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**The history of the lead acid battery has been one of constant improve-ments — very rarely has it been in huge leaps forward but mostly it’s been slow and steady modifications. Or that was until the VRLA battery arrived and the challenges it threw up. By David Rand**

**Moving on from one iteration to the next in lead battery performance**

Gustave Planté’s invention of the lead acid battery came at an opportune time, the availability of industrial-scale electricity was accompanied by a rapid expansion in lead acid manufacture.

A decisive step in the commerciali-zation of the lead acid battery was made by Camille Alphonse Faure who, in 1880, coated the lead sheets with a paste of lead oxides, sulfuric acid and water.

On curing the plates at a warm tem-perature in a humid atmosphere, the paste changed to a mixture of basic lead sulfates which adhered to the lead electrode. During charging the cured paste was converted into elec-trochemically active material (or the active mass) and thereby gave a sub-stantial increase in capacity compared with the Planté cell.

Soon the idea developed of cut-ting rectangular holes out of the lead plates to lighten their weight and also to provide receptacles into which the paste could be packed. So was born the modern pasted-plate battery which is by far the most common type of lead acid battery in use today.

The first major market was for stand-by batteries to provide emer-gency power to essential equipment in electricity-generating stations and at other critical sites. For such large battery applications, it is notable that no other battery chemistry has been able to compete on cost grounds with the lead acid system. Towards the end of the 19th century, electric cars ap-peared on the roads and were pow-ered mostly by lead acid.

Batteries also began to be used for illumination in railway coaches as well as for powering railway signal-ling systems, the electrical equipment of ships, and radio receiving-transmit-ting equipment. With the advent of the internal-combustion engine, the lead acid battery was first employed in road vehicles for lighting, then later also for engine starting, and now ad-ditionally for the whole range of elec-trical duties expected in the modern vehicle.

The market for off-road traction batteries has also expanded and in al-most all cases it is the lead acid system that predominates when the require-ment is for stored energy of more than a few hundred watt-hours.

By 1910, the construction of lead acid batteries involved the use of an asphalt-coated and sealed wooden container, wooden separators, thick plates, and inter-cell connections made through the cover by the use of heavy lead posts and links.

The first important change came in the early 1920s when the more acid-resistant, hard rubber case was devel-oped and came into use. During the next 30 years, basic battery construc-tion changed little, although active-material performance was enhanced through the use of additives and through raw material improvements.

Significant advances were also made in grid technology — it’s worth not-ing that in 1881, J Scudamore Sellon had demonstrated the appreciable me-chanical and electrochemical benefits to be gained by replacing the pure-lead grids of Faure plates with lead antimony counterparts).

Increases in the efficiency of the man-ufacturing process were also achieved during this period, especially following the introduction of machine pasting of plates. During the late 1950s, one-piece covers that were epoxy sealed to the cases were introduced. The case and cover material, however, remained hard rubber and inter-cell connections were still made through the cover.

Lower-resistance separators, which were made of phenolicresin-impreg-nated cellulose fibre, also came into use and obviously raised the electrical performance of cells. Machine stacking of battery plates became common and thereby reduced the level of manual labour involved in battery manufacture.

In the early 1960s, a method was de-vised for automatically joining plates of the same polarity within a cell element. Simultaneously, a technique for connecting the cells within a battery in series through the cell walls was devel-ped. This markedly reduced both the internal resistance of the battery and the amount of connecting or ‘top’ lead needed.

Major advances were also made in plate design and production techniques that gave rise to more efficient batteries with high specific power. In the late 1960s, the injection-moulded polypro-pylene case and cover were introduced and gave the lead acid battery a dura-ble, thin wall, lightweight container.

Moreover, the thin outside walls and cell partitions permitted the use of more active material without increas-ing the external weight or volume of the battery. Finally, the performance and life of the batteries were both enhanced through the availability of low-resistance, highly durable, plastic separators.

Meanwhile, a technological explo-sion was waiting in the wings. Classical lead acid batteries are flooded systems. That is, the electro-lyte medium is a free liquid to a level above the top of the plates and above the busbars. This has the disadvan-tage that the cells have to be vented to release the gases liberated during charging, namely, oxygen at the posi-tive electrode and hydrogen at the negative.

As a consequence, not only is water lost (and thus has to be replaced by reg-ular maintenance operation), but also the battery may be used only in the up-right position, otherwise leakage of the sulfuric acid solution takes place.

Also, the released gases carry a very fine mist of sulfuric acid that is highly corrosive. Thus efforts were made to develop sealed batteries that would not require topping up with water and would be safe under all conditions of use and abuse. At first, such attempts revolved around the catalytic recombination of the gases within the battery, but this idea proved to be impractical.

Success came, however, with the in-vention of the valve-regulated lead acid (VRLA) battery. The first commercial units were introduced by Sonnenschein in the late 1960s and by Gates Energy Products in the early 1970s.

These were, respectively, the gel and absorptive glass mat (AGM) technolo-gies. In the VRLA design, oxygen evolved during charging transfers through a gas space to the negative electrode where it is reduced (recombined) back to water.

This process is known as the in-ternal oxygen-recombination cycle. There are two alternative techniques for providing the gas space. One cell design has the electrolyte immobilized as a gel; the other has the electrolyte held within an AGM separator. Gas passes through fissures in the gel, or through channels in the AGM.

A corresponding recombination cycle for hydrogen is not possible because oxidation of the gas at the positive electrode is far too slow. This feature, together with the fact that oxygen recombination is not com-plete (the efficiency is typically 93% to 99%), requires each cell to be fitted with a one-way valve as a safeguard against excessive pressure build-up — hence, the term valve-regulated.

The VRLA battery can be employed in any orientation, and thus gives equipment design engineers a much greater degree of flexibility. Antimony is not included in the grid alloys of VRLA cells because this element low-ers the hydrogen over-potential and therefore encourages gassing at the negative electrode during charging.

Care must be taken against the intro-duction of other elements that might act similarly. Today, lead calcium tin alloys are preferred by manufacturers of VRLA batteries for float duties, and lead tin for cycling applications. Initially, there was a vexatious prob-lem to be solved, namely, the propen-sity of batteries employing non-anti-monial grids to suffer a rapid loss of capacity early in the projected life of the cell, particularly under deep-dis-charge conditions.

It was found that the adverse be-haviour, loosely termed the ‘anti-monyfree effect’, originated from the positive plate. Given the serious commercial ramifications of the ef-fect, both the lead suppliers and the battery industry soon recognized the need for a consolidated programme, coupled with a forum for the global exchange of ideas on how to eliminate the problem.

This prompted the successive for-mation of the Asian Battery Confer-ence in 1986 (organized by the Aus-tralian lead industry), the European Lead Battery Conference in 1988 (organized by the Lead Development Association, LDA), and the LABAT Conference in 1989 (organized by the Bulgarian Academy of Sciences) — all of which continue to this day.

The knowledge and advice gathered via the scientific and technological network that evolved from the above three conferences proved invaluable to the International Lead-Zinc Research Organization (ILZRO) in establishing the Advanced Lead Acid Battery Con-sortium — ALABC — in March 1992.

Its prime purpose was to combat the threat from the alternative battery sys-tems that were to be developed under the management of the US Advanced Battery Consortium (USABC) follow-ing legislation in California for the im-plementation of zero-emission vehicles (ZEVs). The battery specifications for such vehicles were set by the USABC and included a target life of 500 cycles under the Simplified Federal Urban Driving Schedule (SFUDS) — a performance that VRLA batteries could not achieve at that time.

Consequently, in 1992, a joint ILZ-RO LDA meeting was held during the Third European Lead Battery Confer-ence to develop a consolidated strategy in search of a remedy for the antimo-nyfree effect (which had, in fact, first been diagnosed by Jeanne Burbank way back in 1964!

Since it had been found that batter-ies using lead-antimony alloys with antimony contents < 2 wt.% were also subject to the phenomenon, it was de-cided to refer to the effect as premature capacity loss (PCL), a term that had been recommended by CSIRO’s Tony Hollenkamp in the previous year. The ALABC subsequently formed a PCL Study Group, which first met at the Second LABAT Conference in 1993.

After robust discussion, the compet-ing theories of PCL were defined and grouped under two categories, namely:
• PCL-1, caused by deleterious events at the positive grid | active-material interface;
• PCL-2, caused by gradual inactiva-tion of the active-material itself.
Eventually, a unified explanation of PCL was developed, in which capac-ity loss falls on a continuous scale. The position where a cell lies on this scale is determined by the rate and location at which the connectivity of the active material (ie the apparent density) de-clines to the critical value where con-ductivity is compromised.

The final key to solving the PCL puz-zle, therefore, was to squeeze more life into cells via a controlled level of separator compression to minimize positive-plate expansion. Apparatus such as the CSIRO piston cell was developed to determine the optimum conditions for a given type of AGM separator.

The results of the studies, together with other improvements in cell design, enabled VRLA batteries to meet cycle-life targets. Thus, in 1995, Pat Moseley, the manager of the ALABC, was able to state confidently that: “PCL is in re-treat.”



**BU-201: How does the Lead Acid Battery Work?**

**Learn about the differences within the lead acid family and find out what the cons and pros are.**

Invented by the French physician Gaston Planté in 1859, lead acid was the first rechargeable battery for commercial use. Despite its advanced age, the lead chemistry continues to be in wide use today. There are good reasons for its popularity; lead acid is dependable and inexpensive on a cost-per-watt base. There are few other batteries that deliver bulk power as cheaply as lead acid, and this makes the battery cost-effective for automobiles, golf cars, forklifts, marine and uninterruptible power supplies (UPS).

The grid structure of the lead acid battery is made from a lead alloy. Pure lead is too soft and would not support itself, so small quantities of other metals are added to get the mechanical strength and improve electrical properties. The most common additives are antimony, calcium, tin and selenium. These batteries are often known as “lead-antimony” and “lead­calcium.”

Adding antimony and tin improves deep cycling but this increases water consumption and escalates the need to [equalize](http://batteryuniversity.com/learn/article/equalizing_charge). Calcium reduces self-discharge, but the positive lead-calcium plate has the side effect of growing due to grid oxidation when being over-charged. Modern lead acid batteries also make use of doping agents such as selenium, cadmium, tin and arsenic to lower the antimony and calcium content.

Lead acid is heavy and is less durable than nickel- and lithium-based systems when deep cycled. A full discharge causes strain and each discharge/charge cycle permanently robs the battery of a small amount of capacity. This loss is small while the battery is in good operating condition, but the fading increases once the performance drops to half the nominal capacity. This wear-down characteristic applies to all batteries in various degrees.

Depending on the depth of discharge, lead acid for deep-cycle applications provides 200 to 300 discharge/charge cycles. The primary reasons for its relatively short cycle life are grid corrosion on the positive electrode, depletion of the active material and expansion of the positive plates. This aging phenomenon is accelerated at elevated operating temperatures and when drawing high discharge currents. (See [BU-804:How to Prolong Lead Acid Batteries](http://batteryuniversity.com/learn/article/how_to_restore_and_prolong_lead_acid_batteries))

Charging a lead acid battery is simple, but the correct voltage limits must be observed. Choosing a low voltage limit shelters the battery, but this produces poor performance and causes a buildup of sulfation on the negative plate. A high voltage limit improves performance but forms grid corrosion on the positive plate. While sulfation can be reversed if serviced in time, corrosion is permanent. (See [BU-403: Charging Lead Acid](http://batteryuniversity.com/learn/article/charging_the_lead_acid_battery).)

Lead acid does not lend itself to fast charging and with most types, a full charge takes 14–16 hours. The battery must always be stored at full state-of-charge. Low charge causes sulfation, a condition that robs the battery of performance. Adding carbon on the negative electrode reduces this problem but this lowers the specific energy. ( See [BU-202: New Lead Acid Systems](http://batteryuniversity.com/learn/article/new_lead_acid_systems). )

Lead acid has a moderate life span, but it is not subject to memory as nickel-based systems are, and the charge retention is best among rechargeable batteries. While NiCd loses approximately 40 percent of their stored energy in three months, lead acid self-discharges the same amount in one year. The lead acid battery works well at cold temperatures and is superior to lithium-ion when operating in subzero conditions.

**Sealed Lead Acid**

The first sealed, or maintenance-free, lead acid emerged in the mid-1970s. Engineers argued that the term “sealed lead acid” was a misnomer because no lead acid battery can be totally sealed. To control venting during stressful charge and rapid discharge, valves have been added that release gases if pressure builds up. Rather than submerging the plates in a liquid, the electrolyte is impregnated into a moistened separator, a design that resembles nickel- and lithium-based systems. This enables operating the battery in any physical orientation without leakage.

The sealed battery contains less electrolyte than the flooded type, hence the term “acid-starved.” Perhaps the most significant advantage of sealed lead acid is the ability to combine oxygen and hydrogen to create water and prevent dry out during cycling. The recombination occurs at a moderate pressure of 0.14 bar (2psi). The valve serves as a safety vent if the gas buildup rises. Repeated venting should be avoided as this will lead to an eventual dry-out.

Several types of sealed lead acid have emerged and the most common are *gel*, also known as *valve-regulated lead acid* (VRLA), and *absorbent glass mat*(AGM). The gel cell contains a silica type gel that suspends the electrolyte in a paste. Smaller packs with capacities of up to 30Ah are often called SLA (sealed lead acid). Packaged in a plastic container, these batteries are used for small UPS, emergency lighting and wheelchairs. Because of low price, dependable service and low maintenance, the SLA remains the preferred choice for healthcare in hospitals and retirement homes. The larger VRLA is used as power backup for cellular repeater towers, Internet hubs, banks, hospitals, airports and more.

The [AGM](http://batteryuniversity.com/learn/article/absorbent_glass_mat_agm) suspends the electrolyte in a specially designed glass mat. This offers several advantages to lead acid systems, including faster charging and instant high load currents on demand. AGM works best as a mid-range battery with capacities of 30 to 100Ah and is less suited for large systems, such as UPS. Typical uses are starter batteries for motorcycles, start-stop function for micro-hybrid cars, as well as marine and RV that need some cycling.

With cycling and age, the capacity of AGM fades gradually; gel, on the other hand, has a dome shaped performance curve and stays in the high performance range longer but then drops suddenly towards the end of life. AGM is more expensive than flooded, but is cheaper than gel. (Gel would be too expensive for start/stop use in cars.)

Unlike the flooded, the sealed lead acid battery is designed with a low over-voltage potential to prohibit the battery from reaching its gas-generating potential during charge. Excess charging causes gassing, venting and subsequent water depletion and dry-out. Consequently, gel, and in part also AGM, cannot be charged to their full potential and the charge voltage limit must be set lower than that of a flooded. This also applies to the float charge on full charge. In respect to charging, the gel and AGM are no direct replacements for the flooded type. If no designated charger is available for AGM with lower voltage settings, disconnect the charger after 24 hours of charge. This prevents gassing due to a float voltage that is set too high. ( See [BU-403: Charging Lead Acid](http://batteryuniversity.com/learn/article/charging_the_lead_acid_battery) )

The optimum operating temperature for a VRLA battery is 25°C (77°F); every 8°C (15°F) rise above this temperature threshold cuts battery life in half. ( See [BU-806a: How Heat and Loading affect Battery Life](http://batteryuniversity.com/learn/article/how_heat_and_harsh_loading_reduces_battery_life) ) Lead acid batteries are rated at a 5-hour (0.2C) and 20-hour (0.05C) discharge rate. The battery performs best when discharged slowly; the capacity readings are substantially higher at a slower discharge than at the [1C-rate](http://batteryuniversity.com/learn/article/what_is_the_c_rate). Lead acid can, however, deliver high pulse currents of several C if done for only a few seconds. This makes the lead acid well suited as a starter battery, also known as starter-light-ignition (SLI). The high lead content and the sulfuric acid make lead acid environmentally unfriendly.

Lead acid batteries are commonly classified into three usages: Automotive (starter or SLI), motive power (traction or deep cycle) and stationary (UPS).

**Starter and Deep-cycle Batteries**

The starter battery is designed to crank an engine with a momentary high-power load lasting a second or so. For its size, the battery is able to deliver high current but it cannot be deep-cycled. Starter batteries are rated with Ah or RS (reserve capacity) to indicate energy storage capability, as well as CCA (cold cranking amps) to signify the current a battery can deliver at cold temperature. SAE J537 specifies 30 seconds of discharge at –18°C (0°F) at the rated CCA ampere without the battery voltage dropping below 7.2 volts. RC reflects the runtime in minutes at a steady discharge of 25. (SAE stands for Society of Automotive Engineers.) See also[BU-902a: How to Measure CCA](http://batteryuniversity.com/learn/article/how_to_measure_cca_cold_cranking_amp).

Starter batteries have a very low internal resistance that is achieved by adding extra plates for maximum surface area (Figure 1). The plates are thin and the lead is applied in a sponge-like form that has the appearance of fine foam, expanding the surface area further. Plate thickness, which is important for a deep-cycle battery is less important because the discharge is short and the battery is recharged while driving; the emphasis is on power rather than capacity.

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| http://batteryuniversity.com/_img/content/40-1.jpg | **Figure 1: Starter battery**The starter battery has many thin plates in parallel to achieve low resistance with high surface area. The starter battery does not allow deep cycling.Courtesy of Cadex |

**Deep-cycle Battery**

The deep-cycle battery is built to provide continuous power for wheelchairs, golf cars, forklifts and more. This battery is built for maximum capacity and a reasonably high cycle count. This is achieved by making the lead plates thick (Figure 2). Although the battery is designed for cycling, full discharges still induce stress and the cycle count relates to the depth-of-discharge (DoD). Deep-cycle batteries are marked in Ah or minutes of runtime. The capacity is typically rated as a 5-hour and 20-hour discharge.

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| http://batteryuniversity.com/_img/content/40-2.jpg | **Figure 2: Deep-cycle battery**The deep-cycle battery has thick plates for improved cycling abilities. The deep-cycle battery generally allows about 300 cycles.Courtesy of Cadex |

A starter battery cannot be swapped with a deep-cycle battery or vice versa. While an inventive senior may be tempted to install a starter battery instead of the more expensive deep-cycle on his wheelchair to save money, the starter battery would not last because the thin sponge-like plates would quickly dissolve with repeated deep cycling.

There are combination starter/deep-cycle batteries available for trucks, buses, public safety and military vehicles, but these units are big and heavy. As a simple guideline, the heavier the battery is, the more lead it contains, and the longer it will last. Table 3 compares the typical life of starter and deep-cycle batteries when deep cycled.

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| --- | --- | --- |
| **Depth of discharge** | **Starter battery** | **Deep-cycle battery** |
| 100%50%30% | 12–15 cycles100–120 cycles130–150 cycles | 150–200 cycles400–500 cycles1,000 and more cycles |

**Table 3: Cycle performance of starter and deep-cycle batteries.**A discharge of 100% refers to a full discharge; 50% is half and 30% is a moderate discharge with 70% remaining.

Lead is toxic and environmentalists would like to replace the lead acid battery with an alternative chemistry. Europe succeeded in keeping NiCd out of consumer products, and similar efforts are being made with the starter battery. The choices are NiMH and Li-ion, but the price is too high and low temperature performance is poor. With a 99 percent recycling rate, the lead acid battery poses little environmental hazard and will likely continue to be the battery of choice.

Table 4 lists advantages and limitations of common lead acid batteries in use today. The table does not include the new lead acid chemistries. (See also [BU-202: New Lead Acid Systems](http://batteryuniversity.com/learn/article/new_lead_acid_systems).)

|  |  |
| --- | --- |
| **Advantages** | Inexpensive and simple to manufacture; low cost per watt-hourLow self-discharge; lowest among rechargeable batteriesHigh specific power, capable of high discharge currentsGood low and high temperature performance |
| **Limitations** | Low specific energy; poor weight-to-energy ratioSlow charge; fully saturated charge takes 14-16 hoursMust be stored in charged condition to prevent sulfationLimited cycle life; repeated deep-cycling reduces battery lifeFlooded version requires wateringTransportation restrictions on the flooded typeNot environmentally friendly |

**Table 4: Advantages and limitations of lead acid batteries**. Dry systems have advantages over flooded but are less rugged.

Battery History Lead / Acid

In 1859, Gaston Plante realized the lead accumulator by forming sheets of pure lead in sulfuric acid under the influence of an electric current. It was only in 1880 that the dynamo Gramme was achieved and the oxide battery grid   was also  realized   so that the battery industry starts to develop.

Even though the study of the lead accumulator dates back to 150 years ago, however it can never be considered as an outdated product, It continues to be the core of various research. T he battery is still well - sold. The main reasons for this popularity are not  only the low cost and the maturity of the technology, but also its ability to be recycled (more than 97%.)

Today there are more than one type of battery lead that better meet the necessary specific applications: the lead- battery has improved and specialized over the years, and it still continues to develop.

The battery lead is mainly used for the vehicles ï¿½moving off (currently the most important sector), traction (trolleys), rescue equipments, photovoltaic ...

As far as these sectors are concerned we relied on the lead battery technology, which are characterized in particular by the thickness and alloy grids, liquid or immobilized electrolyte, and the electrolyte concentration, flat or tubular plates...

The global market for batteries (all technologies) includes three categories: laptop, starting and industrial batteries (traction and stationary).

**ELEMENT, BATTERY :**

An element is an electrochemical couple (2 electrodes) immersed in a solution.

According to some technologies, this couple can be {NiOOH / Cd} for nickel-cadmium batteries, the Li {/} metal oxide for lithium-ion batteries, PbO2/Pb {} for lead-acid batteries, and has a different electromotive force. The term semi-element refers to a half-cell electrode.

The term accumulator refers to a reloadable element which is not the same as the pile ( non-reloadable).

A battery is a reversible generator: it can store energy, changing the electric energy into a chemical shape then release it when asked for.

A 2- volt tension lead- battery is rarely used alone. It is  grouped either  in series or in parallel to get  the voltage and desired capacity for use, which make us have battery 2  For example, the starter battery of a thermal vehicle has  "12V" to indicate that it consists of  six batteries, even if the actual motor electromotive force is rather in the range {12.5, 13V}. For backup systems, a standard 48V battery is enough.

**CONSTITUTION OF THE LEAD BATTERY :**

A- 2V accumulator is the basic unit of a lead battery. It consists of positive and negative electrodes, a micro porous separator and electrolyte.

An element of a starter up battery (open lead technology ") includes positive flat plate (2) and negative (1) joined alternately. The platesï¿½ number for each polarity and its surface are the parameters which define the elementï¿½s capacity.

The positive electrode, for instance, comprises four parallel plates joined through a connector (4). A micro porous insulating separator is placed between the plates during assembly (3) in order to avoid short circuits between plates of different polarity.

The positive and negative plates are assembled into bundles (6) and immersed in a solution of sulfuric acid and distilled water. Each bundle  is thus an element.

***Sectional view of an open lead (starter battery)***

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(**1**) A negative electrode, consists of 4- plate sponge lead (Pb)
(**2**) Positive electrode, consists  of 4- plate of dioxide lead (PbO2)
(**3**) Microporous separator (polyethylene cover)
(**4**) Lead Jumper connection
(**5**) A negative terminal
(**6**) An element Pb/PbO2