What's All This Desulfator Stuff Anyhow?

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The following documents were captured from the 'net (links provided) and offered here as a relatively brief description of lead-acid battery functionality along with origins and effects of lead-sulfide (or sulfation) which cripples a battery and ultimately renders it useless.

There are countless examples of battery charger and maintenance products that claim to 'rejuvenate' a sulfated battery or mitigate sulfation of a battery in service. A search through published patents will yield a constellation of devices that claim to prevent or heal battery sulfation. Social and tech media discussion groups are known to discuss the merits of various desulfation products. The writer has observed the evolution of so-called battery desulfation techniques and philosophies for over 20 years. I explored these claims with true battery experts like the marketing and engineering personnel of Concorde Battery Corporation, a large supplier of lead-acid technologies to consumer, industrial and military battery markets. *To date, no such claim has proved to have merit.*

The most interesting feature of all those patents is the wide variation of characteristics of externally applied electrical stimulus claiming to 'break up' lead sulfide crystals. At the time of this writing, the author has yet to witness or discover any desulfation process demonstrably useful in correcting the effects of battery sulfation. A search on Amazon or eBay will yield many products that offer 'repair' or 'desulfation' features. Some with positive reviews numbering in the tens of thousands!

After reading through 100+ reviews, I got what I expected: Everybody talked about performance as a CHARGER; not as a device capable of resurrecting or healing a sulfate damaged battery. As of this date, I'm confident in the opinion that 'battery desulfation' is in the same category of art and science as hydrogen-oxygen generation for improved gas mileage or perpetual motion machines that power your house for free.

Having said that, no doubt there are many charter/maintainers that do a credible job of keeping a battery flight-ready in spite of long storage intervals. When evaluating a charger/maintainer product for suitability to your task, I suggest it's safe to ignore 'repair mode' or 'desulfation' features while concentrating on charge, top-off and sustain modes that prolong the service life of your battery.

I've captured a couple of articles that offer detailed inner and outer workings of lead-acid batteries. Most notable of the Battery University article is a frequent mention of the effects of sulfation while offering no support for the idea behind desulfation.

I encourage all readers to bookmark Battery University in their browser. <u>https://tinyurl.com/38eu8t83</u> Sadly, dearly departed Skip Koss of Concorde Battery is no longer a resource but Battery University is a very capable second-best! Bob . . .

Operation of Lead Acid Batteries

https://tinyurl.com/48r3nxbr

A lead acid battery consists of a negative electrode made of spongy or porous lead. The lead is porous to facilitate the formation and dissolution of lead. The positive electrode consists of lead oxide. Both electrodes are immersed in a electrolytic solution of sulfuric acid and water. In case the electrodes come into contact with each other through physical movement of the battery or through changes in thickness of the electrodes, an electrically insulating, but chemically permeable membrane separates the two electrodes. This membrane also prevents electrical shorting through the electrolyte. Lead acid batteries store energy by the reversible chemical reaction shown below.

The overall chemical reaction is:

$$PbO_2 + Pb + 2H_2SO_4 \stackrel{discharge}{\longleftrightarrow} 2PbSO_4 + 2H_2O_4$$

At the negative terminal the charge and discharge reactions are:

$$Pb + SO_4^{2-} \stackrel{discharge}{\longleftrightarrow} PbSO_4 + 2e^{-}$$

At the positive terminal the charge and discharge reactions are:

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \stackrel{discharge}{\longleftrightarrow} PbSO_4 + 2H_2O$$

As the above equations show, discharging a battery causes the formation of lead sulfate crystals at both the negative and positive terminals, as well as the release of electrons due to the change in valence charge of the lead. The formation of this lead sulfate uses sulfate from the sulfuric acid electrolyte surrounding the battery. As a result, the electrolyte becomes less concentrated. Full discharge would result in both electrodes being covered with lead sulfate and water rather than sulfuric acid surrounding the electrodes. At full discharge, the two electrodes are the same material, and there is no chemical potential or voltage between the two electrodes. In practice, however, discharging stops at the cutoff voltage, long before this point. The battery should not, therefore, be discharged below this voltage.

In between the fully discharged and charged states, a lead acid battery will experience a gradual reduction in the voltage. Voltage level is commonly used to indicate a battery's state of charge. The dependence of the battery on the battery state of charge is shown in the figure below. If the battery is left at low states of charge for extended periods of time, large lead sulfate crystals can grow, which permanently reduces battery capacity. These larger crystals are unlike the typical porous structure of the lead electrode, and are difficult to convert back into lead.



Voltage of lead acid battery upon charging.

The charging reaction converts the lead sulfate at the negative electrode to lead. At the positive terminal the reaction converts the lead to lead oxide. As a by-product of this reaction, hydrogen is evolved. During the first part of the charging cycle, the conversion of lead sulfate to lead and lead oxide is the dominant reaction. However, as charging proceeds and most of the lead sulfate is converted to either lead or lead dioxide, the charging current electrolyzes the water from the electrolyte and both hydrogen and oxygen gas are evolved, a process known as the "gassing" of the battery. If current is being provided to the battery faster than lead sulfate can be converted, then gassing begins before all the lead sulfate is converted, that is, before the battery is fully charged. Gassing introduces several problems into a lead acid battery. Not only does the gassing of the battery raise safety concerns, due to the explosive nature of the hydrogen produced, but gassing also reduces the water in the battery, which must be manually replaced, introducing a maintenance component into the system. In addition, gassing may cause the shedding of active material from the electrolyte, thereby permanently reducing battery capacity. For these reasons, the battery should not regularly be charged above the voltage which causes gassing. The gassing voltage changes with the charge rate.

Lead sulphate is an insulator, and therefore the way in which lead sulfate forms on the electrodes determined how easily the battery can be discharged.

BU-403: Charging Lead-Acid Batteries

https://tinyurl.com/2x8t3e54



The lead acid battery uses the constant current constant voltage (CCCV) charge method. A regulated current raises the terminal voltage until the upper charge voltage limit is reached, at which point the current drops due to saturation. The charge time is 12–16 hours and up to 36–48 hours for large

stationary batteries. With higher charge currents and multi-stage charge methods, the charge time can be reduced to 8–10 hours; however, without full topping charge. Lead acid is sluggish and cannot be charged as quickly as other battery systems. (See <u>BU-202: New Lead Acid Systems</u>)

With the CCCV method, lead acid batteries are charged in three stages, which are [1] constant-current charge, [2] topping charge and [3] float charge. The constant-current charge applies the bulk of the charge and takes up roughly half of the required charge time; the topping charge continues at a lower charge current and provides saturation, and the float charge compensates for the loss caused by self-discharge.

During the constant-current charge, the battery charges to about 70 percent in 5–8 hours; the remaining 30 percent is filled with the slower topping charge that lasts another 7–10 hours. The topping charge is essential for the well-being of the battery and can be compared to a little rest after a good meal. If continually deprived, the battery will eventually lose the ability to accept a full charge and the performance will decrease due to <u>sulfation</u>. The float charge in the third stage maintains the battery at full charge. **Figure 1** illustrates these three stages.



Figure 1: Charge stages of a lead acid battery [1]

The battery is fully charged when the current drops to a set low level. The float voltage is reduced. Float charge compensates for self-discharge that all batteries exhibit.

The switch from Stage 1 to 2 occurs seamlessly and happens when the battery reaches the set voltage limit. The current begins to drop as the battery starts to saturate; full charge is reached when the current decreases to 3–5 percent of the Ah rating. A battery with high leakage may never attain this low saturation current, and a plateau timer takes over to end the charge.

The correct setting of the charge voltage limit is critical and ranges from 2.30V to 2.45V per cell. Setting the voltage threshold is a compromise and battery experts refer to this as "dancing on the head of a pin." On one hand, the battery wants to be fully charged to get maximum capacity and avoid sulfation on the negative plate; on the other hand, over-saturation by not switching to float charge causes grid corrosion on the positive plate. This also leads to gassing and water-loss.

Temperature changes the voltage and this makes "dancing on the head of a pin" more difficult. A warmer ambient requires a slightly lower voltage threshold and a colder temperature prefers a higher setting. Chargers exposed to

temperature fluctuations include temperature sensors to adjust the charge voltage for optimum charge efficiency. (See <u>BU-410: Charging at High and Low Temperatures</u>)

The charge temperature coefficient of a lead acid cell is $-3mV/^{\circ}C$. Establishing 25°C (77°F) as the midpoint, the charge voltage should be reduced by 3mV per cell for every degree above 25°C and increased by 3mV per cell for every degree below 25°C. If this is not possible, it is better to choose a lower voltage for safety reasons. **Table 2** compares the advantages and limitations of various peak voltage settings.

	2.30V to 2.35V/cell	2.40V to 2.45V/cell
Advantages	Maximum service life; battery stays cool; charge temperature can exceed 30°C (86°F).	Higher and more consistent capacity readings; less sulfation.
Limitations	Slow charge time; capacity readings may be inconsistent and declining with each cycle. Sulfation may occur without equalizing charge.	Subject to corrosion and gassing. Needs water refill. Not suitable for charging at high room temperatures, causing severe overcharge.

Table 2: Effects of charge voltage on a small lead acid battery

Cylindrical lead acid cells have higher voltage settings than VRLA and starter batteries.

Once fully charged through saturation, the battery should not dwell at the topping voltage for more than 48 hours and must be reduced to the float voltage level. This is especially critical for sealed systems because they are less tolerant to overcharge than the flooded type. Charging beyond the specified limits turns redundant energy into heat and the battery begins to gas.

The recommended float voltage of most flooded lead acid batteries is 2.25V to 2.27V/cell. Large stationary batteries at 25°C (77°F) typically float at 2.25V/cell. Manufacturers recommend lowering the float charge when the ambient temperature rises above 29°C (85°F).

Figure 3 illustrate the life of a lead acid battery that is kept at a float voltage of 2.25V to 2.30V/cell and at a temperature of 20°C to 25°C (60°F to 77°F). After 4 years of operation permanent capacity losses become visible, crossing the 80 percent line. This loss is larger if the battery requires periodic deep discharges. Elevated heat also reduces battery life. (See also <u>BU-806a: How Heat and Loading affect Battery Life</u>)



Figure 3: Capacity loss on standby ^[2]

Permanent capacity loss can be minimized with operating at a moderate room temperature and a float voltage of 2.25–2.30V/cell.

Not all chargers feature float charge and very few road vehicles have this provision. If your charger stays on topping charge and does not drop below 2.30V/cell, remove the charge after 48 hours of charging. Recharge every 6 months while in storage; <u>AGM</u> every 6–12 months.

These described voltage settings apply to flooded cells and batteries with a pressure relief valve of about 34kPa (5psi). Cylindrical sealed lead acid, such as the Hawker Cyclon cell, requires higher voltage settings and the limits should be set to manufacturer's specifications. Failing to apply the recommended voltage will cause a gradual decrease in capacity due to sulfation. The Hawker Cyclon cell has a pressure relief setting of 345kPa (50psi). This allows some recombination of the gases generated during charge.

Aging batteries pose a challenge when setting the float charge voltage because each cell has its own unique condition. Connected in a string, all cells receive the same charge current and controlling individual cell voltages as each reaches full capacity is almost impossible. Weak cells may go into overcharge while strong cells remain in a starved state. A float current that is too high for the faded cell might sulfate the strong neighbor due to undercharge. Cell-balancing devices are available compensate for the differences in voltages caused by cell imbalance.

Ripple voltage also causes a problem with large stationary batteries. A voltage peak constitutes an overcharge, causing hydrogen evolution, while the valley induces a brief discharge that creates a starved state resulting in electrolyte depletion. Manufacturers limit the ripple on the charge voltage to 5 percent.

Much has been said about pulse charging of lead acid batteries to reduce sulfation. The results are inconclusive and manufacturers as well as service technicians are divided on the benefit. If sulfation could be measured and the right amount of pulsing applied, then the remedy could be beneficial; however giving a cure without knowing the underlying side effects can be harmful to the battery.

Most stationary batteries are kept on float charge and this works reasonably well. Another method is the *hysteresis charge* that disconnects the float current when the battery goes to standby mode. The battery is essentially put in storage and is only "borrowed" from time to time to apply a topping-charge to replenish lost energy due to self-discharge, or when a load is applied. This mode works well for installations that do not draw a load when on standby.

Lead acid batteries must always be stored in a charged state. A topping charge should be applied every 6 months to prevent the voltage from dropping below 2.05V/cell and causing the battery to sulfate. With <u>AGM</u>, these requirements can be relaxed.

Measuring the open circuit voltage (OCV) while in storage provides a reliable indication as to the state-of-charge of the battery. A cell voltage of 2.10V at room temperature reveals a charge of about 90 percent. Such a battery is in good condition and needs only a brief full charge prior to use. (See also <u>BU-903: How to Measure State-of-charge</u>)

Observe the storage temperature when measuring the open circuit voltage. A cool battery lowers the voltage slightly and a warm one increases it. Using OCV to estimate state-of-charge works best when the battery has rested for a few hours, because a charge or discharge agitates the battery and distorts the voltage.

Some buyers do not accept shipments of new batteries if the OCV at incoming inspection is below 2.10V per cell. A low voltage suggests a partial charge due to long storage or a high self-discharge caused by a micro-short. Battery users have found that a pack arriving at a lower than specified voltage has a higher failure rate than those with higher voltages. Although in-house service can often bring such batteries to full performance, the time and equipment required adds to operational costs. (Note that the 2.10V/cell acceptance threshold does not apply to all lead acid types equally.)

Under the right temperature and with sufficient charge current, lead acid provides high charge efficiently. The exception is charging at 40°C (104°F) and low current, as **Figure 4** demonstrates. In respect of high efficiency, lead acid shares this fine attribute with Li-ion that is closer to 99%. See <u>BU-409: Charging Lithium-ion</u> and <u>BU-808b:</u> <u>What Causes Li-ion to Die?</u>



Figure 4: Charge efficiency of the lead acid battery ^[2]

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Argument about Fast-charging

Manufacturers recommend a charge <u>C-rate</u> of 0.3C, but lead acid can be charged at a higher rate up to 80% state-ofcharge (SoC) without creating oxygen and water depletion. Oxygen is only generated when the battery is overcharged. The 3-stage CCCV charger prevents this from happening by limiting the charge voltage to 2.40V/cell (14.40V with 6 cells) and then lowering to a float charge about 2.30V/cell (13.8V with 6 cells) at full-charge. These are voltages below the gassing stage.

Test show that a heathy lead acid battery can be charged at up to 1.5C as long as the current is moderated towards a full charge when the battery reaches about 2.3V/cell (14.0V with 6 cells). Charge acceptance is highest when SoC is low and diminishes as the battery fills. Battery state-of-health and temperature also play an important role when fast-charging. Make certain that the battery does not "boil" or heat up during charge. Put an eye on the battery when charging above the manufacturer's recommended C-rate.

Watering

Watering is the single most important step in maintaining a flooded lead acid battery; a requirement that is all too often neglected. The frequency of watering depends on usage, charge method and operating temperature. Over-charging also leads to water consumption.

A new battery should be checked every few weeks to estimate the watering requirement. This assures that the top of the plates are never exposed. A naked plate will sustain irreversible damage through oxidation, leading to reduced capacity and lower performance.

If low on electrolyte, immediately fill the battery with distilled or de-ionized water. Tap water may be acceptable in some regions. Do not fill to the correct level before charging as this could cause an overflow during charging. Always top up to the desired level after charging. Never add electrolyte as this would upset the specific gravity and promote corrosion. Watering systems eliminate low electrolyte levels by automatically adding the right amount of water.

Simple Guidelines for Charging Lead Acid Batteries

- Charge in a well-ventilated area. Hydrogen gas generated during charging is explosive. (See <u>BU-703:</u> <u>Health Concerns with Batteries</u>)
- Choose the appropriate charge program for flooded, gel and AGM batteries. Check manufacturer's specifications on recommended voltage thresholds.
- Recharge lead acid batteries after each use to prevent sulfation. Do not store on low charge.
- The plates of flooded batteries must always be fully submerged in electrolyte. Fill the battery with distilled or de-ionized water to cover the plates if low. Never add electrolyte.
- Fill water level to designated level *after* charging. Overfilling when the battery is on low charge can cause acid spillage during charging.
- The formation of gas bubbles in a flooded lead acid indicates that the battery is reaching full state-ofcharge. (Hydrogen appears on negative plate and oxygen on positive plate).
- Lower the float charge voltage if the ambient temperature is higher than 29°C (85°F)..
- Do not allow a lead acid to freeze. An empty battery freezes sooner than one that is fully charged. Never charge a frozen battery.
- Avoid charging at temperatures above 49°C (120°F).

References

^[1] Courtesy of Cadex

^[2] Source: Power-Sonic

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