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Development of valve-regulated lead/acid batteries for distributed power requirements

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Abstract

Valve-regulated lead/acid (VRLA) batteries provide the very high levels of reliability required for stand-by service. Various types are available and, in particular, cells with lead–calcium–tin alloy grids and absorptive glass-mat (AGM) separators, cells with pure-lead grids and AGM separators, and cells with tubular plates and gelled electrolyte. The cell types are subject to a number of factors that affect durability in floating service. The factors are reviewed and it is shown that grid corrosion is the usual failure mode. As a result, practical cell and battery designs need to ensure that all other potential causes of failure are either eliminated or occur at a slower rate. Test results based on thermal acceleration are presented and have been correlated with real-time tests. The attainment of satisfactory product life under practical conditions is fully demonstrated. Techniques for battery monitoring and surveillance also have a strong impact on reliability and can be used to define the best strategy for replacement. The overall result is better levels of protection which, together with precise specification and careful consideration of the service conditions, enable user requirements to be met in full.

Keywords: Batteries; Rechargeable batteries; Valve-regulated lead/acid batteries; Lead/acid batteries; Reliability

1. Introduction

Valve-regulated lead/acid (VRLA) batteries have established themselves as the prominent type for all types of stand-by application and yet there is a perception that they are subject to premature failure. Some of this criticism is based on claims for life that could not be substantiated and were found in some instances to be unfulfilled for earlier generations of product. In addition, premature failure modes that were unique to VRLA batteries became evident. These limitations are now well understood, and have been eliminated by design from batteries made in recent years. The product has reached a stage of maturity such that it is meeting the full range of requirements that are specified, given correct selection and a clear recognition that there are various types of VRLA battery appropriate to different applications.

VRLA batteries may be conveniently grouped into four categories [1]: (i) high integrity; (ii) high performance; (iii) general purpose, and (iv) standard commercial. These groupings differentiate products principally by the expected service design life, but also by electrical performance requirements and safety considerations. The specification of these types of batteries has been adopted by Eurobat as a guidance note, and work is in progress on technical standards.

Work has also been in progress to develop an international standard for VRLA batteries. The International Electrochemical Commission (IEC) is working on a standard to be designated as Part 2 of *IEC 896*, where Part 1 defines requirements for vented stationary batteries. The need for properly recognized standards is self-evident and in the UK, *BS 6290: Pt. 4: 1987* [2] has served a useful purpose in defining requirements for VRLA batteries. This was developed several years ago at a time when the level of experience was less extensive than it is today. Methods of testing and appropriate levels of compliance are defined for electrical performance, mechanical integrity, and safety requirements. This standard has served as a benchmark for VRLA batteries for a number of years.

The favoured method of assessing life is an accelerated life test at 55 °C at a specified floating voltage. An Arrhenius relationship is used to extrapolate from this temperature to the service temperature, assuming that a single process with a single activation energy is responsible for degradation across the full temperature range. This can only be assumed by measuring the same level of reduction in performance over a range of temperatures and verifying that the activation energy is unique. In practice, this involves large numbers of trials, and a single temperature has been adopted that is neither too high to make extrapolation prone to error, nor too low to

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make testing times unduly prolonged. Testing of this type may also be correlated with real-time testing, and work in this area provides a useful further basis for verifying results from accelerated life tests.

In this paper, three types of VRLA batteries, all of which are fully capable of meeting the longest specified service life, will be described. The potential failure modes and how they may be overcome will be outlined. The results of accelerated life tests on these types of battery will be presented and strategies for monitoring and surveillance will be discussed. VRLA batteries are recognized as the principal source of stand-by power in many sectors and will continue to provide back-up supply in an ever-increasing range of applications.

2. Types of valve-regulated lead/acid battery

There are three principal types of VRLA battery: (i) cells using lead–calcium alloy grids and absorptive glass-mat (AGM) separators; (ii) cells using pure-lead grids and AGM separators, and (iii) cells using tubular plates and gelled electrolytes.

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

VRLA batteries of this type use flat pasted plates with grids cast in either lead–calcium or lead–calcium–tin alloys. Tin-containing alloys are favoured because they enhance castability and hence the metallurgical integrity of the grid. They also reduce the effects of passivation at the grid/active-material interface. The overall effect is to increase life, and this is achieved without detriment to recombination efficiency or reduction in the corrosion resistance of the positive plate. Plate thickness is important in the achievement of adequate life. Thicker plates increase life, but at the expense of high-rate performance and active-material efficiencies.

The AGM separators are essential to the correct operation of this type of VRLA battery and ensure that the oxygen transfer necessary takes place efficiently. The fibre mix and separator compression are important to avoid stratification effects. Acid volume and plate separation will determine capacity at low and high rates.

Venting systems are used to allow the safe release of small quantities of gas in the forward direction and to prevent ingress of air into the cell in the reverse direction. Pillar seals of high integrity are essential. Containers are generally moulded in flame-retardant acrylonitrile/butadiene/styrene (ABS). This has good mechanical strength, an adequate modulus to resist deflection under pressure, and a high level of fracture toughness.

2.2. Cells with pure-lead grids and absorptive glass-mat separators

The need to reduce the hydrogen overpotential for the negative grid and to increase the corrosion resistance of the positive grid results in pure-lead being an ideal material for VRLA cells. Thinner plates can be used without reducing the service life on float and, in turn, these give better active-material utilization and high-rate performance. The addition of tin has beneficial effects for pure-lead grids in a similar way to lead–calcium alloy grids and provides better cycleability. The difficulty with pure lead is that it cannot be fabricated conventionally. Grid forms are punched from lead sheet, in a continuous process, then pasted and made into plates for assembly. Beyond element assembly, battery construction is similar to that for cells using cast lead–tin–calcium grids.

2.3. Tubular cells with gelled electrolyte

Tubular VRLA cells with gelled electrolyte also used lead–calcium–tin alloys for both the positive spines and for the negative grids. The plates are manufactured in the same way as for flooded tubular cells, microporous plastic separators are used and containers are moulded in flame-retardant ABS. A high-integrity pillar seal is used with synthetic rubber grommets, specially lubricated and conforming to the lid and pillars. 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 transfer from the positive to the negative plate in the gas phase through a network of microscopic fissures and passage ways in the gelled electrolyte. The design of gelled-electrolyte tubular cells is aimed at low-rate applications where the discharge rate is at least 1 h. For higher-rate duties, cells with flat pasted plates and AGM separators are specified.

3. Factors affecting durability in floating service

In floating service, the voltage is set to ensure that full capacity is maintained and to give efficient recharge after a discharge. Part of the current counters internal losses, part drives the recombination reaction, and part will corrode the positive-grid. Pure lead and lead alloys all corrode at low rates and failure will occur through grid corrosion at some stage. The design of the battery has to ensure that other time-, temperature- or voltage-induced failure modes will occur later than positive-grid corrosion.

3.1. Negative group-bar corrosion

Negative group-bar corrosion (NGBC) has been a historic problem that has caused early failures for VRLA cells, but for the majority of manufacturers this problem was fully resolved some years ago. NGBC is unexpected in so far as the negative plate is normally protected against corrosion by virtue of its potential. It occurs uniquely in VRLA cells under the special conditions of gas composition and acid concentration that exist in the headspace of these cells, and with particular combinations of alloys and metallurgical processing. Localized corrosive attack occurs either at the group bar or at the plate lug adjacent to the group bar. This problem is now well understood and may be avoided by careful selection of the alloys for all components and by control of metallurgical processing. The use of cast-on-strap techniques has further improved the reliability of interconnections between plates.

3.2. *Drying out*

Drying out is not a failure mode under normal conditions of float service. The recombination process is very efficient and tends to be self-regulating, as the efficiency increases as the saturation of the AGM separators decreases or more paths for diffusion are created in the gelled electrolyte. The low level of hydrogen evolution at the negative plate and corrosion of the positive grid give rise to water loss. Permeability of the container to water vapour transmission has been considered as a source of water loss, but it is very low for practical wall thickness and moderate ambient relative humidity. Water vapour will also be lost from the cell along with vented hydrogen, but again the effect is very small.

3.3. *Thermal runaway*

VRLA cells are very sensitive to operating temperature, such that service lives are reduced at elevated temperatures and, in extreme cases, an unstable thermal runaway can occur. As the temperature rises, high currents are drawn from a constant floating voltage. These, in turn, generate larger quantities of oxygen that recombine exothermically, produce more heat and, ultimately, the current can rise to a level where the cell gasses and begins to dry out. As the cell dries out, the internal impedance increases, more heat is generated, and failure may occur through softening of the case or, in extreme examples, as a result of melting lead components. These effects can be readily avoided, however, by good installation practice for cooling and venting, by the use of temperature compensation of the floating voltage, and by limiting the available current.

3.4. *Active-material degradation*

The cyclic requirements for stand-by applications are usually moderate, and the positive active-material generally remains in good condition after long periods. Sulfation and capacity loss of the negative plates is a potential failure mode. The oxygen-recombination reaction depolarizes the negative plate such that it never reaches the low potentials normal in flooded batteries, but the inefficiencies of the recombination reaction allow sufficient charge to be applied to the negative plate to keep it in good condition. In addition, cells are designed with augmented negative material to provide a further safeguard.

3.5. *Acid stratification*

Acid stratification can occur in cells with AGM separators. During cycling, sulfuric acid of higher specific gravity sinks to the bottom of the cell and creates a concentration gradient. Recharge becomes acid limited at the top of the cell and occurs at the bottom. Separators with higher levels of finer fibres and higher levels of compression reduce stratification effects. Compression also helps retain the positive active-material. For stand-by applications, the separator is specified such that this is not a failure mechanism.

3.6. *Shorting through the separator*

In VRLA cells, it is possible for short circuits to occur through the separator by leading-through if the electrolyte specific gravity reaches very low levels as a result of overdischarge. Under these conditions, high pH will allow lead species to become soluble and can lead to the formation of lead dendrites. The problem can be avoided by cell design to ensure adequate acid is provided, by special additives in the electrolyte, and by the use of a voltage cutoff during discharge.

3.7. *Premature capacity loss*

Premature capacity loss affects all battery types using antimony-free alloys but for stand-by batteries, where the cyclic duty is moderate, it is not a source of difficulty. Batteries can be designed to provide adequate cyclic life. The whole subject of premature capacity loss is an area of intensive worldwide research effort, and success solving this problem will lead to VRLA batteries with cyclic performance equivalent to flooded-electrolyte counterparts.

3.8. *Cell sealing and venting*

The integrity of the lid/container weld is important and either a heat-sealing process or an epoxy-resin seal is used. Both processes are reliable and proven. Pillar seals use rubber grommets to seal against the container and pillar, which are mechanically clamped into position and, for some designs, are embedded in epoxy resin. The venting arrangements are simple and reliable. All seals are tested by sensitive techniques in manufacture and, in laboratory tests, may be shown to be leak-tight to an order of magnitude greater than that required for satisfactory operation.

3.9. *Manufacturing technology*

VRLA cells required substantial improvements in the level of control and reproducibility in manufacture, as compared with flooded batteries. This has been achieved in all areas of manufacture. In particular, plate manufacture has been placed under very close control. The adoption of cast-on-strap has brought higher reliability and the inter-cell welds are all tested as they are being made. Seal integrity is monitored in-line and the acid-filling technique has a very high precision. Fully-charged batteries are tested for open-circuit voltage, discharge performance and capacity. Through these procedures, very high levels of reliability have become well-established.

3.10. Grid corrosion

As summarized above, all of the other components in a VRLA cell may be designed such that their life is greater than the corrosion life of the positive grid. In a VRLA cell, the positive grid experiences conditions that are more corrosive than in flooded cells. This is because: (i) the float current is higher (due to the depolarizing effect of the recombination reaction on the negative electrode); (ii) the rate of polarization is different. As a result, for the same applied voltage, the current is increased and the voltage supplied to the positive plate is increased. This, in turn, will influence the rate of corrosion.

Grid growth will also occur as the grid corrodes. The oxide corrosion product has a greater volume than the metal, and as the stressed metal becomes thinner, grid growth will tend to increase in the later stages of life. The rate of growth is determined by the creep rate of the alloy. The morphology of the corrosion product will also be affected by alloying elements. Grid growth will eventually lead to loss of contact between the grid and active material.

4. Life testing

Some studies of the projected life of VRLA batteries are based on studies of grids in sulfuric acid at specified voltages. These studies often fail to recognize the impact of the environment in a VRLA cell. The effect of polarization of the negative electrode and grid growth can only be validated by cell testing.

Product life may only be effectively validated by accelerated life testing or by real-time testing of complete cells and monoblocs. The test that has been adopted is based on an accelerated life test at 55 °C, with a capacity check at ambient temperature after 40 day intervals. After known numbers of intervals, cells are subjected to a teardown and the degree of corrosion of the positive grids is measured. This is correlated with a teardown of cells of identical construction after known times on float at room temperature, to measure the corrosion of the positive grids.

This method was originally developed by Oldham France [3] in collaboration with Electricité de France (EDF) to validate the life of flooded lead–calcium tubular cells for electric utility installations. The 40 day testing interval was shown to be equivalent to 1.6 years at room temperature on the basis of the correlation with actual corrosion rates.

This method was applied to VRLA cells with lead–calcium–tin pasted plates and AGM separators. The test was conducted as described, i.e. 55 °C and 2.27 V/cell, with discharges carried out at $1.5C_{20}$ to 1.70 V per cell at 20 °C. A life (to 80% capacity retention) of 9.5 cycles was obtained. Correlation of the measured corrosion at 55 °C and room temperature gave an acceleration factor of 1.14. A service life of 11 years at room temperature is predicted. These data were obtained with cells using the grid alloys and grid profiles in use some years ago. By contrast, recent data from improved products show 40 to 50% improvement in life, based on accelerated testing.

The same tests have been applied to tubular gel VRLA cells with lead–calcium–tin grids and spines. In this case, the cells were floated at 2.23 V/cell and discharged at $0.5C_{10}$ to 1.80 V/cell at 20 °C. The same acceleration factor derived for tubular flooded cells may be used in this case to validate a room-temperature life of 15 years.

The C_{10} capacity of cells using pure-lead grids and AGM separators, established by 55 °C accelerated life testing and by the same test for cells that had previously been exposed to five years floating service at 2.27 V/cell and an average temperature of 26 °C, shows that a lifetime of 17 years is achieved. This is exceeded for cells where only the latter part of the life has been accelerated.

These data show that VRLA batteries are capable of 15 years life on float at 20 °C, or 10 years of life at 25 °C. Service temperature is the key factor in determining corrosion life. A good guide is for every 10 °C increase in temperature, service life is reduced by 50%. The importance of good installation practice is clearly evident. It should also be noted that life will be shorter at high discharge rates (5 to 30 min) than at low discharge rates (>3 h) because more grid metal is required to sustain high-rate performance.

5. Monitoring and surveillance

The integrity of installed batteries can only be assessed fully by carrying out a measured discharge. For large populations of batteries, this may be done on a sampling basis by age, but other techniques are useful to indicate that end-of-life is approaching and to support replacement strategies.

Continuous monitoring of voltage, current, temperature and time will result in identifying fault conditions prior to failure. Data-logging equipment will measure individual cell and monobloc voltages, both on float and during planned or unplanned discharges. Faulty batteries can be identified by reference to an acceptable voltage window and, on discharge, batteries with a higher rate of voltage decay can be identified. Charger faults and temperature can be recorded. Data can be interrogated to obtain a full operating history and alarms set to meet any local or remote requirement.

Conductance or impedance can be measured to give an indicated of battery condition. The battery is analysed as a small network of resistive and capacitative components. The a.c. techniques give a measure of the resistive element and eliminate the capacitative elements expressed either as conductance or impedance. Impedance will increase as the cell ages and corrodes and, therefore, it will give some indication of battery condition. In practice, impedance measured by various techniques follows the reduction of capacity with life, but does not indicate accurately when the capacity has fallen to 80% of the original value. Impedance or conductance measurements can be used to identify when a battery requires further investigation and to detect conditions that will lead to rapid failure. A continuing record of impedance and temperature against time will give an indication of the security of the system.

6. Conclusions

VRLA batteries have been developed to a stage where they provide safe, reliable, space-efficient and cost-effective power systems for virtually all applications. The product is significantly differentiated for various market sectors. Cells with plates cast in alloyed lead, or punched from pure-lead sheet with AGM separators or tubular gel cells are applied in different market sectors.

Reliability is assured by careful design and a full understanding of the factors that can contribute to failure. Cells are designed such that positive-grid corrosion is the normal end-of-life failure mode. All other potential failure modes are either eliminated or occur at a lower rate than grid corrosion.

Life testing is the only way to validate reliability. Accelerated life tests, correlated with corrosion studies, provide a good basis for ensuring that actual service life is achieved. It has been shown that > 15 years life at 20 °C or > 10 years life at 25 °C can be obtained.

Monitoring and surveillance of in-service battery populations are important. Impedance or conductance measurements are useful as an aid to identifying incipient failures, and systems for continuous monitoring are widely used. All of these techniques enhance reliability, but it is vital to recognize that VRLA batteries do require maintenance checks from time to time to ensure the integrity of the system.

Sealed VRLA batteries are, in many ways, an enabling technology for a variety of industries, particularly telecommunications and information technology. They have become a key factor in facilitating the establishment of new networks; the battery industry has been at the forefront in this area and will continue to break new ground.

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