High gelled-electrolyte quality with polyacrylamide polymer: limitation of cycle-life through water loss

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Abstract

A gelled-electrolyte battery, with lead–calcium grids and over-pressure valves, has to be well designed, accurately manufactured, and charged with an optimized charging system in order to obtain a reasonable lifetime. Besides this detail know-how, which is necessary to reach the present state-of-the-art, the following two factors are critical to performance: (i) gel quality and distribution; (ii) water loss and cycle-life. The gel stiffness as well as the distribution and the correct acid concentration, can be optimally adjusted by the addition of a polyacrylamide-emulsion polymer and a reduction in the silica component. A well monitored and consistent gel quality is important in achieving equal behaviour between all cells in the battery. Water-loss tests have shown that different charging methods result in different lifetimes, from 550 to 2000 cycles.

Introduction

The performance of maintenance-free traction batteries is not determined solely by the gel or glass-fibre technique, the lead–calcium alloy, or the charging method; there are many more critical features in design, manufacturing and application (Table 1). Each single parameter within this complex system can cause early failure of the battery. Furthermore, it is very difficult, and sometimes impossible, to clearly detect the cause of battery failure. Only accurate monitoring and evaluation of a reasonable number of batteries over their lifetime can help to improve the performance and efficiency of maintenance-free batteries. This paper deals with two critical factors:

(i) minimization of the manufacturing tolerances by using polyacrylamide-emulsion polymer as a gel component;

(ii) minimization of water-loss problems through better charging methods.

Polyacrylamide polymer

A well monitored and consistent gel quality is, together with other parameters, necessary for all the cells in the battery to exhibit identical electrical behaviour. From an analysis of the filling mechanism in general and determination of the optimum physical and chemical characteristics of

TABLE 1

Critical parameters relevant to the performance of gelled-electrolyte traction batteries

Design	Manufacture	Application
Mass of positive and negative active material and amount of acid per A h	Grid casting and grain structure	Voltage behaviour of cells within battery
Geometry of separation	Positive plate quality and tolerances	Charging method
Design of manufacturing conditions for a good interaction between the positive grid and the active material	Lug welding	Deepness of discharge cycles
Gel quality, filling principle	Terminal casting	Danger of mixing up chargers for wet and dry batteries (coded plugs)
Grid, lug and terminal alloy	Valve quality	Temperature effects at a higher cycle-life
Cell tightness	Tolerances in gel preparation	
Valve opening pressure and hysteresis	Accuracy of filling process	

the gel, it is concluded that the following three factors are important for the final battery quality: (i) correct amount of acid between the plates; (ii) good gel distribution; (iii) high gel stiffness.

The filling mechanism proceeds via the following sequence.

Step 1. The liquid gelled electrolyte is pumped on to the plates in the cell.

Step 2. The liquid gelled electrolyte spreads between the plates at acceptable speed and with limited forces of inertia that affect the position of the plates. There is a speed limit depending on the type of battery.

Step 3. Some liquid is separated from the liquid gel and penetrates into the small pores (filtration effect). This concentrates the gel components between the plates.

Step 4. Gas escapes from the plates and from the inter-plate space, flowing against the direction of the liquid.

Step 5. The gel solidifies to such a degree that it becomes insensitive to shocks, even at low acid densities (discharged battery), and holds all the absorbed liquid.

There is considerable movement and action taking place within the cell during the filling process. The latter requires energy and time, but the mechanical energy available for distribution of the gelled electrolyte is very limited. There is only a slight pressure impact as well as a small difference in potential energy between the top of the cell and the final resting place of the gel. The main factors hindering these actions are the forces of inertia and the viscosity of the liquid. Therefore, it is necessary to have a gel that, for a reasonable time, offers a very low viscosity, but later a high and constant stiffness.

The solution to the above problem is to use an acid-resistant organic polymer, with long chains and limited active groups within the chain, that acts as a pumpable liquid that polymerizes in the final gelled electrolyte with a certain time lag. This criterion can be realized by means of a polyacryl-amide-emulsion polymer (PEP) with a molecular weight of about 1 million, or more. After inverting the emulsion, the polymer originally included in the water phase of the water-in-oil emulsion requires a given time to expand until the active groups of the polymer react with the silica, or with other polymer molecules, thus forming the gel. Because of this time lag in the reaction, the characteristic of the viscosity increase is completely different from that of a gel with pure silica.

Figure 1 shows measurements of gel development with different recipes. The gel with PEP requires only 55 to 60 wt.% gel generating components, but maintains much lower viscosities during the first 200 s after filling. Later on, however, it is much stiffer and not thixotropic compared with a gel containing silica only. The latter is thixotropic and can become fluid again by shocks to a discharged battery [1–3].

During the development of maintenance-free Dryflex® batteries with PEP in the gel other positive effects of PEP were observed. In summary, use of PEP results in the following five advantages.
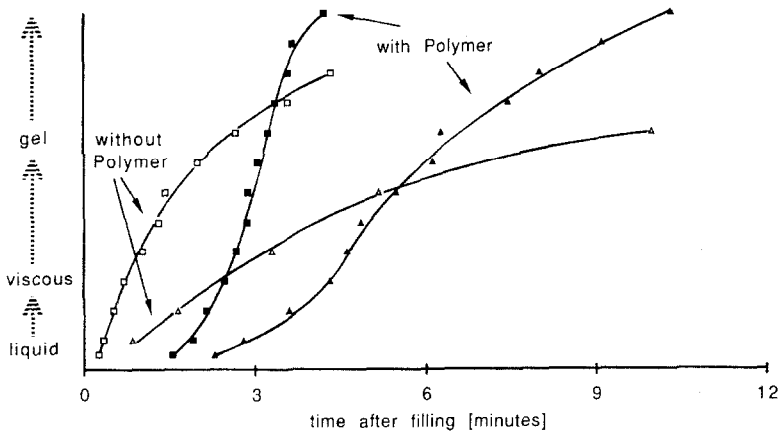
Fig. 1. Fig. 1. Gel development after introduction into the cell; different recipes, with and without polymer.

1. The amount of silica can be reduced by about 40 wt.% when using only a very small quantity of polyacrylamide as additive.
Effect: about 3% more acid in the cell.
2. The prepared liquids for the mixture, including the total quantity of acid required and the mixture itself, have a very low viscosity (about 3.5×10^{-3} Pas). Thus, cells with dry and fully-charged plates can be filled without any problems.
Effect: very low manufacturing tolerances in the form of fluctuations in the final acid concentration and variations in the amount of acid between the plates.
3. The final cross-link of the emulsion polymer with the silica occurs with a delay, because of the inverting time of the emulsion. Therefore, the viscosity of the liquid acid during the filling and degassing processes is extremely low.
Effect: fast distribution of the liquid acid, speedy degassing of the cell, very good filling results, reduced tolerances.
4. During the start-up charge for gel cells with silica only, there is usually a considerable liquid separation on top of the plates. This has to be sucked off. With PEP this adverse effect is reduced by more than 80%.
Effect: after filling the cell with gel, no separated liquid has be be removed. The manufacturing tolerances can again be kept very low.
5. The stiffness of the final gel in a new cell is about 2 to 3 times higher than that without PEP. The gel is not thixotropic.
Effect: with PEP, it is impossible for the gel to move between the plates under shock conditions. This avoids problems that are otherwise experienced when a PEP-free battery is discharged, i.e., low acid concentration and reduction in stiffness of the silica gel.

Limitation of cycle-life through water loss

Reduction in cell life brought about by the loss of water can occur through: (i) use of an incorrect charger; (ii) leakages of the cells; (iii) an inadequate charging method. The first possibility originates from problems in organization of the systems, the second from inaccuracies in the cell manufacture or failure of the over-pressure valve. These difficulties are never a problem of the dry system itself. They can be easily detected by weighing the cells. The difference in the weight after production can be compared with the water loss that is acceptable during normal battery life.

The main questions connected with water loss are:

Is the correct charging method being used?

Is the battery life being limited by water loss or some other factor?

To investigate these questions, long-term water-loss tests were conducted on 24 V, 5 PzS 500 A h batteries. Assuming that a very low overcharge current does not produce serious corrosion at the positive grid, the water loss was created without cycling the batteries (Fig. 2). A capacity test was carried out periodically (Fig. 3). After 12 to 15% water loss (related to the amount of water in the acid) the capacity reduced dramatically to below 60%. Opening and inspection of the cells showed that this fall in capacity was not caused by grid corrosion and, therefore, was attributed to the loss in water.

The measurement of water loss during the intermediate capacity tests and comparison between the total water loss in these special tests and that experienced during normal cycling and with different charging methods enabled the effect of water loss on cell cycle-life to be determined. Figure 4 shows that, with a simple IUIa charger (0.8 C/5, 2.4 V, 0.08 C/5 for 3 h), the cycle-life is restricted because of water loss to 550 to 700 cycles. By contrast, the DETA charging method [4–6] minimizes the water loss and generates 65
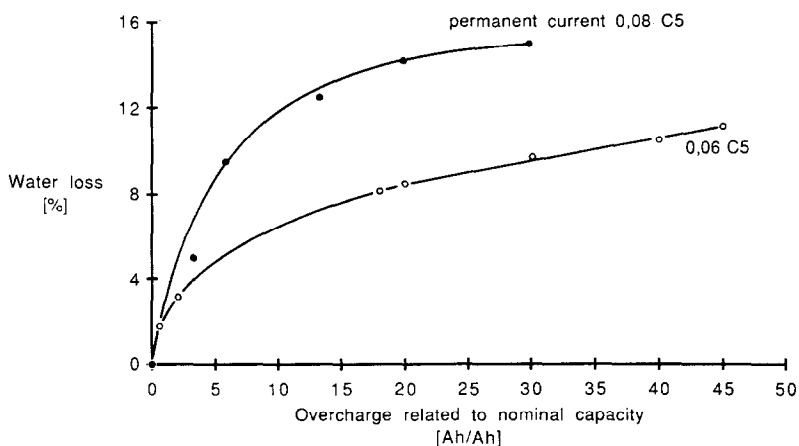

Fig. 2. Water loss of a gelled-electrolyte battery during permanent overcharge at different currents.
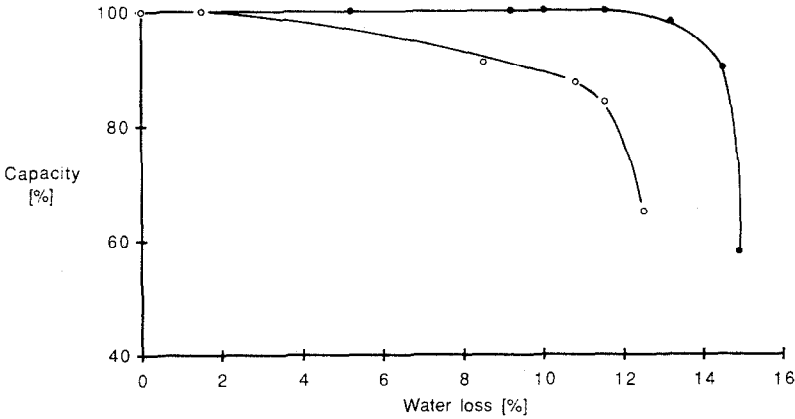
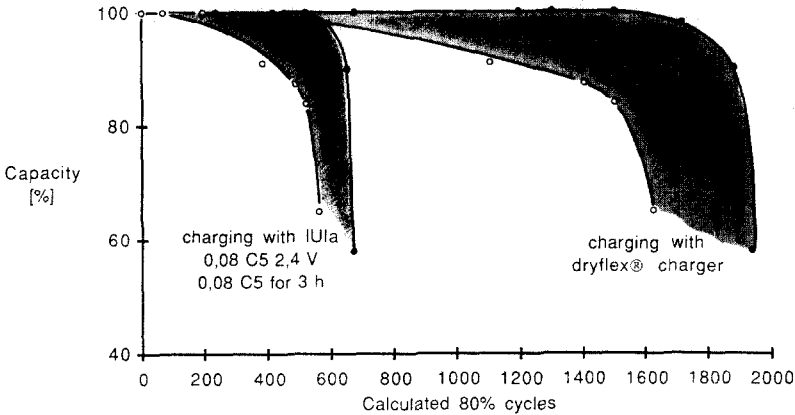Fig. 3. Capacity drop in gelled-electrolyte cells because of water loss.

Fig. 4. Calculated cycle-life (determined by water loss) with IUIa and Dryflex® charging method.

to 75% less water by using a pause-charging method in the second charging phase. This charging method (see below) gives the battery more time for recombination. The cycle-life limitation because of water loss for the DETA Dryflex® charging method therefore lies somewhere between 1500 to 2000 cycles. With this performance, other life-limiting parameters, e.g., manufacturing tolerances, grid corrosion etc., are more important.

There are two critical areas within a IUIa charging curve (see Fig. 5) where the valves of the cells open and gas is emitted: one shortly before 2.4 V is reached and the other during the Ia region. To minimize water loss a DETA Dryflex® charging method has been developed. In this, the 2.4 V is reduced to 2.35 V and pauses of different length are installed in the Ia schedule in order to give the gas more time to recombine and to reduce the voltage of the cell, see Fig. 6. The effect is less water loss and better electrochemical efficiency.
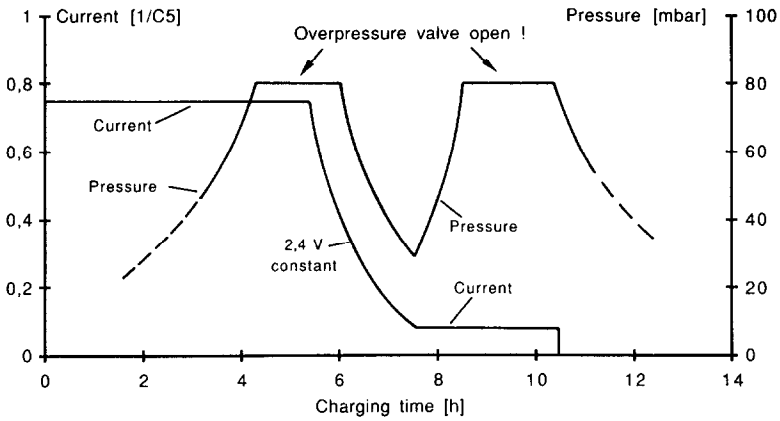
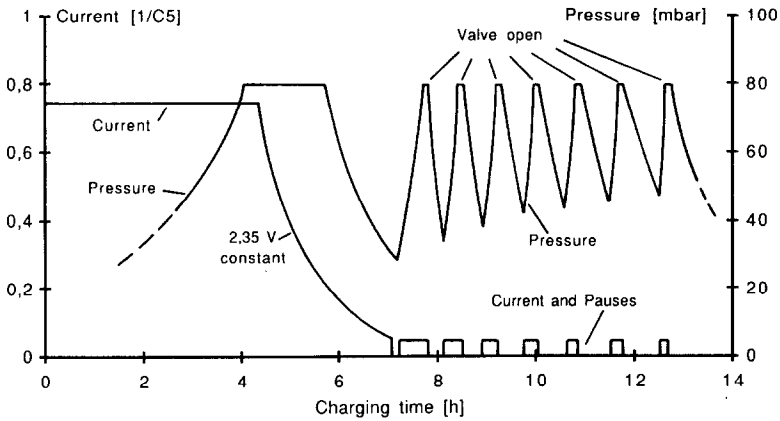Fig. 5. Critical areas within the IUIa charging method for gelled-electrolyte cells.

Fig. 6. Optimized charging method, with minimum water loss, for maintenance-free Dryflex® batteries.

References

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