HYBRID ADVANCED GEL VRLA BATTERIES

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ABSTRACT

The VRLA battery can be produced using two differing technologies. Absorbed glass mat technology has lower resistance, while gel technology has better thermal stability and cycle life. A new hybrid technology that combines gelled electrolyte with AGM separators to provide the benefits of both technologies is described.

ADVANCED GEL CHARACTERISTICS

The concept of the Hybrid Advanced Gel VRLA battery is to mate the advantages of both technologies into one superior battery. The Absorbed Glass Mat battery has a lower resistance due to its construction and, thus, has much better high rate capability. This makes it a better candidate for the UPS market where rates can be typically fractional hours—quarter and half hours. The gel batteries, however, cycle well and would be preferred in any application that requires any significant number of cycles. However, their microporous polymer separators tend to increase their internal resistance and, thus, they have limited usefulness for high rate discharges. Standby systems in industrialized countries generally do not demand frequent cycles and the AGM batteries cycle well enough for that application. However, if the power infrastructure is not totally secure, then the enhanced cyclability of a gel battery is required. For equivalent capacity, the gel battery will be physically larger than the AGM, since the gel takes up space, and this must translate to larger volume or decreased capacity. This will depend on the gel concentration, as we will show in a later graph.

Thus, each battery derives advantages from its inherent design and compares favorably against flooded designs when the costly issue of maintenance is introduced. The Hybrid Advanced Gel possesses the cyclic ability of a gel, but without the volumetric penalty. The extra heat capacity due to the extra water from the colloidal gel gives these batteries an advantage in harsh, fluctuating temperature environments, since their temperature swings are moderated. An important failure mode for all lead acid batteries is water loss. The flooded batteries evolve hydrogen and oxygen and need to be periodically refilled with water. The VRLA batteries recombine oxygen to form water, and their life is determined by the rate of increase of the acid concentration and, thus, the open circuit voltage of the battery. There will be no charging when the open circuit voltage reaches the float voltage of the charging system. Thus, if recombination can be made efficient, the battery with more electrolyte will have the longer life. The AGM separator inherently recombines, as does a properly prepared gel, since it will possess cracks that allow the oxygen to reach the negative plate and react to form water. The battery containing the most electrolyte has the advantage if recombination has similar parameters, since the acid will concentrate at the same rate. The amount of extra life should be proportional to the amount of extra electrolyte designed into the battery. The problem is that recombination efficiency cannot be sacrificed for extra electrolyte or the battery behaves like a flooded one and can evolve large quantities of hydrogen, which should be avoided in most applications.

ADVANCED GEL HISTORY

The late Frank Vaccaro started this Advanced Gel battery development in 2000 and was continuing it at the time of his untimely death. Frank and the technical team had been designing AGM batteries since the 80's and identified improvements that would help widen their customer base. The AGM VRLA batteries have evolved over the years as the Fiberglas separators have improved. Customers indicated that more capacity and service life with less maintenance would be expected in the future. Small incremental changes in design were deemed not enough to insure continued company growth and, so, broader transformations were started. An important transformation was to immobilize or gel the electrolyte throughout the battery.

Silica gel can be prepared in various ways, but if one wants to disperse it throughout the entire battery, then colloidal silica is the simplest choice. The various powders available could be dispersed as colloids, but it made more sense to purchase the colloids, since they were available in tank car quantities. Since the capacity of the batteries were very important, only a limited concentration of gel should be used. Ten percent gel would lower the battery capacity by about 15%, and that was unacceptable for most applications.

The major breakthrough was to disperse the gel throughout the entire active material of the battery. The Fiberglas separator was vital, but the "pores" are fairly large. Thus, a colloid size was chosen that would fit into the pores in the lead dioxide and lead. The simplest method to accomplish this dispersal was to mix the colloid and the acid and fill the battery under vacuum. Mixing is easy, since the density of the colloidal silica is similar to the sulfuric acid and both have low viscosities. The mixture of colloid and acid will gel as the battery reaches end of formation and the acid becomes more concentrated. The battery may have other gel added, but is ready to use just after formation. These steps and procedures are the subject of a United States patent application.

CHARGING CHARACTERISTICS

The concentration of sulfuric acid in the Hybrid advanced gel is the same as in a conventional AGM battery and, thus, the charging parameters remain the same. The acid concentration can be changed to match other requirements, but, generally, about 40% is considered standard. This value is designed to provide sufficient polarization in a new battery so that charging is easily accomplished.

Since these batteries are expected to be deployed outdoors, the question of temperature compensation of the float or charging voltages must be addressed. To maximize the service life of the battery, the charging or float voltage should be decreased as the battery temperature increases. The rate of change or coefficient should be kept at the low end of an adjustable scale if one is provided. A fixed value of between 1¼ and 2 mV per degree Centigrade will help increase life. Over compensation at higher temperatures will decrease polarization and lead to diminished life. Temperature compensation should not be the only defense against thermal runaway. At colder temperatures, the float voltage can be gently increased with the same slope, but an offset of 15 degrees Centigrade will help match currents to need.

The best forms of charging are generally the simplest. Ac ripple should be avoided, if possible; the batteries can act as a filter, but their life will be affected if they become warmer. Float voltages should match the acid concentration in the battery. Batteries can be manufactured with a range of acid concentrations, but it is probably easier to adjust the float voltage than the acid gravity. Engineering is needed to avoid the problems that surfaced when VRLA batteries were first introduced and 23 cell strings had to be used in the Central Offices, since the float voltages were designed for the 30% acid in use then in the larger flooded lead acid batteries. Subsequent generations of power systems used higher float voltages based on the 40 % acid used in VRLA batteries.

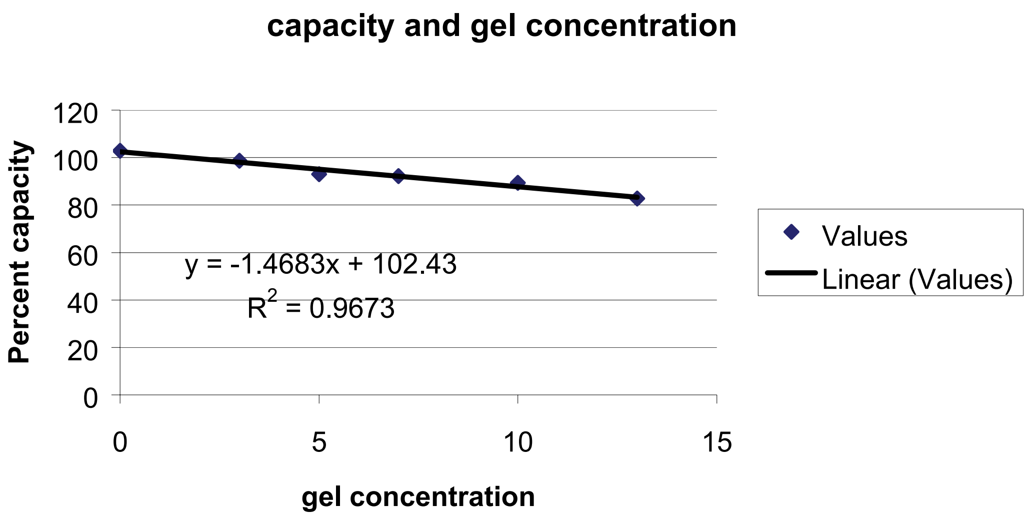
HYBRID ADVANCED GEL LIFE EXPECTANCY

A major advantage for the Advanced Gel is the extra water in the battery. As long as recombination is good, the extra water simply translates to extra life. Dry out can be a major failure mode in VRLA batteries and can be countered by good recombination efficiency and adding water to the battery. Unfortunately, just adding water to the battery will lower the efficiency of recombination so that it approaches that of flooded batteries. The gel facilitates recombination, since it cracks and provides pathways for the oxygen to reach the negatives. Laboratory tests show the recombination efficiency to be similar and, thus, the Advanced Gel will last longer before dry out.

Measuring the polarizations in VRLA batteries is difficult, but it was found that the values in Advanced Gel showed a very small decrease in positive polarization (3 mV) that would point to a decreased corrosion rate and, thus, if the polarization difference remains, then the growth rate would also slightly favor increased life. These are difficult measurements to make, and we continue them as the technology evolves. Grid growth is another failure mode, but is related to corrosion rate, and this will also favor Advanced Gel. These measurements are generally made under accelerating conditions at high temperature and the results extrapolated back to room temperatures. The battery designers will continue both accelerated tests and room temperature tests to optimize the percentages and characteristics of the gels used in the Hybrid Advanced Gel batteries.

EFFECT OF GEL ON CAPACITY

The silica does not participate in the electrochemical reactions and can be viewed as a dilutant for the sulfuric acid. Thus, every percent of silica would not be available as sulfuric acid and would decrease the capacity by one percent if weight were the controlling criterion. The problem is that we probably need some form of volume percent, not weight percent, and will have to factor in the effect on the quantity of sulfuric acid available for discharge inside the plates. This is in the Advanced Gel, since the gel permeates the active materials. The actual results show that the effect is slightly greater since 5% gel decreases the capacity by 7%, while 10% gel lowers the capacity by 15%. Thus, the lower the concentration of gel, the higher is the battery capacity.



HEAT CAPACITY OF BATTERY

The heat capacity of a VRLA battery resides mostly in the electrolyte, and this provides an opportunity to increase the overall heat capacity by using gel. The electrolyte has over 65 % of the heat capacity and that can be increased, since the gel can be added in differing quantities. This extra heat capacity can help the battery survive fluctuating outdoor temperatures, since the excursions will be minimized and the battery temperature moderated. We will quantify this in the next part of the presentation.

THERMAL ADVANTAGES OF ADVANCED GEL

Outside applications fluctuate in temperature both seasonally and daily. The battery has a high heat capacity due to the electrolyte and, thus, lags the temperature. The life of the battery follows the well-known Arrhenius equation that indicates that the reactions in the battery have their logarithms dependent on the absolute or thermodynamic temperatures. This simply means that high temperatures hurt the battery more than cold temperatures help it. Thus, 12 hours at 35°C and 12 hours at 15°C actually do 45 % more damage to the battery than 24 hours at 25°C. However, the Advanced Gel battery can avoid some of the damage due to the increased heat capacity. A moderation of only 3 degrees to 18°C and 32°C will cut the damage in half (22%). Thus, the gel can help extend life in outdoor applications and can be modified to match the application. The response of the Advanced Gel batteries to temperature changes is being studied as part of a more comprehensive treatment of outdoor conditions and their effect on battery life and performance.

TEMPERATURE COEFFICIENT OF CAPACITY

The capacity of lead acid batteries is temperature dependent because the rates of the reactions are temperature dependent. A rough guideline is about 1% per degree Centigrade. However, VRLA batteries and, in particular, Advanced Gel are less temperature dependent than flooded batteries. This merits further investigation, but the advantages of the gel should be used in applications in colder climates. When engineering a system, the battery must be sized for the expected low temperature and, thus, a larger battery is frequently specified. The Advanced Gel does not require as much a change and may thus prove very cost effective and space efficient. Another important parameter must be the freezing point of the electrolyte on discharge, and since the Advanced Gel contains more electrolyte, the concentration must remain higher during the discharge, and the freezing point must be lower. These considerations are very broad-based, and each application should be analyzed to be certain that the best gel is used. Tradeoffs will be made in the design of systems, and the Advanced Gel offers an advantage in electrolyte volume and cyclability over the standard VRLA battery. These advantages should be incorporated early in the design process. This temperature coefficient of capacity may also be a function of the molecular structure of the colloid used, but the standard colloid does provide some improvement.

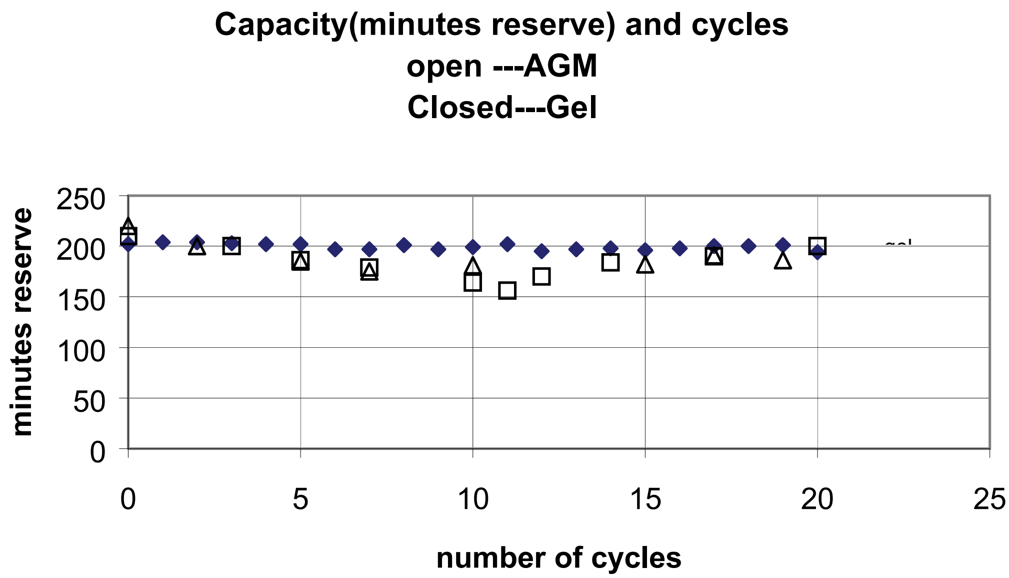
COLLOIDAL SILICA GELLING TIMES

Colloidal silica is available in a variety of particle sizes and concentrations. A useful range for the Advanced Gel batteries is 4-20 nanometers (40 Angstroms)

The gelling time depends on the particle size and concentration of the colloid along with the concentration of the acid present and their resulting temperature. The gelling times can range from seconds to many tens of hours. Temperature has a rate effect, but since the colloid contains water, there is also an appreciable heat of mixing with the sulfuric acid. Cooling the sulfuric acid can slow the gelling, but, generally, the colloid cannot be frozen and this limits the increased time achievable. The goal of permeating the active materials with gel can be achieved by choosing combinations that gel very slowly. Thus, diffusion has time to work, and the increase of acid concentration at the end of formation actually finishes the gelling. This provides a uniform gel that, since it permeates the battery, provides protection against acid stratification.

The battery can also benefit from other layers or structures of gel with different characteristics than the main dispersed gel. These extra gels could be used to simply increase the heat capacity of the battery or to simply act as a source for water to delay dry out and thus extend life.

CYCLIC ADVANTAGES OF ADVANCED GEL



Since the gel permeates the active material and separator of the battery, its structure will decrease the acid stratification. The gel behaves like a very fine Fiberglas separator (0.1 micron diameter) and, thus, the battery can cycle more effectively. This is seen in the graph where repetitive daily cycles show that the Advanced gel capacity remains constant, while AGM batteries initially lose capacity. Putting the batteries on their side or "pan caking" them and thus dramatically lowering the acid diffusion length by over an order of magnitude (factor of 10) can recover this capacity. One AGM battery also seemed to have recovered most of its capacity without pancaking, but has not been fully analyzed yet.

This advantage in cyclability has been used in the wheelchair market, where the Advanced Gel has received wide acceptance. Solar applications are also being studied to determine where various Advanced Gels might prove beneficial.

SECOND GEL PARAMETERS

There are opportunities to use the characteristics of the colloidal gels to further improve the Advanced Gel batteries at modest cost increases. The gels can be configured from differing particle sizes and concentrations. This allows considerable flexibility in modifying or customizing a battery for a specific application. A major goal could be to increase the amount of water in the battery to provide more heat capacity and longer float life. More gel could be added to increase the thermal conductivity of the battery by filling any voids that may have occurred during manufacturing and forming. This would help a battery subjected to harsh cyclic temperatures by conducting heat better and increasing the heat capacity that lowers the effect of the harsh temperatures. These extra gel layers can also help recombination, since they will dry and crack and provide pathways for oxygen recombination.

Some very concentrated gels can form quite fast and, so, they can be added as a final manufacturing step just as the batteries are readied for shipment. The colloidal particle size and concentration are the rate determining parameters, along with battery temperature, and the variables can be adjusted to meet the application. Standard Advanced Gels could be modified just before shipping to meet a specified requirement for a particular application.

SUMMARY

This new blending of established technologies should provide benefits to the battery using community. These Advanced Gel batteries will discharge at high rates, since their internal resistance remains low. The increased electrolyte quantity provides a measure of enhanced thermal stability and the potential for longer life. The gel provides enhanced cyclability that could prove useful in environments where the primary power source is compromised or functioning in an erratic manner.