Journal of Power Sources 59 (1996) 119–121

External recombination system for vented lead/acid batteries used in float service

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Received 13 November 1995; accepted 12 December 1995

Abstract

There is a major demand for maintenance-free lead/acid batteries, i.e. batteries that do not require periodic additions of water. A catalyst-based system is described, the Aqua-Gen System, that externally recombines the oxygen and hydrogen evolved during battery charging to water. Vented (flooded-electrolyte) batteries fitted with this device and operated under normal conditions, do not require topping-up with water during the course of their lifetimes. Other benefits include the avoidance of risks and mistakes in battery operation, simplified inspection of the battery, and cost savings.

Keywords: Lead/acid batteries; Gas recombination; Palladium; Cycle life; Water maintenance; Catalysts

1. Introduction

One of the long-standing main objectives of battery manufacturers has been to extend the service interval for lead/acid and nickel–cadmium batteries, or to make the batteries completely maintenance-free, without any adverse effects on performance. The author's company addressed this problem successfully in the early 1970s by developing an external solution: the Aqua-Gen System (AGS).

To date, more than 100 000 stationary cells, both industrial lead/acid and FNC (fibre-structured nickel–cadmium) batteries with capacities of up to 3000 Ah, have been equipped with Aqua-Gen plugs. This has converted all the types of vented batteries into maintenance-free units. The development of valve-regulated lead/acid (VRLA) technology in the 1980s was an important step towards maintenance-free operation. This approach is based on the principle of internal recombination, whereas AGS technology is based on the external recombination of hydrogen and oxygen gases.

In January 1995 at the INTELEC Conference in The Hague, The Netherlands, Feder presented the latest results from the most extensive study of battery failure that has been undertaken to date. This study was performed on 24 000 VRLA cells from nine major brands. In the present author's view, Feder's results underline the necessity to establish, also in Asia, a far more reliable, safer and less costly alternative to the VRLA battery by using external recombination, especially for batteries with high capacities.

0378-7753/96/$15.00
SSDI 0378-7753(95)02311-9

The following observations were made in the Feder investigation:

- In 60 to 80% of the cells, premature failure occurred at ages that were only a fraction of the intended design lives. This was despite the fact that the cells had been operated in benign environments of Telecom central offices and environmental-controlled UPS installations
- The cell failure rates were more than 41% by the sixth year. For battery strings, the failure rate was 50% at four years of operation
- Given the complexity of VRLA technology, the exact cause of these 'generic' failures has still to be determined

Other experience has shown that cells equipped with AGSs deliver maintenance-free service over the total length of their traditional lifetime under normal, European conditions, i.e. 10 to 12 years for flat-plate batteries; > 15 years for tubular-plate batteries, and ≫ 15 years for Planté-type batteries. An example of such service is given in Table 1. Given such performance, this paper describes how the Aqua-Gen plug is designed and how it functions under various operating conditions.

2. Aqua-Gen recombination

Energy is needed to break down substances into their individual constituents. This process always takes place when a fully charged battery is constantly charged further to com-

Table 1
An example of how the Aqua-Gen System can reduce the water-maintenance requirements of vented lead/acid batteries

a) *Basis for the calculation of water loss*
Stand-by operation (constant float-charge conditions of 2.23 V/cell)
Electrolyte temperature of 20 °C
Assumed float-charge current of 15 to 20 mA per 100 Ah of nominal capacity (average value used for calculations: 17.5 mA/100 Ah)
During overcharge, 1 Ah decomposes 0.336 mg (ml) of water into 0.418 l hydrogen and 0.209 l oxygen
b) *Example*
Tubular-plate cell (type 7 OPzS 490) with an electrolyte volume of approximately 1.1 l between 'max' and 'min' levels
c) *Calculation without AGS*
Decomposition of water: 0.69 ml/day
Electrolyte level drops from 'max' to 'min' level after ~1609 days (4.5 years)
Water refilling required after ~4 years (and any other negative consequences)
d) *Calculation with AGS*
Owing to the efficiency of the recombination system, the cell is maintenance-free over its entire service-life

pensate for self-discharge. It should be noted that, in Europe, constant-voltage charging at 2.23 V/cell ('float' charging) has become a standard for vented lead/acid batteries.

Various levels of float current can occur. These depend on the voltage, electrolyte temperature and capacity of the battery cells. The currents compensate for self-discharge and for water electrolysis, whereby heat is generated. The larger part of the current is responsible for water decomposition. In general, 1 g of water will be decomposed by 3 Ah of overcharging energy.

A great deal has been done to lower the float-charge currents of lead/acid cells by reducing the content of antimony in the grids. In HOPPECKE DIN-type cells (1.7 wt.%Sb), for example, the reserve of electrolyte solution is sufficient for a period of about five years without the need for topping-up with water. This performance applies to European environmental conditions with an average electrolyte temperature of 20 °C and a relative humidity of 60%. In dry, hot climates, the cells suffer an additional loss of water by evaporation, but only in small amounts.

The AGS is designed as a device for the catalytic recombination of hydrogen and oxygen gases that evolve as a result of the electrolysis of electrolyte water during the float charging of lead/acid batteries (see Fig. 1). At a hydrogen concentration of 4% or more, the gases that escape from the cells during the float charge will form an inflammable and, hence, explosive gas mixture. As a protection against possible dangers, appropriate regulations for the ventilation of battery rooms exist, both for the producers and for the operators of stationary battery systems. The costs of ventilation facilities can be reduced by 50% (according to *German Standard DIN VDE* 0510, part 2) when using Aqua-Gen catalysts on vented lead/acid batteries or when using VRLA batteries. The AGS recombines gas mixtures even under non-stoichiometric conditions because the device uses oxygen from the outside air.

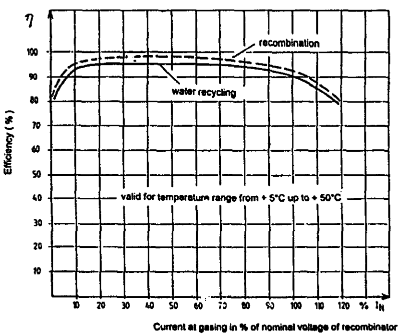

Fig. 1. Efficiency of Aqua-Gen recombinators in permanent use.

In VRLA batteries (both AGM and gelled-electrolyte types), only oxygen is reduced at the lead (negative) electrode. This reaction is frequently described as 'gas recombination', but the term is not completely accurate because there is no 'recombination' reaction for the hydrogen. The hydrogen evolved in VRLA batteries does not react, and can thus present some danger. In addition, a certain loss of water will occur. Therefore, the working parameters must be optimized to give an oxygen-reduction efficiency of 94 to 98%. Unlike vented lead/acid cells, both types of VRLA battery have no surplus volume of electrolyte solution. Gelled-electrolyte cells require up to two years to increase their oxygen-reduction efficiency from about 75 to 94%, or more. This causes a corresponding decrease in cell lifetime.

Attention must also be drawn to the significant rise in the float current due to the oxygen reaction at decreasing electrolyte volumes. The oxygen-reduction reaction generates heat. If this heat cannot be dissipated out of the cells because of the existing environmental conditions, e.g. hot climate, thermal runaway will occur. The AGS recombines hydrogen and oxygen to water outside of the cell. Therefore, unlike the situation with VRLA cells, the reaction heat generated during this process is not emitted to the electrolyte.

3. Design and operation of Aqua-Gen system

The structure and function of an Aqua-Gen plug is shown in Fig. 2. The hydrogen/oxygen gas mixture, charged with

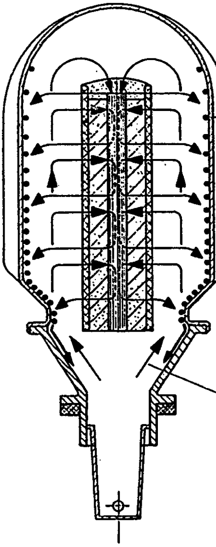

Fig. 2. Design and function of Aqua-Gen recombinator.

traces of catalyst toxicants, flows into the plug. The plug has a layer of particles that contain copper and manganese. These are held within a porous ceramic tube. Gases reach an embedded, thin cylinder that is coated with palladium catalyst. Here, the gases react to produce water. The reaction heat causes the water to flow back as steam through the ceramic tube and into the plug shell where it condenses as droplets on the walls (these droplets provide a simple performance control) and then returns to the cells, cooled down to 30 to 35 °C.

The AGS has a number of self-protective functions. These are as follows:

- In float-charge service with non-stoichiometric gas volumes, i.e. hydrogen surplus, oxygen is admitted through an opening in the plug shell that is normally closed with a porous ceramic part (due to being under pressure as a consequence of the reaction), and hydrogen is completely burned with oxygen
- In the case of larger gas quantities, the palladium-coated catalyst rod may reach very high temperatures. An ignition of the in-flowing gas mixture is prevented by the porous ceramic tube
- Under very heavy loads, e.g. a fivefold gassing stream, the quantity of steam that develops in the counterflow will limit the admittance of more hydrogen and oxygen. As an emergency measure, the steam is evaporated to the outside through the shell opening

One benefit of the AGS is obvious. Topping-up with water may be dispensed with for the whole life of the batteries. For users, the advantage lies not only in the savings associated with the absence of the need for water addition, but also in the fact that the risk of using contaminated water is eliminated. Moreover, overfilling of the cells is no longer possible. Consequently, there are no variations in electrolyte density and, therefore, no variations in cell behaviour. In summary, the benefits for the user lie in the avoidance of risks and mistakes, in the simplified inspection of the battery, and in the resulting cost savings.