

# UNDERSTANDING THE REAL DIFFERENCES BETWEEN GEL AND AGM BATTERIES - *YOU CAN'T CHANGE PHYSICS*

**Dr. Wieland Rusch**  
Research & Development  
BAE Batterien GmbH  
Berlin, Germany

**Keith Vassallo**  
General Manager  
BAE Corporate  
North America

**Gary Hart**  
Entrepreneur  
G.K. Hart POWER Inc.  
Ontario, Canada

## INTRODUCTION

The majority of Valve-Regulated Lead Acid (VRLA) batteries on the market or being manufactured today are AGM batteries. The electrolyte is immobilized by a micro-fibre glass mat. Their usable life usually runs between 5 and 10 years, with a cycle life rating between 200 and 500 cycles (80% DOD). Their life is restricted by the increase of internal resistance and, consequently, the drop of the capacity. Often, a part of the battery fails by sulphation of the negative plate.

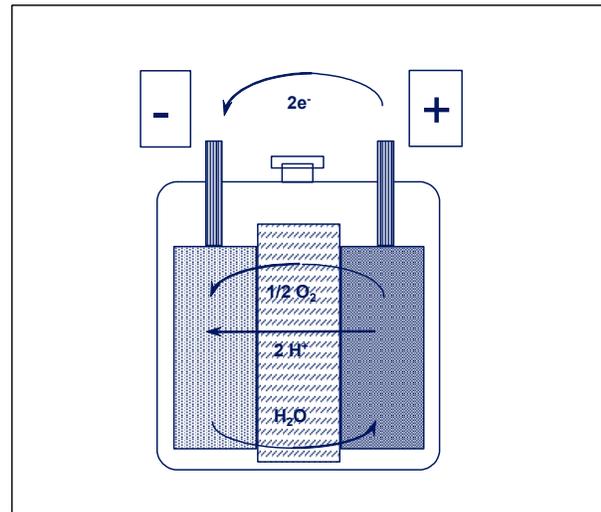
The minority of VRLA batteries are GEL batteries, where the immobilization of the electrolyte is made with pyrogenic silica. Their usable life is between 10 and 20 years; cycle life is between 500 and 1500 cycles (80% DOD). Thermal run-away effects are not reported, the cells keep their capacity and internal resistance stable over life [1]. Tubular plates can be used with GEL VRLA technology.

Why do GEL and AGM batteries behave so differently? Is it a question of workmanship and design, of different manufacturers? If not, can we explain the characteristics by the different immobilization system?

Yes. We can.

## PROCESSES IN VRLA BATTERIES DURING FLOAT CHARGE

If the positive plate is fully charged, water is decomposed in oxygen, hydrogen ions and electrons. In **flooded cells**, the oxygen gas is released from the cell, and the hydrogen ion moves in the electrolyte to the negative plate and is reduced there to hydrogen gas, which also leaves the cell. This results in water loss. Only a very small amount of the oxygen gas finds the way to the negative plate for recombination to water, because the solubility of oxygen in water is very low. In **VRLA cells** exist two phases between positive and negative plates: First, a liquid one, where the hydrogen ions can be transported. Second, a gaseous one, where oxygen gas diffuses to the negative plate. There, oxygen is reduced to water, which is far more likely than the reduction of hydrogen ions to hydrogen gas. This formed water diffuses back. Only 5-10% of the hydrogen ions are reduced to hydrogen gas, which leaves the cell through pressure sensitive release valves.



**Figure 1.  $O_2$  recombination in VRLA cells**

The realization of the liquid phase, as well as the gaseous phase at the same place between the positive and negative plates, was the breakthrough for the VRLA cell. Now, the recombination was strong enough to carry 90% of the float current, and water refilling was no longer necessary. The “easy-going” reaction of the hydrogen ions to water caused another effect, depolarization of the negative electrode. At the start of the VRLA development, often a zero negative polarization was observed. Having zero polarization at the negative electrode in a battery, in average, means that, in some cells (cells with thinner plates and less acid), negative polarisation was below zero; in other words, these cells were steadily slightly discharged during float. These are the cells that were sulphated. They could be located using impedance and conductance meters and they provoked a new effect, the PCL 3 (premature capacity loss due to negative plate sulphation).

### The basic “law” of float charge

The basic “law” of float charge conditions shows that both electrodes have to be polarized to keep them charged. This remains undoubtedly valid. The difference between float charge voltage and open-circuit voltage is the polarisation voltage, and this polarization voltage has to be shared between both electrodes. Example:

$$\text{Float voltage } 2,25\text{V} - \text{open-circuit voltage } 2,11\text{V} = \text{polarization } 140\text{mV}$$

At the beginning of their development, flooded lead calcium cells had a lack of polarization of the positive electrode. Very low impurities of the antimony-free negative plate resulted in such a high hydrogen over voltage that all the polarisation was consumed on the negative side, leaving the positive electrode at zero polarization, sometimes below zero, i.e., in the discharged state. Experts could see the lead sulphate crystals in the darkness, pointing with a light onto the positive plates. With palladium chloride additions, the negative polarization was reduced, leaving at least 50 mV for the positive polarization.

In VRLA cells the **negative plate** is in danger of low polarization. What can be done to increase it?

First, the negative electrode has to be “clean”, i.e., there should be present only a low amount of impurities which reduce the hydrogen over voltage. Then, also with low hydrogen current, we get a substantial negative polarization. Second, the depolarization effect by the oxygen recombination should be restricted and should be equal for all cells of the battery. This is where we have differences between AGM and GEL batteries. GEL batteries have generally a lower recombination current, because the microporous separator restricts the oxygen flow to the negative plate. Further, all cells start with a wet GEL, and the recombination is built up step by step. There is also a regulatory effect insofar as cells with lower recombination ability get higher float voltages, resulting in more water loss and bringing them in line with others. AGM batteries have generally a higher float current, a higher recombination current, and a higher depolarization. It is one of the most difficulties to give all AGM cells in a battery the same recombination ability by leaving in all cells 5% free space in the AGM separator. It is interesting that M. Fernandez [2] published a costly procedure: All AGM cells are overfilled with acid and then overcharged. Due to water loss, the recombination starts after some time and the charging voltage reduces. If the voltage of one cell or one block has reached a defined level, the overcharge of this cell or block is stopped.

The polarization effects can be summarized with the graph in Fig.2.

For simplicity, all cells were equipped with an acid gravity of 1,30g/ml. Consequently, the OCV is about 2,15V, leaving no polarization at a **float voltage** of 2.15V. At a float voltage of 2.30V, we see a total polarization of 150mV. Now the question arises, what is the proportion of the negative and positive polarization? This is shown by the curves on the right. At 2.30V, the flooded battery has a positive polarization of 80mV and a negative polarization of 70mV, totalling 150mV. Here, we have satisfied the basic “law” of float charge conditions best with nearly equal positive and negative polarisations.

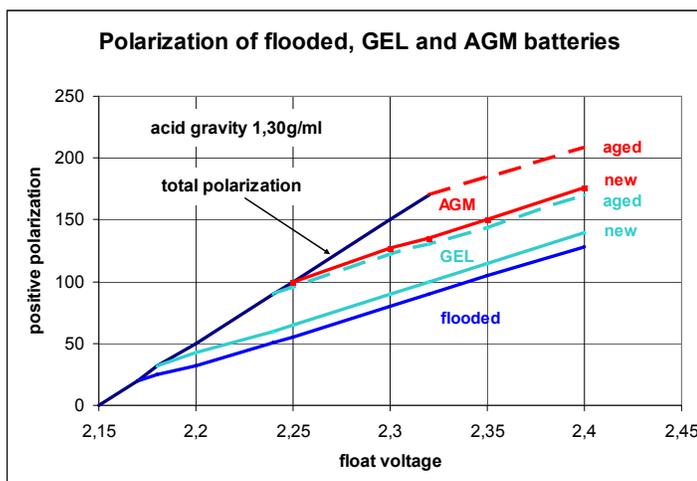


Fig. 2 Polarization of flooded, GEL and AGM batteries

The situation is similar with GEL batteries: The negative polarization starts at 60mV and, at the end of operational life, it is 30mV. AGM batteries start at 25mV negative polarization, which is reduced to zero during life, coming into an unstable condition. One should add that not all AGM batteries are alike. AGM batteries with thicker separators and smaller pores have a lower oxygen recombination and become more GEL-like.

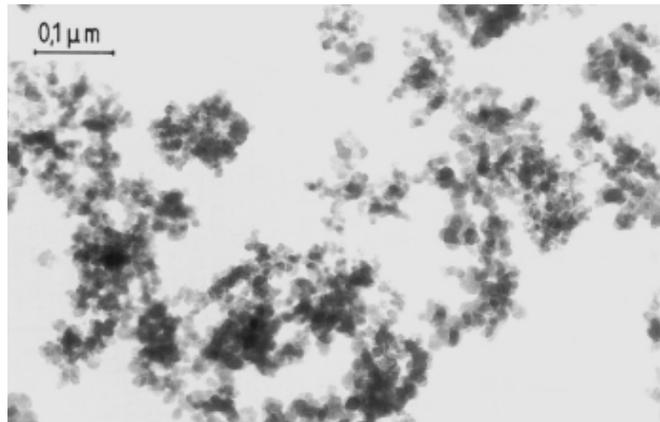
What is the reason for the different behaviour of GEL and AGM batteries?

**GEL: ELECTROLYTE IMMOBILIZATION WITH PYROGENIC SILICA**

Pyrogenic silica is a powder of very fine dispersed SiO<sub>2</sub> with an apparent density of 0,05g/ml. It consists of primary compact particles with a diameter of 10nm or 0,01µm in average. This can be seen with Transmission Electron Microscopy (TEM) in Figure 4. Due to the small size of primary particles, the internal surface is very high, measured as BET- surface: 200m<sup>2</sup> per gram.

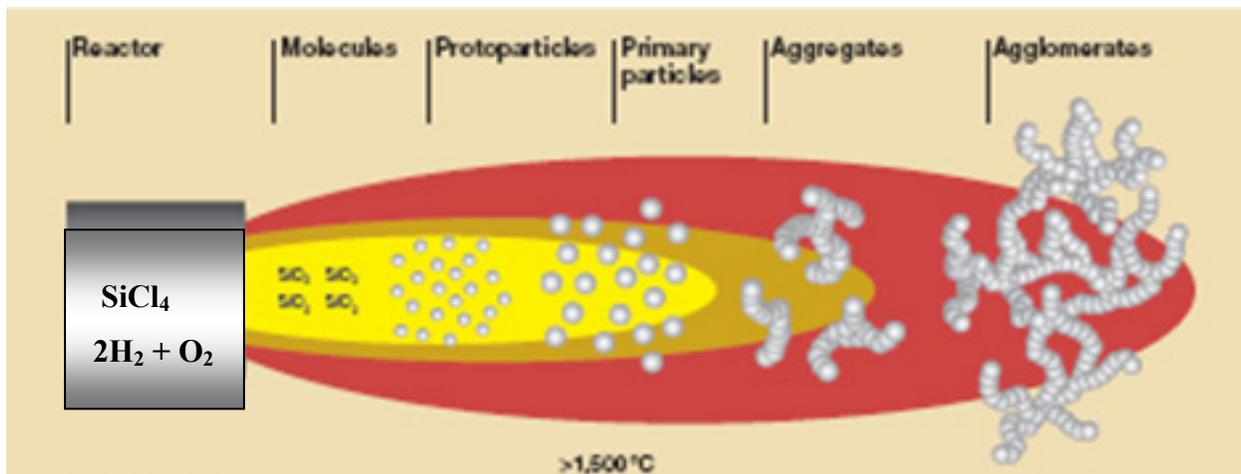


**Fig. 3 Powder of pyrogenic silica**



**Fig. 4 TEM of pyrogenic silica**

The primary spherical particles of 10nm diameter are bonded together in chainlike aggregates. These aggregates have a loose contact to each other, forming Agglomerates. This morphology is a direct consequence of the manufacturing process:



**Fig. 5 Manufacturing process of pyrogenic silica**

Evaporated silicon chloride is blown in an oxygen-hydrogen flame. At temperatures above 1500°C SiO<sub>2</sub> molecules are formed. Around 10.000 SiO<sub>2</sub> molecules strongly bond in siloxane groups (Si – O – Si), bind together to spherical primary particles of 10nm size. As the particles move to colder areas, they bind together to chain-like aggregates with a length of approximately of up 1µm. By further cooling down, they form agglomerates with a diameter of 10 to 250µm. The binding force **between** the primary particles is the hydrogen bridge linkage. The silanol groups (Si – O – H) of two particles come in contact and create the bridge linkage by exchange of their hydrogen molecule (Fig. 6).

These agglomerated aggregates of SiO<sub>2</sub> particles are mixed with acid and water, forming a liquid GEL (SOL) as seen in the left part of Fig. 7. After keeping it for several hours, on setting, the hydrogen bridge linkages form a three-dimensional structure. This is the GEL, seen in the right hand side of Fig. 7.

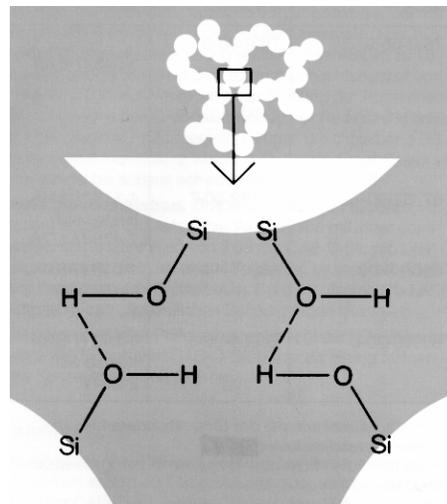


Fig. 6 Hydrogen bridge linkage between particles

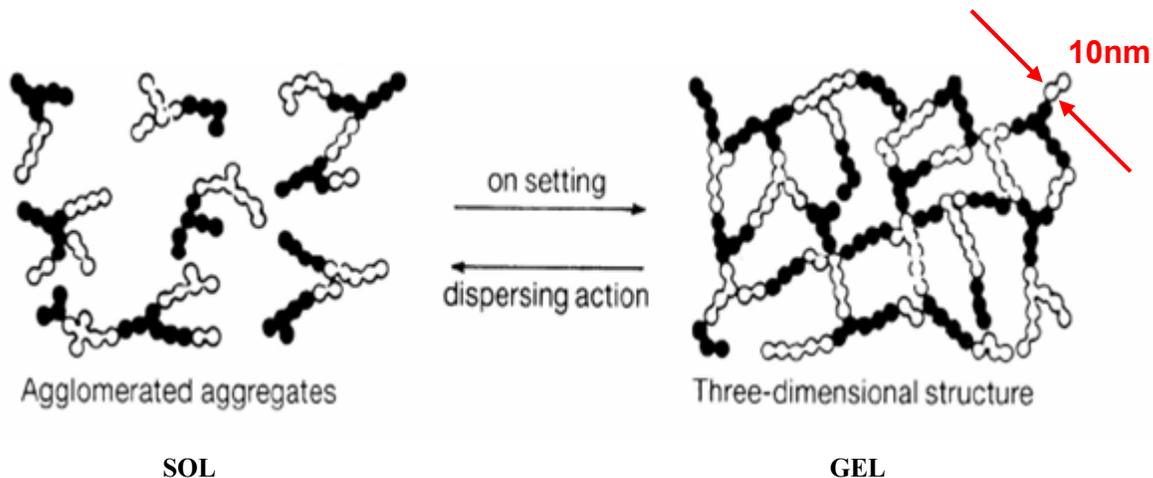


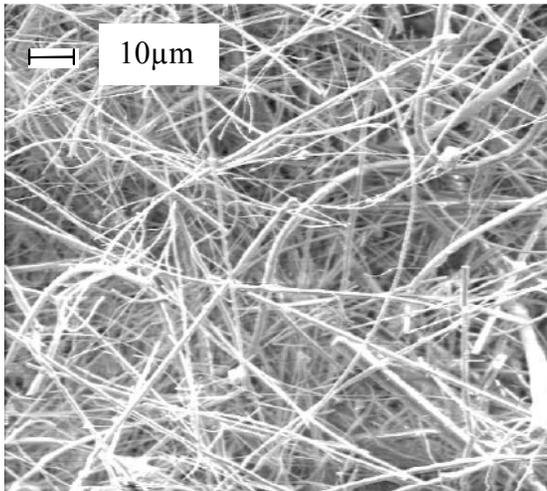
Fig. 7 The GEL structure is at the beginning reversible, by dispersing SOL and by setting GEL

The most important information we should keep in mind is that water and sulphuric acid are trapped in a structure, which is formed by chains with a diameter of **only 10nm** or 0,01µm. We will see later that the glass matt of AGM batteries consists of SiO<sub>2</sub>-fibers of 1µ diameter, which are 100 times thicker. This factor 100 counts.

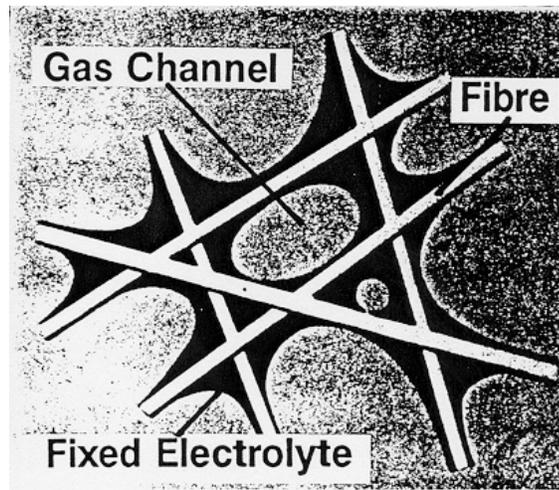
The GEL structure is formed out of a liquid sol within the cell. This allows all gaps to be filled between the separator and between the plates, no matter which tolerance in thickness the plates have, both flat and **tubular**. The slow water loss in a VRLA GEL cell causes the GEL to form “cracks.” This process is very important for the oxygen recombination, as we see below.

There are also other kinds of silica, like colloidal silica. This silica is produced in the liquid phase. It has a particle size of about 15nm. It is much smaller than agglomerated aggregates of pyrogenic silica, with a size of 10 to 250µm. As a result, the colloidal silica enters the pores of the positive and negative mass, which restricts the mobility of the sulphuric acid ions and reduces the overall capacity.

## AGM: ELECTROLYTE IMMOBILIZATION WITH GLASS FIBRES



**Fig. 8** REM picture of a glass fibre mat



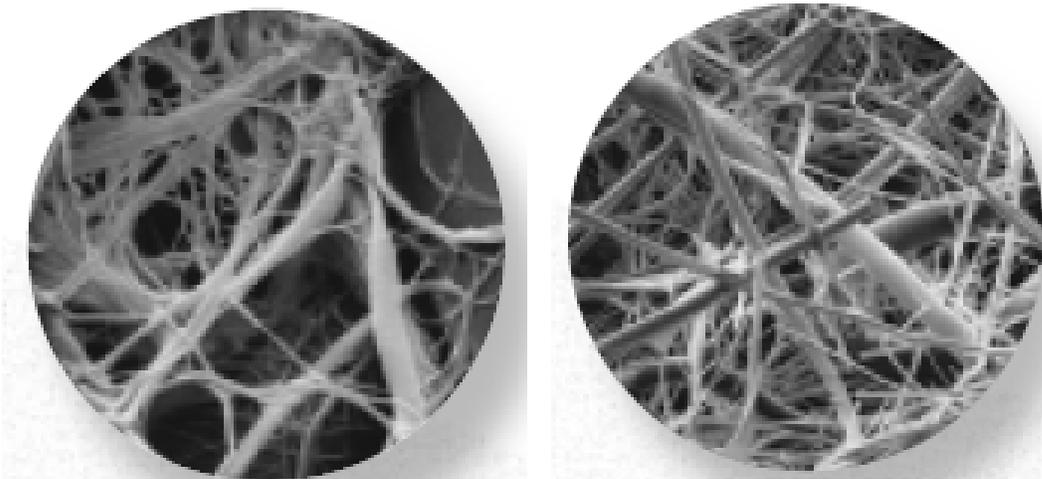
**Fig.9** Liquid distribution due to surface tension

AGM separators consist of a paper-like arrangement of glass fibers with a thickness of 1 to 4mm. The glass fibers have a diameter of 0,5µm to 3µm. Due to their hydrophilic behavior, the diluted sulphuric acid is trapped on the glass fibers. (See Figure 9.) The larger pores remain open until the AGM separator is 100% saturated and are the first to open if dry-out starts to happen.

The thicker fibers are used to build up an elastic spring. The elasticity is necessary because the separator has to be pressed onto the plates for a good ionic path or, in other words, a good cell's impedance. Also, the tolerance of plate's thickness has to be balanced with the elasticity.

The thinner fibers are used to get better adhesion of the acid in the separator. During charging, the emerging concentrated acid has a tendency to sink down due to the gravity force and create acid stratification. The smaller the pores and the fiber diameters are, the fewer problems there will be with acid stratification.

AGM cells have no extra microporous separator, so the AGM separator is the only separation between the plates. To avoid damage of the separator during manufacturing of the cell, which would lead later to short circuits, organic binders are common in thinner AGM separators. They give more mechanical stability, but reduce the portion of small pores.



**Fig. 10** AGM separators with (left) and without (right) organic binder

## MORPHOLOGY OF THE IMMOBILIZATION SYSTEM CHANGES BATTERY CHARACTERISTICS

The electrolyte immobilization structure for AGM as well as for GEL batteries consists chemically of SiO<sub>2</sub>. The structure and the pores in between the structure are 100 times smaller in a GEL battery (Table 1). According to Table 1, the pores of AGM are larger than those of the active material, while the pores of Gel are smaller as the pores of the active material.

**Knowing that the pore system with the smaller pores attracts the liquid stronger**, we can easily conclude that AGM is subject to dryout earlier as the active material, while GEL dries out later as the active material. It has severe consequences for the inner resistance and the capacity decay, as we see below.

<b>Table 1. Morphological Differences of AGM and GEL</b>		
	AGM	GEL
Diameter SiO <sub>2</sub> fibres	1µm	0,01µm
Pore size of the active mass	pos. 0,1µm, neg. 0,3µm	pos. 0,1mm, neg. 0,3µm
Rigid microporous separator	no	yes
Plate thickness tolerance	critical	Not critical
Plate contact	Elastic properties are essential	SOL / GEL fills all gaps

### Consequences of the different pore size of AGM and GEL batteries

- AGM batteries have a height restriction. Plates with a height above 200mm suffer from acid stratification, while GEL batteries can be built without practical restriction. Submarine batteries with a plate height of 1000mm are already being built.
- AGM batteries have a lower cycle life. Even for cells with plate heights of 100mm up to 200mm, acid stratification may occur, if thinner plates are used unintentionally or the container bulges out.
- AGM batteries have a shorter operational life. Dryout during aging is concentrated in the AGM separator (see above). By losing water, the separator will shrink, which reduces contact between the plates and the separator; therefore increasing the impedance. As a result, dryout is the main failure mode of AGM batteries. This explains why the impedance data of the AGM battery correlate better with the residual capacity vs. for flooded or GEL batteries.

### Consequences of the extra microporous separator in GEL batteries

- The microporous separator in GEL batteries acts as a barrier for the oxygen recombination. As we have discussed together with the measuring results documented in Figure 2, the lower oxygen recombination reduces the depolarization of the negative electrode and avoids the PCL 3 effect, the premature sulphation of the negative plates.
- The tendency for thermal runaway is strongly reduced for GEL batteries. In Figure 11 and 12, we compare the behaviour of two blocks 6V 68Ah, using the same plates, containers, lids etc. One block has AGM separators and the other microporous separators and GEL. They were artificially aged by overcharge until they have lost 10% of their water content. Simulating the situation of bad heat transfer to the environment or of a large battery in a small room, we increased the heat evolution in the cells by applying a charge voltage of 2.60V/cell. Having identical conditions for both types, the oxygen recombination for GEL batteries is around 1.5A current - equivalent, while for AGM batteries the oxygen recombination is around 10A current – equivalent. Having a six fold higher heat evolution in the AGM cells let the temperature go up to 100°C after 5h, while the temperature of the GEL cells remained below 50°C even after 28h. (See Fig.11 and Fig. 12.)
- The float charge voltage of GEL batteries can be kept constant up to 50°C without any danger of thermal runaway. By keeping the voltage high, we avoid discharge of the negative plate at higher battery temperatures.
- During deep discharge or pole reversal, the microporous separator of GEL batteries helps to prevent short circuits by dendrite growth between the plates.
- The internal resistance of GEL batteries is higher as of AGM batteries at the beginning of their lives.

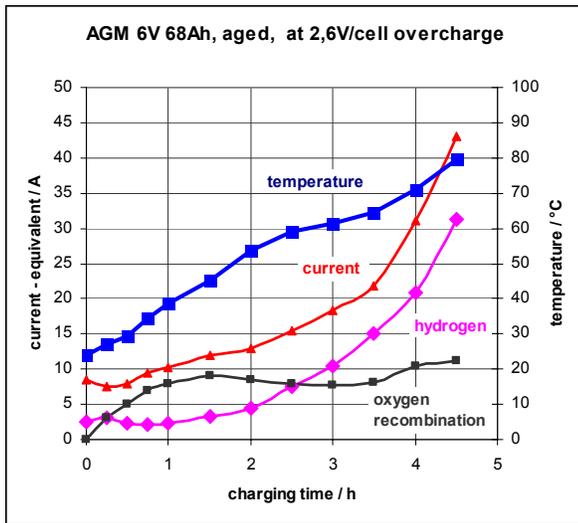


Fig. 11 Thermal run-away simulation of AGM

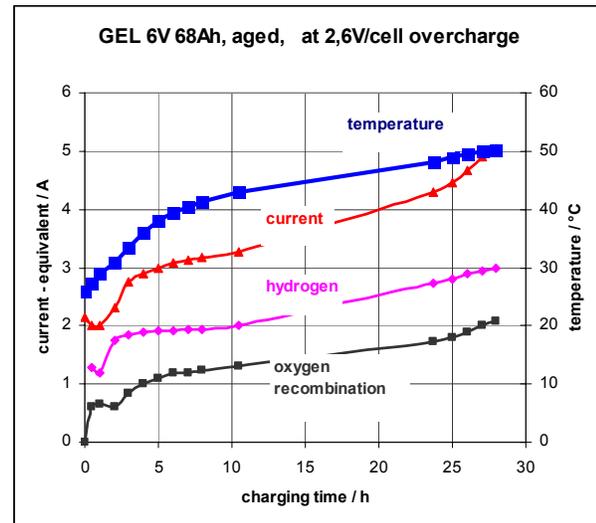


Fig. 12 Thermal run-away simulation of GEL

**The SiO<sub>2</sub> structure of the GEL is filled into the cell as SOL**

- The fixed electrolyte in the GEL system is filled in a liquid form into the cell. It can fill the gap between plates, even if the thickness tolerance is above 0,1mm. The ionic contact is secured in any case.
- Tubular plates get good contact around the whole tube. The advantages of the tubular plate is long life, low corrosion, and high cycle life [1].
- The fixed electrolyte can also cover the plate lugs and the pole straps, avoiding corrosion due to a shifted electrochemical potential.

## CONCLUSION

The different behaviour of AGM and GEL batteries can be attributed to the different electrolyte immobilisation. The SiO<sub>2</sub> – chains in AGM have a diameter of 1µm, while in GEL they have a diameter of 0,01µm. This factor 100 is mainly responsible for the different battery characteristics.

From a user's point of view, for a low cost UPS battery with an expected life of 5 to 10 years, the AGM battery is a good choice.

For applications where life times exceeding 10 years are expected, GEL batteries are the better choice. Flat plate GEL types are for high current discharges, and tubular plate types should be used for discharges of one hour or more. This allows a choice for different application and environmental conditions. Not only battery life time should be evaluated, but also the critical nature of the site, re: the cost for dropping the site from open circuit, should be taken into account.

For all high cycle applications (solar, load levelling etc.), the GEL batteries are best suited.

## REFERENCES

1. Rusch, W, Vassallo, K, Hart, H, BATTCON 2006, "Flooded, sealed, flat plate, tubular plate: How does the end user decide on the best solution?"
2. Fernandez, M, Batteries & Energy, Winter 2007, "VRLA batteries: An in-depth analysis of the oxygen cycle", 101-114
3. Berndt, D, Meißner, E, Rusch, W, "Aging effects in valve-regulated lead-acid batteries," 15. INTELEC 1993, Paris, Volume 2, 139 – 145