency (%)	97.0	98.8	99.4	99.7

years, the cost of the shorter product life is more than offset by the savings arising from having a totally maintenance-free product.

### Future prospects

The market for sealed, maintenance-free products shows continual growth. In addition to applications already mentioned, other areas include consumer durables, and commercial and industrial uses, as demonstrated in Table 3. Clearly, the prospects are that the sealed, maintenance-free battery will have an important contribution to make for the foreseeable future.

TABLE 3

Markets for sealed lead/acid batteries

#### *Consumer durables*

Portable power tools

Video cameras

Portable telephones/walkie-talkies

Cassette recorders

Toys

Leisure equipment -- sport, boating, etc.

#### *Commercial*

Electronic cash tills

Security and alarm systems

#### *Industrial*

Automatic guided vehicles using opportunity recharging techniques.