OVERVIEW OF SULPHATION AND ELECTROLYTE STRATIFICATION

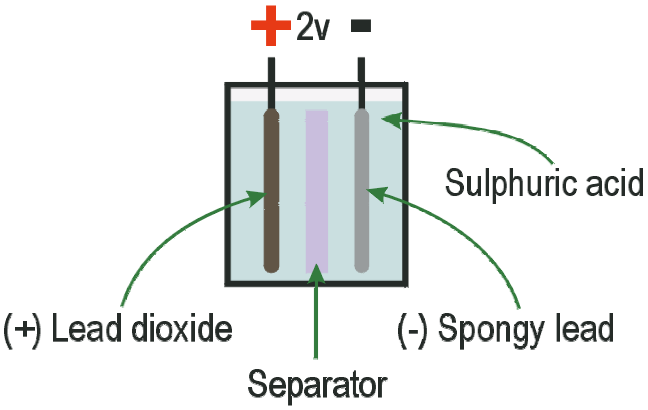
Sulphation and **electrolyte stratification** are the two principle avoidable causes of battery performance degradation. (In contrast, natural battery failure results from plate corrosion, the long-term consequence of the metal plate structure being immersed in an acidic electrolyte.)

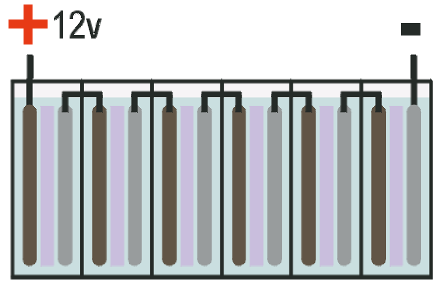
The problem of sulphation affects all types of automotive starter and deep-cycle lead-acid battery, whether of the flooded, sealed, VRLA, gel or AGM design. Electrolyte stratification occurs principally in both sealed and conventional flooded batteries. Both of these impairments can be prevented or reversed by taking the appropriate action.

First, a brief overview of the way lead acid batteries work:

BATTERY CONSTRUCTION

All lead acid batteries are created from 2v cells. Thus a 6v battery comprises 3 x 2v cells linked together internally; a 12v battery has 6 x 2v cells.





6 cells in a 12v battery

The voltage of each cell when fully charged is about 2.13v, or 12.8v for a 12v battery. Note that the precise voltage depends on temperature and trace elements in the battery's plates such as antimony (Sb), calcium (Ca) and silver (Ag).

The positive plate in a fully charged lead acid battery cell is made of lead dioxide (PbO_2), while the negative plate is made from a spongy form of lead (Pb). In between the plates is a separator which prevents the plates from touching while allowing electrolyte to pass through freely. The above diagrams are rather simplistic: in order to maximize the capacity (measured in amp-hours, or Ah) in the minimum case size, modern battery cells contain multiple plates packed tightly.

In the conventional flooded battery, both plates are surrounded by sulphuric acid (H_2SO_4), the electrolyte. As the battery discharges, both plates start converting to lead sulphate ($PbSO_4$) while the sulphuric acid converts into water (H_2O), diluting the electrolyte. The difference between starter, deep-cycle, flooded, sealed, VRLA, gel and AGM batteries is primarily one of construction. The basic chemistry of the lead-acid cell applies equally to all these battery types.

BATTERY STORAGE CAPACITY

The capacity of a battery to store charge is measured in ampere-hours (Ah), which defines the current in amps (A) that can be supplied for one hour until the battery runs flat. In reality, things are not that straightforward: the Ah value depends on the current drawn, and the temperature of the battery among other things. To avoid premature failure of a battery, it should not be discharged to more than 50% of its capacity. Expressed another way, the capacity required of a battery for a particular function should not exceed 0.5 x Ah rating.

BATTERY CURRENT CAPABILITY

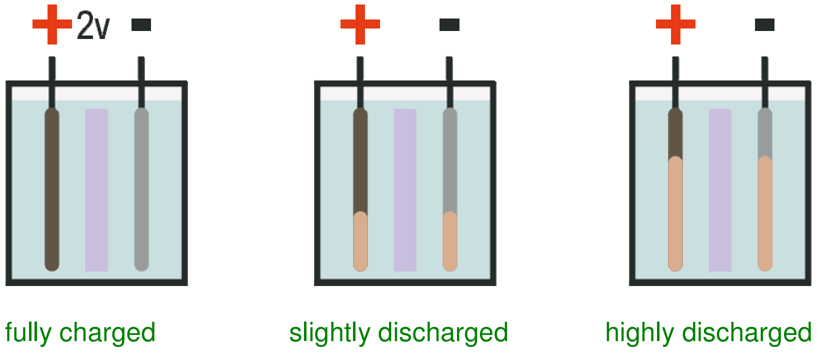
One of the characteristics defining a battery's performance is the maximum current that it can deliver over a given period of time. The cold cranking amps (CCA) is one such measure. The precise definition of CCA is

> "the amps that a battery can produce at –18°C for a 30-second period while maintaining a cell voltage of at least 1.2v".

Automotive starter batteries are usually rated this way, where the CCA rating provides an indication of the ability to power a starter motor on a diesel or petrol engine. Starter batteries are designed for short bursts of high current discharge followed by immediate recharging, whereas deep-cycle batteries are designed to withstand regular discharging over a prolonged period of time between charges.

SULPHATION

Sulphation is the name given to the build-up of normally irreversible lead sulphate crystals on the plates in a battery that adversely affect the performance of the cells.



As the battery is discharged, lead sulphate builds up on the plates, coloured brown in the above diagrams. If the battery is quickly recharged after use, nearly all the lead sulphate is changed back to the lead / lead dioxide of the fully charged battery. Usually some residual lead sulphate will remain on the battery plates, which over time builds up as a hard crystalline structure: this process is known as sulphation. The rate at which sulphation occurs depends on many factors, such as:

- How long the battery remains partially discharged after use
- The depth of discharge that occurs between recharging
- The temperature of the battery during use and when idle

EFFECTS OF SULPHATION

Reduction of Ah:

The $PbSO_4$ crystals comprising sulphation have been taken out of circulation, and therefore contribute nothing to the operation of the battery. In other words, they represent lost plate material, which means that there is less active lead / lead dioxide in the battery plates. This represents a reduction in the storage capacity (Ah) of the battery, which as a result will run down more quickly and require frequent charging.

Reduction of available current (CCA)

The $PbSO_4$ crystals comprising sulphation form an insulating layer around the battery plates. The more extensive this layer, the more limited is the maximum current that the battery can deliver. In severe cases of sulphation, the CCA rating can be reduced to very low values, for example 10% of the design value. The practical implication is that the battery is no longer capable of driving the loads for which it is required.

Sludge:

Lead sulphate ($PbSO_4$) is a relatively soft material; it falls out of the battery plates much more easily than lead / lead dioxide, forming the sludge often found collecting in the bottom of batteries.

The rate at which sludge forms depends on the degree of sulphation in a battery: the worse the sulphation the quicker sludge accumulates.

MINIMIZING SULPHATION

- Keeping the battery fully charged to reduce the build-up of lead sulphate
- Preventing high ambient temperatures during the life of the battery
- Using Megapulse to prevent the build-up of the hard crystalline lead sulphate

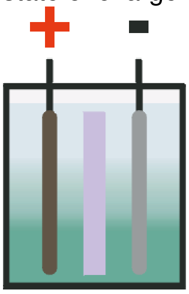
While the way a battery is used can minimize sulphation, it cannot be entirely prevented from occurring and will build up during the life of a battery.

THE BEST SOLUTION

By connecting Megapulse to a battery, the build-up of sulphation can be prevented over the life of the battery.

ELECTROLYTE STRATIFICATION

As a battery is discharged, the sulphuric acid is converted to water. H_2SO_4 is more dense than H_2O, so as a battery discharges, the electrolyte becomes less dense. This effect can be measured using a hydrometer: the height of the calibrated float shows the density (SG) of the electrolyte, hence the ratio of H_2SO_4 to H_2O. By inference, this indicates the state of charge of the battery, which is commonly what a hydrometer is used to determine.



As long as the acid and water components of the electrolyte are evenly mixed, the battery behaves as expected, but if the acid and water separate into layers, battery performance can be dramatically reduced. As mentioned above, acid is more dense than water; over time it will tend to accumulate at the bottom of the battery. Contributing factors to electrolyte stratification are:

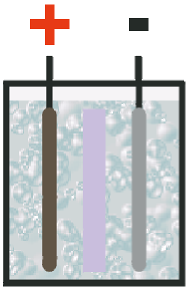
- Battery never being fully charged (i.e. always undercharged)
- Battery lying unused for extended periods

Stratification will occur more readily if the charging voltage is too low, and where the charging time is insufficient to replace the charge used up during the operation of the battery. Under-performing chargers and failing alternators can contribute significantly to this problem.

ELIMINATING ELECTROLYTE STRATIFICATION

Put simply, the water and acid need to be mixed up into a homogenous solution for proper battery operation.

Gassing:



One way to do this is by using an ***equalization charge***, which requires charging the battery at a voltage well above the gassing limit of 2.43v per cell (or 14.6v for a 12v battery). In practice, this means a voltage of around 2.6v per cell (or 15.6v for a 12v battery).

By allowing the battery to gas vigorously, the bubbles stir up the electrolyte creating the required homogenous solution.

Warning: *Only flooded cell batteries that can be topped up should be equalized. Never equalize gel, VRLA or AGM batteries.*

This process must be very carefully controlled as the elevated voltage will result in a higher-than-normal charging current, which will generate heat internally raising the temperature of the battery. Excess heat concentrated in the battery plates can cause mechanical damage - typically plate warping - which can lead to one or more shorting cells. Once mechanical damage has occurred, the battery has no value and must be replaced.

The gas generated during equalization is due to the electrolysis of the water in the electrolyte, producing hydrogen (H_2) and oxygen (O_2). The water used up in this way needs to be replaced to keep the electrolyte level constant. The gases themselves form a highly explosive mixture, so the process of equalization requires adequate ventilation and the elimination of all sources of ignition.

SOLUTION - Equalizing charger:

Use a multi-stage battery charger that applies an equalizing voltage every so often. With Megapulse controlling the sulphation, a short equalizing charge lasting 30 minutes or so applied every few months or after a given number of discharge cycles is usually all that is needed.

Vibration:

The natural vibration due to vehicle movement that occurs in automotive applications will go some way to preventing electrolyte stratification. However, excessive vibration such as found in the construction and mining industries can actually be harmful to a battery by increasing the production of sludge from lead sulphate within the battery.

By connecting Megapulse to a battery, the build-up of sulphation can be prevented, minimizing sludge formation.

It is interesting to speculate whether controlled, gentle vibration can be applied to a static battery to achieve the mixing of the electrolyte. This would be preferable to using an equalization charge which can overstress a battery and results in the emission of explosive gases. The vibration would have to be carefully applied to avoid causing internal mechanical damage and accelerating the production of sludge deposits.

Other techniques:

- Bubbling air through the battery using a pump and thin pipes - could be tricky to do.
- Draining then replacing the electrolyte would also eliminate stratification - could be an arduous task.

Battery problems are the most common in motor vehicles

German car manufacturers dominate in reliability for price and won 8 out of the top 10 spots (Source ADAC 2008). Of the breakdowns that occurred on 1.95 million in 2007 vehicles that are six years or less in age, the causes are as follows:

52% battery
15% flat tire
8% engine
7% wheels
7% fuel injection
6% heating & cooling
6% fuel system

A breakdown due to the battery remains the number one cause.

Acid stratification, a problem with luxury cars

A common cause of battery failure is acid stratification. The electrolyte on a stratified battery concentrates on the bottom, causing the upper half of the cell to be acid-poor. This effect is similar to a cup of coffee in which the sugar collects on the bottom when the waitress forgets to bring the stirring spoon. Batteries tend to stratify if kept at low charge (below 80%) and never have the opportunity to receive a full charge. Short distance driving while running windshield wiper and electric heaters contributes to this. Acid stratification reduces the overall performance of the battery.

Figure 1 illustrates a normal battery in which the acid is equally distributed form top to bottom. This battery provides good performance because the correct acid concentration surrounds the plates. Figure 2 shows a stratified battery in which the acid concentration is light on top and heavy on the bottom. A light acid limits plate activation, promotes corrosion and reduces performance. High acid concentration on the bottom, on the other hand, artificially raises the open circuit voltage. The battery appears fully charged but provides a low CCA. High acid concentration also promotes sulphation and decreases the already low conductivity further. If unchecked, such a condition will eventually lead to battery failure.

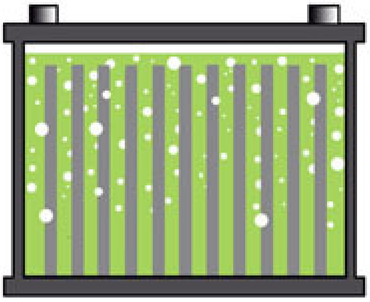


Figure 1: Normal battery

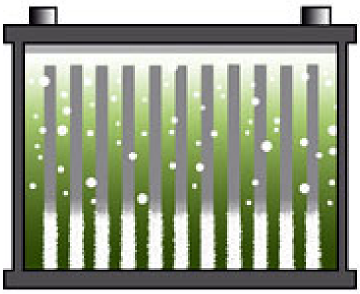


Figure 2: Stratified battery

The acid is equally distributed from the top to the bottom in the cell and provides maximum CCA and capacity.

The acid concentration is light on top and heavy on the bottom. High acid concentration artificially raises the open circuit voltage. The battery appears fully charged but has a low CCA. Excessive acid concentration induces sulphation on the lower half of the plates.

Allowing the battery to rest for a few days, applying a shaking motion or tipping the unit over tends to correct the problem. A topping charge by which the 12v battery is brought up to 16 volts for one to two hours also reverses the acid stratification. The topping charge also reduces sulphation caused by high acid concentration. Careful attention is needed to keep the battery from heating up and losing excessive electrolyte through hydrogen gassing. Always charge the battery in a well-ventilated room. Accumulation of hydrogen gas can lead to an explosion. Hydrogen is odourless and can only be detected with measuring devices.