Meeting European requirements with advanced designs of valve-regulated lead/acid batteries

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Abstract

Valve-regulated lead/acid (VRLA) batteries now meet the majority of requirements for stand-by applications. There are two principal technologies for VRLA batteries; (i) cells with gelled electrolyte and (ii) cells with absorptive glass-mat (AGM) separators. New developments in both of these areas are described. Tubular-plate cells using gelled electrolyte offer many advantages over conventional counterparts and extend the available capacity range of VRLA batteries. New types of VRLA batteries using AGM separators have also been developed in larger capacity ranges and offer improvements in high-rate performance. For smaller capacities, recent achievements in the capability of batteries using pure lead plates will be compared with cast-alloy plates. These offer better high-rate performance and other unique advantages for a number of critical applications. All of these developments are set in the context of the relevant standards, and the importance of correct specification to ensure overall system reliability is discussed. VRLA batteries have evolved rapidly in recent years and continuing development will ensure that increased demands for stand-by power can be met.

Introduction

Valve-regulated lead/acid (VRLA) batteries have been developed for a range of applications over recent years. For stand-by power, such batteries have achieved a dominant position and have effectively displaced traditional technologies. This has resulted directly from the real user benefits that are provided with VRLA batteries. The elimination of the need to add water at regular intervals, reduced levels of gas emission allowing new freedom for battery installation, and better high-rate performance have all contributed to a high degree of market acceptance. This development has run in parallel with an enormous expansion in telecommunications and in networking of computers that has placed new demands on batteries. The result of this has been a wide variety of products being introduced to the marketplace, and it is only recently that a clear understanding of the different types of product required for particular applications has become fully appreciated.

This paper will describe the construction and electrical characteristics of the principal types of VRLA cells and their preferred application. A simple classification is also described. This has been developed to ensure that users specify batteries correctly, particularly with regard to service life, safety and performance.

There are three principal types of VRLA batteries: (i) batteries with gelled electrolyte; (ii) batteries with cast lead–calcium alloy plates and absorptive glass-mat (AGM) separators; (iii) batteries with pure-lead plates and AGM separators. Each type has been developed to serve different forms of duty.

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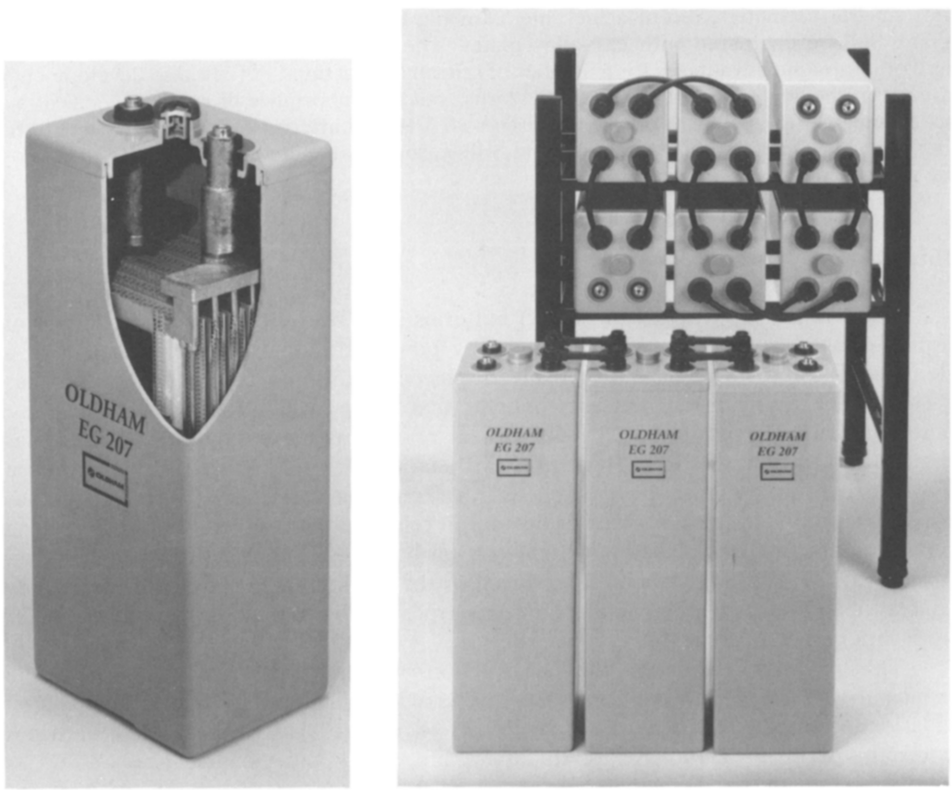
Tubular stand-by cells with gelled electrolyte

Tubular stand-by cells with gelled electrolyte (Fig. 1) may be constructed with lead–calcium–tin alloys for both positive spines and the negative grid. The preferred alloys lie in the range 0.06 to 0.08 wt.% calcium and 0.3 to 0.8 wt.% tin and have good mechanical properties as a result of dispersion and solid-solution hardening. Careful control over the casting process and subsequent thermal processing is required to ensure that the preferred microstructure is produced, which also leads to a high degree of corrosion resistance. Tin has the effect of avoiding passivation at the grid/active material interface and these alloys also have a high hydrogen overpotential which is necessary to suppress hydrogen evolution at the negative plate.

The positive and negative plates are manufactured in a manner similar to those used for flooded cells. Microporous polymeric separators are used and the container is moulded in flame-retardant acrylonitrile butadiene styrene (ABS). The pillar seal has a very high degree of integrity and uses a closely conforming synthetic rubber grommet. The pressure-relief valve operates through a Bunsen valve and incorporates a flame arrestor. The electrolyte is gelled with finely-dispersed silica. The recombination reaction takes place by virtue of oxygen transport from the positive to the negative plate in the gas phase through a network of microscale fissures in the gelled electrolyte.



(a) (b)

Fig. 1. Valve-regulated lead/acid cell with tubular positive plates and gelled electrolyte: (a) cutaway showing cell configuration, and (b) cells may be installed horizontally or vertically.

Cells of this type conform to DIN 40736 Part 3, under the general designation OPzV, and are available in a range of capacities from 200 to 3000 A h. The cells may be installed horizontally or vertically. For horizontal installation, however, the plates must be vertical and this is indicated on the cell lid. Intercell connection is by bolted, flexible connections.

The design of gelled electrolyte tubular cells is optimized for low-rate applications where the discharge duration is one hour, or more. For higher-rate applications, cells using flat pasted plates and AGM separators are specified.

Cells with lead–calcium alloy grids and absorptive glass mat separators

The majority of VRLA batteries are manufactured with flat pasted plates that are cast in lead–calcium or lead–calcium–tin alloys (Fig. 2). The plate thickness will be a key factor in determining the high-rate performance of the cell which, in part, will be a compromise between design life and discharge behaviour. Where the product is designated for telecommunications service, discharge rate requirements are generally in the range of one to three hours, and cell designs need to be closely matched with service requirements to achieve optimum life. For higher-rate applications, grid and element designs become more critical and attention is needed to ensure that intercell connections and pillar configurations have the lowest possible resistance.

The AGM separators are the key feature of this type of VRLA battery. The separator retains the acid that is not within the active material and contains sufficient connected porosity to permit rapid diffusion of oxygen in the gas phase from the positive to the negative plate. There is a critical balance between the pore size of the active material and the separators to ensure that the pores in the active material are filled preferentially by capillarity. These properties are achieved with glass microfibre mats (often referred to as AGM) that are made by wet paper-making processes from sub-micron glass fibres. Porosity levels are very high and the separator resistance is very low. Smaller amounts of coarse glass and polymeric fibres may be added to obtain better mechanical properties and to permit thermal bonding during fabrication. Separator compression needs to be controlled within critical limits. Acid filling is sufficient to

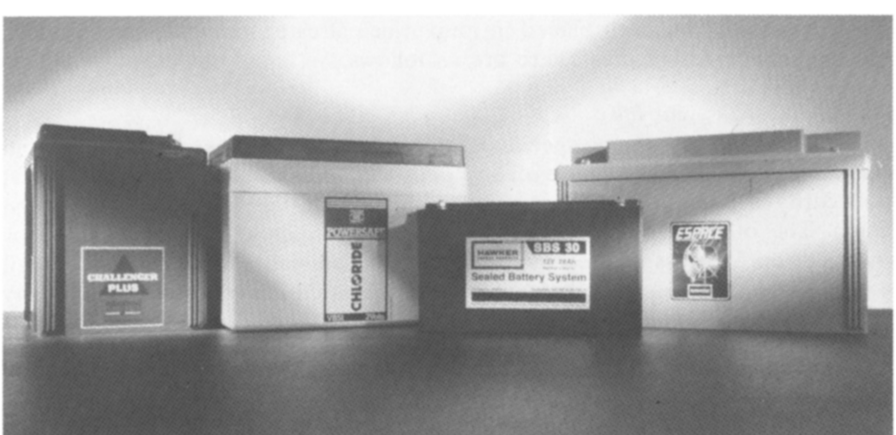


Fig. 2. Valve-regulated lead/acid cells with absorptive glass mat separators and either a lead–calcium–tin or pure-lead grid.

ensure full saturation of the plates, but an adequate level of retained porosity in the separators.

Similar venting systems to those used for gelled-electrolyte cells are employed. The vent must prevent ingress of air to the cell in the reverse direction but allow safe venting for small quantities of gas in the forward direction. It must also allow safe venting of larger quantities of gas in the event of abusive overcharge. A Bunsen valve design is generally used to achieve the required characteristics.

The pillar seal is also an essential feature. Mechanical seals that involve the compression of thermoplastic rubber grommets are effective, but coating of the sealing surfaces and the condition of the conforming surfaces are also important factors.

Flame-retardant ABS is generally selected for the container. It has good mechanical strength, an adequate modulus and excellent fracture toughness. A number of studies have shown that it has a higher permeability to water than some other polymers. For practical purposes, however, the water loss through the container at ambient temperatures is negligibly small.

Cells with pure-lead grids

VRLA cells can also be built with pure-lead grids. The corrosion resistance of pure lead is superior to lead–calcium–tin alloys and, in consequence, much thinner plates can be used without reducing the expected life in floating service. This gives better active-material utilization and the potential for enhanced high-rate performance. Pure-lead grids cannot be fabricated in a conventional manner and so the grid is punched from cold-rolled sheet in a continuous process, pasted and then cut into individual plates. Special paste formulations and plate processing are employed to optimize performance. Battery construction follows similar principles to cells using cast lead–calcium–tin grids, except that handling systems need to be tailored to deal with thin plates and that cell designs have been developed to achieve higher performance for short durations.

Categorization of product types

VRLA batteries have been placed in four principal categories that are based on the expected service design life. These are as follows.

(i) High integrity, 10+ year life

Batteries in this group are specified for telecommunications, for nuclear and conventional power plants and in the oil and petrochemical industry where the highest level of security is required. They are required to provide the full rated capacity on installation. The other electrical performance characteristics will be as declared by the manufacturer. Safety is assured by the use of nonflammable materials for the cell case, a safe venting pressure, safe behaviour under short-circuit conditions, and a very low level of gas emission. This is defined as less than 10 cm^{-3} per A h of capacity at the 10-h rate per 30 days. Seal integrity needs to be very high and batteries are required to be resistant to severe mechanical abuse.

(ii) High integrity, 10 year life

These batteries have a comparable design life with batteries in category (i), but the requirements for performance and safety are not as exacting. For example, the need to use a fully flame-retardant polymer for the case is not specified and the level of permissible gas emission from the cell is increased by a factor of three. The electrical performance is generally equivalent to products in the first category, but rated capacity may not be achieved immediately on installation and a period in service on float may be required.

(iii) General purpose, 5 to 8 year life

Batteries of this type also have lower safety requirements, but electrical performance is equivalent to batteries in category (ii) and tests to establish life may not be as exacting. These batteries may have higher power and energy densities, particularly at shorter discharge times, but these characteristics may be achieved at the expense of life relative to higher categories.

(iv) Standard commercial, 3 to 5 year life

VRLA batteries of this type are used in a wide variety of applications that require a stand-by battery. Their use, performance and safety characteristics are entirely fit-for-purpose. The batteries are very widely used in domestic and industrial equipment where initial price is a key issue.

This categorization has been developed by Eurobat and is based on the technical test and performance information of International Electrotechnical Commission (IEC) 896-2 which is in the form of a final draft. The standard commercial types of battery are also described by an IEC standard. The careful use and specification of these categories will go a long way to ensuring that the correct types of VRLA batteries are used.

Reliability

The reliability of VRLA batteries has improved substantially as they have matured and many of the defects that were apparent, when the technology was in its infancy, have been eliminated by design and process changes. Recombination technology is, however, radically different to conventional flooded lead/acid technology. There are potential failure modes that either do not occur or are of no significance for flooded cells that become important for VRLA cells.

Overdischarge is an area for potential problems. VRLA cells may be acid-starved and, on deep discharge, lead sulfate is deposited within the separator and this leads to short circuits. This should be prevented by the use of a voltage cutoff, but the effect can be reduced by the use of an additive in the electrolyte to inhibit the formation of lead dendrites.

Although electrolyte stratification can occur on cycling with AGM separators, it is not a problem for standby applications in float service. It does not occur with gelled electrolyte and, therefore, if there is a requirement for more regular cycling, a tubular gel cell would be preferred.

Corrosion of the plate-lug/group-bar interface has been observed for both the positive and negative group bar. This problem may be eliminated by careful selection of the alloys that are used for the components, together with control of the microstructures. Localized attack resulting from various metallurgical phenomena is now understood and will not lead to premature failure.

Drying out is not a problem as a failure mode. The recombination process is highly efficient and tends to be self-regulating in so far as the efficiency increases markedly as the saturation of the separators with AGM separators decreases or more paths for gaseous diffusion are created by the formation of microscopic fissures in the gelled electrolyte. Small losses of hydrogen occur in service and while these are at a very low level, there is a need to ensure safe convective venting at all times to avoid build-up of potentially flammable mixtures.

VRLA cells are sensitive to operating temperature. Service lives are substantially reduced at elevated temperatures and the problem can be exacerbated by thermal runaway. The process can become unstable. At higher operating temperatures, higher currents are drawn. These generate more oxygen which recombines exothermically, generates more heat internally and ultimately the current can rise to a level where the cell gases and begins to dry out. At this stage, the resistance rises and more heat is generated such that failure will occur through softening of the case and, in extreme examples, as a result of melting of lead components. These effects can be avoided by good installation design for cooling and ventilation, by the use of temperature compensated chargers, and by limiting the available current.

As a result, end-of-life failure modes are related to corrosion of the positive grid and degradation of the active material, as dictated by the service conditions; corrosive failure dominates in floating service. Experience in service is now being closely correlated with laboratory-based accelerated life testing. The intrinsic reliability of the system is being achieved, but it is important for the correct type of cell to be selected for each application.

Battery monitoring

Battery monitoring is becoming an important tool for assessing the reliability of stand-by batteries. Equipment is available that will record time, voltage, current and temperature, and then provide alarm signals as required. Continuous recording of data will also allow access to discharge data that arise from unplanned outages rather than test discharges. This is a useful tool for condition monitoring of a battery. These discharges can also be initiated remotely and the stored data can be interrogated as required.

Impedance measurements are becoming an interesting technique for battery monitoring. The a.c. impedance of cells can be correlated with residual capacity or the presence of defects and although the correlation is in some cases poor, data are being accumulated in sufficient quantity for this type of technique to become more useful.

Conclusions

VRLA batteries have evolved rapidly over the last several years to become a mature technology with significant differentiation between various types of product. Cells with tubular plates and gelled electrolyte, flat pasted plates cast in alloyed lead, and flat plates punched from pure lead provide products for different market sectors. Within each sector, products are tailored for specific application areas. This allows the user the opportunity to specify the precise type of battery required and to achieve the service life and reliability that is expected.

Battery monitoring is an important method for increasing the overall reliability of the system. It is the electrical equivalent to condition monitoring for complex pieces of mechanical equipment and will produce the same benefits in early diagnosis of potential problems before failure has occurred.

Continuous development of VRLA batteries will move in two directions: (i) for telecommunications and related applications, long-term durability is the key issue, whereas (ii) for uninterruptible power supplies (UPS), high-rate performance will be optimized. Lead/acid batteries are now used for a greater variety of duties than a few years ago and the development of VRLA batteries has been a powerful factor in ensuring that customer requirements can be met.