

Maintenance-free motive-power cells using gas-recombination technology

J. M. Stevenson, F. Wilson* and J. I. Dyson

CMP Batteries Ltd., P.O. Box 1, Salford Road, Over Hulton, Bolton BL5 1DD (U.K.)

Abstract

This paper summarizes the maintenance-free product development programme of CMP Batteries Ltd. (U.K.). This programme started in 1984 and is still under continual development and improvement. Its evolution together with the product's concept and technology are discussed and some of the initial field experience data are presented.

Motive-power technology — general principles

Two motive-power technologies for all maintenance-free (MF) products are currently on the market. These are gelled-electrolyte (silica gel) and absorbed-electrolyte (absorptive glass micro-fibre mat, AGM). Both make claims in the use of gas recombination.

Considering CMP Batteries Ltd.'s (now part of the CEAc Group, France) past links with the Chloride Group, it is not surprising that CMP are following the absorbed-electrolyte approach. A general description of the MF product technology is given in Table 1. The technology is explained in more detail in the following sections.

Effect of alloy

Standard alloys used in the manufacture of motive-power cells tend to contain relatively high levels of antimony.

In motive-power applications, a recharge to gassing voltages generally occurs every cycle. This is necessary to maintain a healthy cell and capacity in service, but results in water losses and the need for regular maintenance. As antimonial cells 'age', the processes of corrosion of positive spines and contamination of negative plates increasingly take place. The cell voltage falls, resulting in progressively more over-charge on a standard charge and, hence, increased maintenance as cycle-life progresses.

By changing to calcium alloys, the cell voltages become 'stable' and it would be expected that regular maintenance intervals would be maintained. Therefore, the product would not become 'maintenance free', just by changing the alloy.

*Author to whom correspondence should be addressed.

TABLE 1

CMP technology for motive-power batteries using gas recombination

Spines and negative castings	lead-tin-calcium alloy
Pillars and burning strip	lead-tin-selenium alloy
Separation	AGM, 200 g m ⁻² , 1.2 mm thick
Vent	rubber cap and retaining washer at approx. 3 psi pressure; non-return valve
Top packing	expanded polystyrene, to reduce explosion hazard

For a complete MF cell, the amount of recharge to limit water loss and keep the cell healthy almost certainly results in under-charging, rather than over-charging. The basic design of CMP's MF product —AGM (to give gas recombination), pressure vent (reduces water loss and atmospheric oxidation of the negative plate), dedicated controlled charging (to limit over-charging)— produces a difference in operation that far outweighs any alloy differences. Although, for reasons explained, the use of calcium is still an important part of the MF product design.

Effect of charger and pressure vent

A critical step in achieving the MF product is the development of a dedicated charger. The CMP charger has voltage control that reduces gassing levels with a carefully regulated, constant-current, charging period to ensure limited over-charge up to 110%. To limit water loss to an absolute minimum, a pressure vent is also included. Even with calcium alloys, a dedicated charger and a pressure vent, however, the design is still prone to drying out and premature failure due to water loss. Obviously, the period to drying out is considerably longer than if a standard flooded product was used.

Gas recombination using AGM

The depth-of-discharge (DOD) will control the cycle-life of a lead/acid product, flooded or MF. The recharge of the product will have, however, a greater bearing on the ultimate 'life' in the MF application, as previously explained. Water loss must be seen as the major failure mode of the MF product. The objective, therefore, has been to extend the period to 'drying-out'. By using AGM, a gas-recombination mode is introduced. In the CMP design, this is when the product goes into the 'starved' electrolyte condition. In adopting the gas-recombination technology, the useful life of the cell/battery is prolonged by extending the drying out period of the flooded design. Over-charge in the gas-recombination phase of operation results in reduced water loss. Even so, the AGM design of motive-power cell will still ultimately fail due to water loss, or the effects brought about by water loss (loss of capacity and positive spine corrosion).

CMP Batteries are currently manufacturing sealed lead/acid motive-power cells. These cells are being evaluated in the market place in, mainly, selected applications. The package is battery, charger, and a recommended application. A regime of up to 60% DOD and 12–14 h recharge is suggested.

Battery design details

The following summarizes the design and manufacturing details.

- Positive plate, employs square carrots, square-form gauntlets and bottom bars. Careful control of weights is ensured.
- Negative plates are pasted to weight giving good thickness control.
- Plates are tank-formed to optimize initial capacities.
- Assembly by individual plate separator wrap, element separator wrap, polythene sheet and pack sizing.
- Elements are burned up in a universal jig and boxed by ram. Head packing is inserted prior to lid sealing and all cells are leak tested under water.
- Electrolyte filling by vacuum-pulsing techniques with weight control on acid.
- A conditioning cycle and capacity check on all cells before shipment to the customer.
- Cells are produced with bolted connectors and pillar caps to offer a 'dead top' product.
- Range of cells presently being assessed is 200 mm DIN, 5 plate to 13 plate in 370, 460, 500, 605 and 750 mm heights.

How did CMP arrive at this design? The approach has been practical rather than theoretical, but theory has not been entirely neglected.

History of battery development

Battery design

During 1985, CMP was requested to test MF batteries that were intended for operation in a special truck for exhibition purposes. The battery was a 24-V unit and of a non-standard height. The details of the construction were: (i) 2.3 mm diameter spine, 24 tube, 6.1 mm internal diameter tube; (ii) lead-tin-calcium alloy; (iii) AGM 200 g m⁻², 1.2 mm plate and element wrap; (iv) screw-in vent housing cap-retaining washer, 2–3 psi venting pressure. This product was, in effect, modified 'Classic 25' (DIN) CMP technology and is referred to as the DIN Mark 1 (Table 2).

Initially, six batteries were made and put into service: three with customers and three internally within CMP. Two of these batteries are still in use. A further 10 batteries were placed with customers between Aug. and Dec., 1987. Three of these batteries were operated in the U.K., the others elsewhere. Experience with this experimental product was favourable and the indications were that a two-year life was to be expected.

TABLE 2

Design details of DIN Mark 1 battery

Single cell, not a range of cells	
9-plate box dimensions	
length	83 mm
width	198 mm
Height	non-standard, 260 mm
Positives	24 tube/6.1 mm ID/6.9 mm OD/162 mm height
Negatives	
inter	3.7 mm plate thickness
end	2.2 mm plate thickness
Separator	200 g m ⁻² /AGM, nominal 1.2 mm
Capacity	140 A h/14.4 g per A h nominal positive active-material utilization
11-plate assembly	

The low-cost, low-risk route to product/scale-of-manufacture of a MF cell was via modification of existing components. To improve the contact of separators to the positive plate and equalize the compression, a square-tube positive plate was designed. Gauntlets were obtained to fit (8.1 × 8.1 mm) and a new bottom-bar seal was used. Using existing negative grid moulds and the modified positive spine mould, plates were produced with lead-tin-calcium alloy spines and castings. The capacity of these DIN size cells (referred to as DIN Mark 2, Table 3) was between 90–95% of the corresponding 'Classic' (DIN) range cells. Between 1988–1989, approximately 1000 cells were placed with customers, for field experience. The mode of assembly of these components into cells is given above, but with the addition of solid plate supports.

The limitations of this approach were recognized and the capacity of the cell was increased by further modification of the positive plate. Coincidental with this, new negative inter- and end-plates were commissioned to match the longer positive plates (this product is referred to as DIN Mark 3, Table 4). This development was seen to be an intermediate solution to the capacity shortfall, as the positive active-material utilization was still poor.

TABLE 3

Design details of DIN Mark 2 battery

Range of cells; 5–13 plate; 5 plate lengths	
9-plate cell	370 mm height
Positives	19 tube/8.1 × 8.1 mm internal/248 mm height
Negatives	
inter	5.3 mm plate thickness
end	2.65 mm plate thickness
Separator	200 g m ⁻² /AGM, nominal 1.2 mm
Capacity	200 A h/18.1 g per A h nominal positive active-material utilization

TABLE 4

Design details of DIN Mark 3 battery

Range of cells; 5-13 plate; 5 plate lengths	
9-plate cell	370 mm height
Positives	19 tube/8.1 × 8.1 mm internal/271.5 mm height
Negatives	
inter	5.3 mm plate thickness
end	2.65 mm plate thickness
Separator	200 g m ⁻² /AGM, nominal 1.2 mm
Capacity	220 A h/20.0 g per A h nominal positive active-material utilization

A programme is now in hand to optimize the positive plate by 'normalizing' the positive active material to current standard utilization values. The tube profile has been fixed as rectangular, maintaining the same tube pitching, and adopting a thinner plate section.

Battery charging

Initial charging profiles were developed during bench-testing of prototype cells. These profiles became the basis for the subsequent charger modifications and dedicated MF chargers. The principle assumes that between 105 and 110% input over previous output is necessary to maintain performance without excessive water loss. The charging regime is divided into three stages.

- (i) current limit to battery voltage maximum;
- (ii) change to timed period of constant-potential charge with current reducing;
- (iii) final stage of limited constant-current charge.

Stages (i) and (ii) have the objective of returning near to 100% of the previous output within the shortest time period and with minimum water loss. The time stage (iii) will return a fixed over-charge per cycle with limited theoretical water loss.

The charging profiles have optimum efficiency at 60% DOD: at DODs greater than 60%, under-charging is observed; at DODs less than 60% over-charging is observed (Table 5). Thus, the recommended use of the cells is up to 60% DOD.

Operational information

In this paper only the initial Mark 1 prototype batteries experience is reported. The results of field trials are given in Table 6. It can be seen that the Mark 1 charger profile has been modified to produce over-charge predominantly in Stage 3.

The water loss results over the majority of time in use are given in Table 7.

Although the application of the batteries has been light usage, the 'life' with customers has been very encouraging. Of special interest is the water-

TABLE 5

Typical results of return of charge (Mark 2 charger)

<i>80% DOD</i>			
Discharge 116 A h = 83% DOD			
Recharge 120.6 A h = 4% excess			
	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	30 → 21.5	21.5 → 0.7	1.8
Voltage (V)	20.5 → 27.9	27.9 → 28.2	29.5 → 31.0
Time above gassing voltage (min)	0	0	149
Time (min)	190	482	149 (821)
<i>50% DOD</i>			
Discharge 70 A h = 50% DOD			
Recharge 75.6 A h = 8% excess			
	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	29.5 → 21.6	21.6 → 0.4	1.8
Voltage (V)	26.0 → 27.9	27.9 → 28.2	30.0 → 32.0
Time above gassing voltage (min)	0	0	149
Time (min)	101	481	149 (731)
<i>20% DOD</i>			
Discharge 28 A h = 20% DOD			
Recharge 34.7 A h = 24% excess			
	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	28.4 → 21.6	21.6 → 0.3	1.8
Voltage (V)	26.4 → 27.9	27.9 → 28.2	31.4 → 32.5
Time above gassing voltage (min)	0	0	149
Time (min)	32	481	149 (662)

loss profile for the Field Trial No. 1 dust kart over the closely monitored period (Table 7). It seems that the winter periods tend to produce relatively low water loss, whilst the summer periods are responsible for the majority of the losses. It is hardly likely to be due to evaporative losses, but may be due to the greater DOD during the winter and the subsequent fall in excess charging.

The Field Trial No. 2 application appears to have a relatively uniform pattern of water loss and the onset of a steady recombination state is indicated between 2.5 to 4 years. This may well indicate the low usage of this truck. Field Trial No. 3 shows a similar water loss over the initial 12-month period, but thereafter, practically no increase. This again may well be due to the low usage of this truck.

Problems in service

The examined cells have exhibited some breakdown of the AGM material. The points of maximum compression are severely weakened.

TABLE 6

Field trials on Mark 1 prototype motive-power batteries

Field Trial No 1

Typical duty daily, collection of waste from bins located on a sea front. Vehicle returns to depot at lunch-time for opportunity charging, further duty in the afternoon. Seasonal variation, wet sand carried and lights operated during winter months

Morning

Discharge 30.7 A h = 22% DOD

Recharge 9.7 A h = no excess

	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	26.9	2.3 → 1.1	–
Voltage (V)	28.7 → 30.0	26.4	–
Time above gassing voltage (min)	17	–	–
Time (min)	17	52	– (69)

Evening

Discharge 12.4 A h⁺ = 8.8% DOD

21.0 A h = 23.8% DOD

Recharge 36.5 A h = 9.3% excess

	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	26.9	2.3 → 1.1	0.5
Voltage (V)	29.3 → 30.0	26.3 → 28.5	27.7
Time above gassing voltage (min)	13	18	–
Time (min)	13	795	23 (821)

Field Trial No. 2

Pallet truck usage, daily but variable, dependent upon deliveries

Typical duty

Discharge 53.4 A h = 38.0% DOD

Recharge 60.1 A h = 9.3% excess

	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	27.0	2.7 → 1.1	0.3
Voltage (V)	28.1 → 29.2	26.8 → 29.8	27.0
Time above gassing voltage (min)	49	268	–
Time (min)	71	749	49 (869)

Field Trial No. 3

Pallet truck usage, variable both when and how, but light

Duty measured

Discharge 15.2 A h = 10.9% DOD

Recharge 20.5 A h = 34.9% excess

	Stage (i)	Stage (ii)	Stage (iii)
Current (A)	22.2	2.3 → 0.8	0.4
Voltage (V)	27.5 → 30.0	27.2 → 31.0	28.1
Time above gassing voltage (min)	10	595	–
Time (min)	12	778	69 (859)

TABLE 7

Water loss data

<i>Field Trial No. 1 (Oct. 1985-Mar. 1990)</i>														
Time in use (months)	1	2	3	4	6	7	9	12	14	16	18	25	33	54
Average water loss (g)	-	-	-	-	4	15	55	74	77	89	93	152	150	400
<i>Field Trial No. 2 (Nov. 1985-Feb. 1990)</i>														
Time in use (months)	1	2	3	5	8	10	12	15	17	24	30	51	169	
Average water loss (g)	8	19	22	33	40	47	50	52	63	78	156			
<i>Field Trial No. 3 (Nov. 1985-June 1988)</i>														
Time in use (months)	3	5	7	10	12	14	19	25	32					
Average water loss (g)	13	21	32	42	51	55	63	68	62					

The corrosion of the calcium positive spines has been uniform and with a 2.3 mm diameter has not caused problems. Of interest, there has been an increased corrosion of the positive top frames, but not the positive lugs.

Failure has tended to be more of a mechanical nature, such as broken pillars due to vibration effect, although shorts have also been observed. The latter tend to be observed at points of weakness rather than due to 'leading through' in the body of the separator.

Further improvements

The present product can be improved by further design refinements to offer a VRLA cell with recombination characteristics. At present, we are uncertain of the implications on life.

Without opting for the 'starved' gas-recombination application, improvements can be made to the AGM material. These would concentrate on the 'wet-strength' of the material and the use of hydrophobic fibres/binders to enable, or encourage, the recombination characteristics of 'flooded' designs.

The greatest problem area is seen to be the battery management: the correlation of 'charge in' over 'charge out' has to be closely monitored and controlled. Without the ability to recombine, the problem of charging will always tend to be over-charge and water loss, or under-charge and capacity loss. It is obvious that the way forward is to evolve the product into a recombination design and improve the battery management by charger development.