

# ABOUT THE CHALLENGES FOR CHARGING TECHNIQUES WITH LEAD-ACID BATTERIES IN THE AUTOMOTIVE INDUSTRY\*

Dr. rer. nat. Jonny Dambrowski  
R & D Department  
Deutronic Elektronik GmbH, Adlkofen, Germany

16.10.07 - Version 1.0  
05.03.09 Revision 1.2

## Abstract

Changes in operating conditions, technology and production methods of starter batteries during the last 10 - 15 years has accelerated specific aging mechanisms, leading to an increasing number of premature failures, as the German automobile association ADAC has unmistakably documented in its breakdown statistics. In particular these are:

- (i) Use of antimony-free lead-acid grids  $\Rightarrow$  leads to a reduction in the charging capacity<sup>1</sup> and cycling lifetime.
- (ii) Changes to the load profile through considerably increased energy and power consumption in vehicles in conjunction with a simultaneous supply-deficit due to the alternator  $\Rightarrow$  lower discharging levels of lead-acid batteries, especially during the summer and winter months.
- (iii) Increase of the standby current in vehicles  $\Rightarrow$  resulting in low discharge levels and even deep discharge.
- (iv) Cycling in a partially discharged state *Psoc operation* due to charging deficiencies.

The resulting aging mechanisms are:

1. Aus (i)  $\Rightarrow$  drastic form of the so-called PCL effect (Premature Capacity Loss)
2. Aus (iii), (iv)  $\Rightarrow$  accelerated sulphation as the most common aging phenomena
3. Aus (ii), (iv)  $\Rightarrow$  favours acid stratification and thereby sulphation
4. Aus (ii), (iii)  $\Rightarrow$  favours sludging and dendrite-formation, which in turn can lead to short circuits inside lead batteries

A suitable charging strategy can however prevent the first mentioned ageing mechanisms and thereby drastically increase the serviceable life of a starter battery. Forasmuch as new requirements appear in the technology surrounding the charging of lead-acid-batteries in the automotive industry, which, as long as the battery voltage remains limited to ca. 15V, make the utilization of external chargers with special refresh algorithms a necessity. Numerous publications have described the reversibility of the so-called ageing mechanisms also giving discrete information and thereby providing the fundamental knowledge of how to develop an, up to now, nonexistent algorithm.

---

\*Please take notice of the references to copyrights 5.

<sup>1</sup>This can be seen in the latest standards requirements [EN06], where before the capacity test is carried out, the starter batteries are charged at 16V for a period of 24h.

## Contents

<b>1</b>	<b>Introduction</b>	<b>3</b>
<b>2</b>	<b>Operating Strategy</b>	<b>4</b>
<b>3</b>	<b>Ageing Mechanisms</b>	<b>6</b>
3.1	Sulphation - Re-crystallisation . . . . .	7
3.2	Acid Stratification . . . . .	8
3.3	Short Circuit - Dendrite Formation . . . . .	9
3.4	Technology and Production Processes . . . . .	10
3.4.1	Influence of the Grid Technology . . . . .	10
3.4.2	Influences of the Production Processes . . . . .	11
<b>4</b>	<b>Influence of the Charging Technology</b>	<b>11</b>
<b>5</b>	<b>Conclusions and Outlook</b>	<b>14</b>

## 1 Introduction

The automotive (or automobile) sector includes all vehicles with a combustion engine. This is for example common motor cars, motor cycles and lorries. Also included are however are busses, boats and agricultural vehicles, especially tractors and mowing machines.

**Definition 1.** A rechargeable energy storage with basic electrical functionality

1. starting a combustion engine, especially at low temperatures,
2. energy supply for lighting with the engine switched-off,
3. stability of the energy supply for the ignition process

in a vehicle combustion engine is called a **automotive battery** or **starter battery**, in short SLI = Starting, Lighting, Ignition.

Nevertheless NiMH or Lithium-ion batteries are also used in modern hybrid vehicles, should we continuously talk here about lead-acid batteries with liquid electrolyte, which are still the most often used today. For the so-called start procedure very high currents are required for short periods, in motor cars these can lie between 500-1000A for 0.3-3s [Eh05],[Ki03] chap.9. To achieve this, such storage batteries have a technologically optimised performance. The extremely low internal resistances required are accomplish by:

- extremely thin plates, higher porosity,
- thin separatorsthin separators<sup>2</sup> with very low crossover resistance, whereby very small plate distances can be realized.

The resulting limited cycle stability is insofar unproblematic, as long as the alternator can nearly completely assume the supply of all loads after the combustion motor has been started. The starter battery is designed accordingly for the standby operation, more precisely they are operated with a relatively high state-of-charge (ca.80% – 90%), flat cycles where full charging or complete discharging are seldom. However, in practice the situation concerning extremely low charge volumes has not happened for a long time. Currently the on board network supply is more than 2kW and will double by 2010 [Eh05]. Furthermore, until now increases in alternator performance have not kept pace with the increase in vehicle energy requirements [Wa05]. Therefore apart from the cold start capabilities current starter batteries should also possess high cycle stability and due to the limited charging times by the alternator a very good charge acceptance. Both characteristics are so far not present and furthermore due to technological changes are additionally stressed. Altogether during the past 10-15 years the starter battery has significantly changed, on one hand the operating conditions (cf. Def.2) and on the other hand the technological/manufacturing procedures, whereas the charging technology, especially that of the alternator have remained almost unchanged. Particularly this has had an influence on the life span of the energy source, in other words: other operating conditions or other technological/manufacturing procedures also implicate other requirements on the charging technology respectively and the battery management system. The consequence of this development is premature battery failures, which can occur in new vehicles after only 1-2 years [ADAC06], and in large executive models within a few months [Sp04],[Ra04]. A question therefore arises as to what can the user himself do, i.e. the car workshop, the vehicle owner but also the automobile manufacturer, to avoid a premature battery failure. Even though the user has no influence on the charging technology respectively the vehicle's battery management system, he however has the possibility to introduce an external charger unit to prevent premature failure of the starter battery.

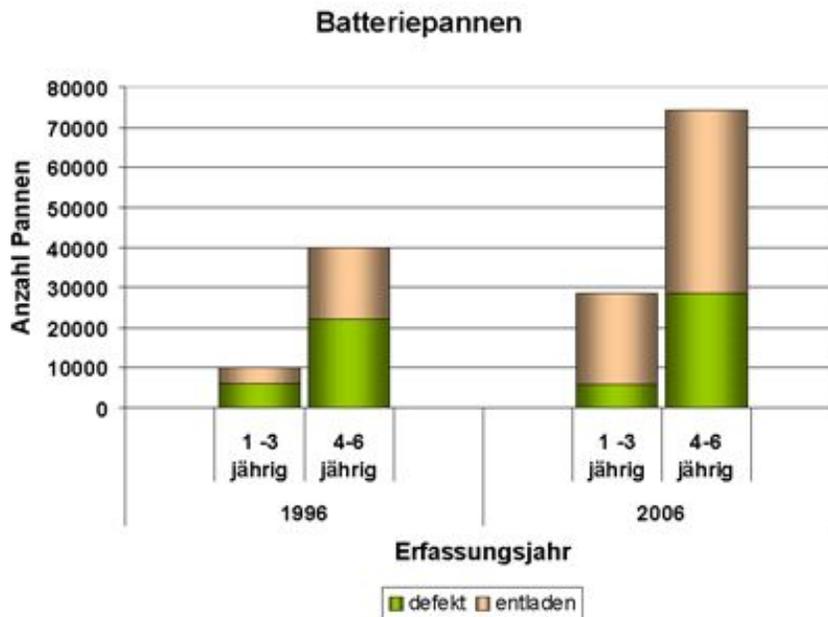
<sup>2</sup>Typical PE separators from traction batteries are double so thick and have a 4 times higher resistance as starter batteries. Typical values [Boe99]:  $d_{SLI} = 0.25mm$ ,  $R_{SLI} = 60m\Omega cm^{-2}$  respectively  $d_{Tr} = 0.5mm$ ,  $R_{Tr} = 280\Omega cm^{-2}$

## 2 Operating Strategy

**Definition 2.** Under **operating strategy** of a storage battery we understand

1. the operating conditions for the specific application, i.e. the typical mechanical, thermal and electrical load profile,
2. the necessary monitoring and charging strategies for the functioning of the energy storage device, in short the **Battery Management System = BMS**.

Briefly: operating strategy = operating conditions + BMS. From this we conclude that the operating strategy is an crucial factor in the life span of an energy storage device. Even when we often have no influence on 1, there are enough optimisation possibilities in the sphere of the battery management system, which are often insufficiently utilized. That 1 cannot be changed without adapting 2, is shown in the following german ADAC breakdown statistic.

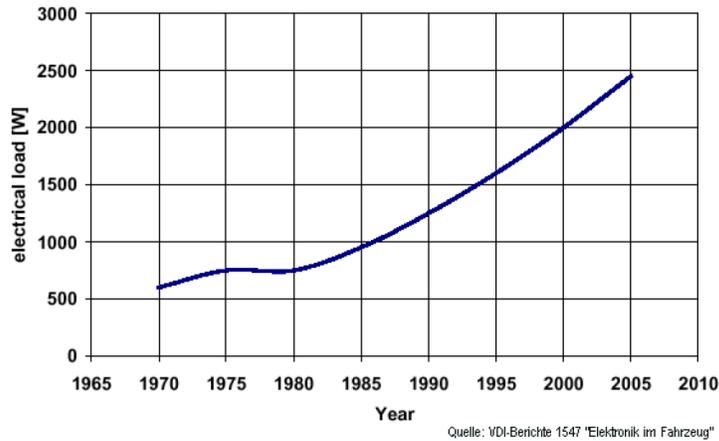


**Figure 1:** Battery failure in Germany in a 10-year comparison [ADAC06]

Hereafter are the commonest documented electrical failures due to defects or discharged batteries [ADAC06], [ADAC05], (Abb.1).

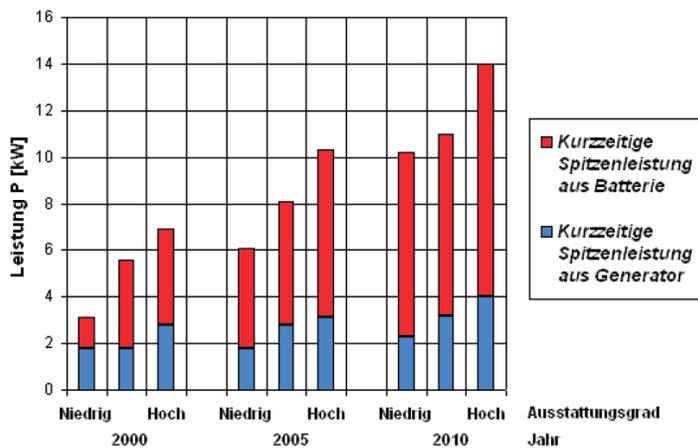
Whereas during the year 2000 primarily vehicles of the executive class were affected, in the meantime middle class vehicles are appearing in the statistic. The main reason for this is a rapid increase in electrical components in vehicles (Fig.2), that influence the starter battery operating conditions as follows:

- (i) Due to the negative energy balance between the alternator and the loads, starter batteries are reaching ever lower states-of-charge (Fig.3), i.e. the energy and performance consumption in the vehicle is occasionally greater than that which the alternator can deliver. As a consequence, the difference must be supplied from the starter battery, which as a result is moved to a lower cycle. This is especially prevalent in the extreme seasons of the year such as summer and winter, where due to the use of air conditioning systems, heated seats (up to 130W), rear window heating (up to 350W), windscreen heating (up to 1.3kW), etc. more energy is consumed.



**Figure 2:** Increase of the medium power consumption in vehicles

- (ii) Even in parked vehicles there is a discharge due to the connected monitoring and control electronics, which require a low current, the so-called closed-circuit current, that in turn by extended standing time can lead to a deep discharged energy storage device. For example the closed-circuit current of a motor car lies between ca. 10 - 100mA. The same level of deep discharge is suffered by seasonal vehicles such as motorbikes, mowing machines, tractors, etc. whereas here the reason for the discharging of the energy storage device is not necessarily the electronics. Due to long standing times, self-discharge of lead-acid batteries forms a contributing factor, which cannot be neglected.
- (iii) Because vehicle journey times are on average no more than 30 minutes, and hardly ever last 3 hours or more [Sa06], the starter battery is only seldom fully charged.



**Figure 3:** Increase of power consumption in vehicles [Fa06]

The operating strategy described in (iii) is also called cycling in a partial state of charge (PSOC). This, for example, is also the case in solar applications. In the course of fuel economy today's vehicles are constructed according to ergonomic principles. A result of this is a drastic increase in the temperature under the engine bonnet, caused by reduced air circulation and lack of cooling. As starter batteries are also today often mounted under the motor bonnet, they are consequently operated at higher temperatures.

In summarizing; resulting from the classical and contemporary operational strategy requirements of starter batteries we obtain the following comparison:

**Classical requirements:**

1. High cold cranking capability
2. Standby operation
3. Overcharge stability
4. Temperature stability

**Contemporary requirements:**

1. High cold cranking capability
2. Hohe Zyklenstabilität im PSOC sowohl durch sehr hohe als auch niedrige Lade- und Entladeströme
3. High charge acceptance
4. Maintenance freedom
5. Over-charging and over-discharging stability, the last means robust against deep discharge
6. Improved temperature stability, above all at high temperatures

From the above comparison it is clear that the once classically well defined border between the automotive and traction is becoming more blurred. This melting can be more clearly seen when one considers the nascent development in hybrid and electrical vehicles (=HEV/EV). According to this development it is also clear why the classical definition of the starter battery in 1 is no longer valid. A definition that meets today's standards is given in [Ra04] pp 389-399.

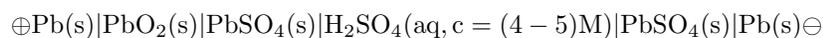
### 3 Ageing Mechanisms

**Definition 3.** Under **ageing** of a storage battery we understand the decrease of the following characteristic parameters during the operational or storage life:

- performance and thereby its high current capacity
- actual capacity, i.e. the specified nominally available capacity
- charge acceptance
- efficiencies
- rate of self-discharge

The ageing process begins at the point of time when the storage device is completed. Its depreciation is however dependant both on the operating strategy as well as selecting the technological implementation for the battery application. An unsuitable selection also implies an accelerated ageing. For example it makes no sense to use an automotive battery in a stand-by application, then to provide the necessary level of the cold cranking power, extremely thin grids are required, which provide nearly no corrosion reserves. Within a short time the grid will be corroded through, hence the normal life expectancy in stand-by operation of 15-20 years are fully illusionary.

For the following observation it is sensible to consider both the phase diagram as well as the electrode



fraction for the absorption and dissipation of energy from lead-acid batteries.

The operating strategy of the energy storage device result in specific ageing mechanisms. In the automotive sector these are primarily:

1. sulphation (re-crystallisation, i.e. formation of large lead sulphate crystals at the expense of the smaller ones)
2. acid stratification (vertical concentration-gradient of sulphuric acid)
3. cell short-circuit (due to dendrite formation)

### 3.1 Sulphation - Re-crystallisation

Sulphation is the most common ageing phenomenon in the automotive sector [Sa06]. Hereby this is understood as the formation of nearly insoluble (electrochemically partially active) lead sulphate crystals ( $\text{PbSO}_4$ ), which during re-charging of lead-acid batteries are only with great difficulty or not completely converted into the charged active mass, that is to say they cannot be converted in the lead sponge ( $\text{Pb}$ ) respectively porous lead-oxide ( $\text{PbO}_2$ ). This leads to a capacity reduction and in addition an increase in the internal resistance, which in turn causes a reduced start capability of the battery. The negative plates of lead batteries have a great tendency to sulphate into positive ones [Ru04]. A preferably high charge acceptance i.e. charging capability, is an important requirement in the automotive sector and sulphation is one mechanism from many (see 3.4), which significantly degrade the charging acceptance. This has been proved for the negative electrode from Y. Yamaguchi et al [Ya01] through morphological investigation and postulated by M. Thele et al [Th07] using pure electrical measurement methods.

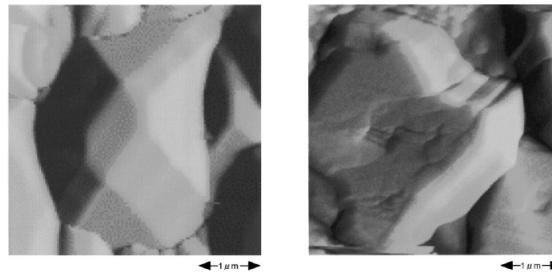
Sulphation is accelerated due to the following operating strategy:

- (i) Cycling in PSOC (especially with deficient charging)
- (ii) Discharging with small currents
- (iii) Long standing times in a discharged state
- (iv) High temperatures

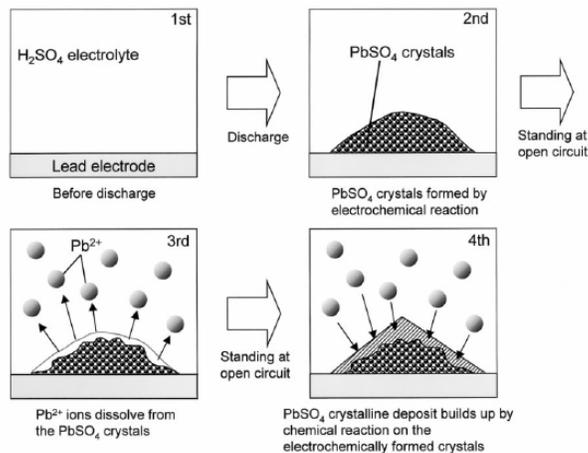
In the first instance the lead sulphate crystals formed during discharging are not completely converted in the active mass. A subsequent discharging cycle does not lead to a new nucleus generation, but rather increases the existing  $\text{PbSO}_4$  crystals, causing them to grow. In the second instance, the formation of  $\text{PbSO}_4$  both  $\text{Pb}^{+2}$  as well as  $\text{SO}_4^{2-}$  ions are necessary. With low discharge currents, the concentration of  $\text{Pb}^{+2}$  ions in the electrolyte is low, so that an accumulation on the existing crystals is more probable, than enough lead and sulphate ions concentrating to form new crystals. The third and fourth cases are as a result of the fact that the lead sulphate solubility increases by a decrease in the acid concentration respectively an increase in temperature cf. (Fig. 6).

The woolly definition leads to the conjecture that sulphation is reversible to a certain degree. It follows that the larger the non-conducting lead sulphate crystals the more difficult it is to convert them back into the active mass during a charging cycle. This condition is common but unnecessary, as there are also sulphated electrodes, whose sulphate crystals are small [Ya00]. As a consequence it must be assumed that the electrochemical activity of the  $\text{PbSO}_4$  is not only dependant on the crystal size. Morphological research on the negative plates by Y. Yamaguchi et al resulted in the verdict that there are two types of lead sulphate crystals. One type is formed by chemical means with a smooth surface and the second by an electrochemical reaction, resulting in a rough surface.

A smooth surface implies a low surface energy and a higher strength, so that the lead sulphate crystals formed via chemical means during charging, can only be dissipated with difficulty as opposed to those with



**Figure 4:** Difference between the formation of  $\text{PbSO}_4$  crystals; chemical (left) and electrochemical (right) [Ya00]



**Figure 5:** Sulphation model according to [Ya00]

a rough surface. Due to this observation, Yamaguchi and co-authors have proposed a new sulphation model (Fig. 5).

Similar results have been reached by M. Thele et al in [Th06], [Th07] using electrical measurements. Due to the fact that the charge acceptance of a charged lead-acid battery with a flat cyclising increases with time. It can be concluded that the younger lead sulphate crystals are absorbed into the active mass more easily than the older ones. Accordingly, so-called *hardened* lead sulphate crystals with lower electro chemical activity are formed.

### 3.2 Acid Stratification

With lead-acid batteries the electrolyte, diluted sulphuric acid, participates in the electrode reactions (see (1)), with the consequence that both during charging as well as discharging a decaying acid concentration is developed due to local concentration differences from the bottom up. With acid stratification we understand the formation of a vertical concentration gradient and hence a density gradient of the sulphuric acid in the electrolyte. With each charging respectively discharging cycle the density difference is intensified and thereby level of the acid stratification. This can be explained as follows. The resistance of the upper electrode regions to the connecting studs is lower than in the lower electrode region. Therefore, the acid density at the top sinks more than at the bottom during discharging. Additionally, due to the low acid density at the top the  $\text{H}_2\text{SO}_4(\text{aq})$  reserves are exhausted sooner as at the bottom and the lower regions will be further discharged, dependant on the end-of-discharging voltage.

Analogue behaviour is observed during charging. The low resistance in the upper region near the battery

studs, allows the acid density to increase more rapidly than at the bottom. Then due to gravity and diffusion this area of high acid density sinks to the bottom. Because during the previously mentioned discharging where less sulphations were present at the top, the conversion of the discharged active mass into the charged active mass is more likely to occur there than at the bottom. Therefore with a not correct adapted end-of-charge voltage, the lower regions will not be completely charged.

From the above mentioned considerations it follows that the actual capacity decreases more rapidly dependent on the degree of the acid stratification.

An extreme example is described by Tuphorn, a 55cm high lead-acid battery with an acid density of  $1.24g/cm^3$  had reached after only 6 full cycles  $1.13g/cm^3$  at the top and  $1.31g/cm^3$  at the bottom. In comparison, an empty starter battery had an acid density of ca.  $1.10cm^3$  and a full one ca.  $1.28g/cm^3$ .

Because the electrochemical potential of lead-acid batteries is dependent on the acid density and this is concentrated in the lower electrode region, then the battery's open-circuit voltage here is correspondingly high. Hence, generally with lead-acid batteries the open-circuit voltage has no correlation on the state of charge. A lead-acid battery aged due to acid stratification can have a higher open-circuit voltage and simultaneously a lower state of charge.

Further, the acid stratification leads to an electrochemical potential dependant on the electrode height, which results in discharging processes within the battery. Here the upper regions with low acid density are charged and the lower regions with high acid density are discharged. Dependant on the level of acid stratification this can lead to sulphation of the lower active mass.

Collectively the acid stratification is accelerated by the following operating strategy:

- (i) Low cyclic duty of lead-acid batteries, especially cycling in PSOC
- (ii) High charging and discharging currents

The acid stratification resulting for the sulphation mechanism is dependent on the operating strategy from [Gu07]. For example long standing times or low discharge currents lead to deep discharge of the lower electrode regions and thereby sulphation of the lower active mass. On the other hand, higher discharge currents cause sulphation in the upper regions. This is because in areas of lower acid density the discharging causes due to re-crystallisation tend to increase and therefore to sulphation (see .6). As shown in section 2 both variants are present in the automotive sector.

### 3.3 Short Circuit - Dendrite Formation

The acid density in starter batteries varies between "empty"  $\Leftrightarrow 1.10g/cm^3$  and "full"  $\Leftrightarrow 1.28g/cm^3$ . Within this range the solubility of the lead sulphate increases with a lowering of the acid density cf.(.6).

With high sulphate solutions not only is lead sulphate present on the electrodes, but also in a soluble form it can even reach as far as the separator. During an renewed charging process the separated lead sulphate particles are converted there in Pb and  $PbO_2$  and can lead to a short circuit here while they arrange themselves in the form of dendrites. In this case dendrites are classified as needle-like growth of Pb and  $PbO_2$ .

The irreversible dendrite formation is thus fostered due to long standing times in a discharged state respectively when the starter battery is re-charged from a low state of charge.

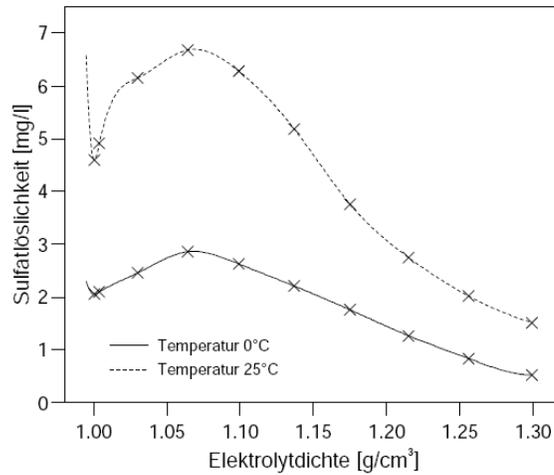


Figure 6: Solution of lead sulphate dependant on the acid density at different temperatures

### 3.4 Technology and Production Processes

By employing special technological designs, lead-acid batteries can be optimised to suit their purpose. That is for example the geometry and size of the electrodes, additives in the active mass and the electrolyte or special alloy constituents in the grids. But also optimisation around the separators and the production process play a roll.

Besides the similarly applicable technological characteristics for all starter batteries, such as the high power density due to extremely thin grids (in which the highly porous and soft active mass is pasted), as well as the very thin separators for as smaller plate spacing as possible, but additionally in the last 20 years technological changes have taken place, not only in the grid alloys themselves but also in their production. Both have had a direct consequence on the operational behaviour which is contrary to the present day requirements of automotive batteries (cf. section 2). This will be discussed in the next two sections.

#### 3.4.1 Influence of the Grid Technology

The following considers the pure technological aspects and hence various influences dependant on the operating conditions will be set aside for the time being. Table 1 shows an extremely simplified view of the changes in the grid technology and its effects<sup>3</sup>.

	PbSb	~>	PbSb-Low	~>	Hybrid-Typ	~>	PbCa	~>	PbCa-Low
Maintenance freedom	--	~>	o/+	~>	+	~>	++	~>	++
Cycle stability	++	~>	+	~>	o	~>	--	~>	--
Charge acceptance	++	~>	+	~>	o	~>	-	~>	-

Table 1: Change from lead antimony to lead calcium grids in starter batteries

**Definition 4.** A starter battery is called **maintenance-free** when during the whole serviceable life the water does not need to be refilled.

<sup>3</sup>Legend: ++ :<math>\Leftrightarrow</math> "very good", + :<math>\Leftrightarrow</math> "good", o :<math>\Leftrightarrow</math> "satisfactory", - :<math>\Leftrightarrow</math> "poor", -- :<math>\Leftrightarrow</math> "very poor"

Accordingly, all maintenance-free starter batteries are not necessarily sealed. On the other hand, every sealed lead-acid battery is maintenance-free. The freedom from maintenance was an important requirement from the automobile industry and ultimately responsible for the successive conversion from PbSb to PbCa grid technology (Table 2). However this change is associated with a substantial deterioration in the cycle stability and the charge acceptance (Table 1), both due to a complex ageing mechanism called PCL meaning **premature capacity loss**. The PCL effect is basically due to two mechanisms:

PCL1: Development of non-conducting (passive) layers between the grid and the positive active mass.

PCL2: Loss of the electrical conductivity of the positive active mass (= PAM)

From the work of D. Pavlov [Pa93] and L. Apateanu et.al. [Ap93] it follows that with antimony-free grid alloys, such as PbCa grids, the PCL effect is especially noticeable. For example the US Navy Research Laboratories found that under their common cycling conditions, the PbCa grids were rendered useless within 10 cycles [Ho96]. By the variation of the Ca concentration and also the addition of alloy ingredients such as Al, Zn or Ag the mechanical stability, corrosion resistance, grid growth, charge acceptance and cycle life can be improved (Tab.2). However, they still lie under PbSb(Sn) performance, because tin reduces the rate of corrosion in positive PbSb grids and improves the electrical contact and therefore the electrical conductivity between the grid and PAM [Pr06]. Also the electrical conductivity in the PAM with PbSb grids is increased due to the fact that during the course of operation the antimony finds its way in the PAM [Pa01].

### 3.4.2 Influences of the Production Processes

The grids of the positive and negative electrodes of a starter battery are no longer cast, rather predominantly manufactured using the stretched metal process. The traditional casting technology is not suitable for the soft grid material for example a low PbCa grid (Table 2). In such cases the metal stretching method is employed, which additionally brings higher quantities with consistent quality and a reduced reject rate [Wa05].

Basically, concerning the performance of the battery, the roll which the manufacturing process plays should not be underestimated, then they give as it were a gauge for the resistance against misuse due to incorrect operating management. Apart from the mechanical stability, corrosion rate/grid growth of the positive grid also the temperature stability and electrical properties are dependant on the production process. Positive PbCa grids produced using the stretch metal technology are, compared with the cast PbCa grid, more robust with respect to overloading and storage at high temperatures, however they possess a worse charge acceptance from a deeply discharged state. The charge acceptance is appreciably dependent on the concentration of the alloy additives calcium, tin and silver [Fo99].

As a whole, the observed reduction in cycle stability and also the charge acceptance due to the changes in grid technology and the production process are seen as a contradiction to the operating strategy presented in section 2.

## 4 Influence of the Charging Technology

The charging of re-chargeable batteries is not only to replace the amount of energy removed, but also to reverse the ageing process or at least to minimize it. In other words the charging technology has a decisive role to play in determining the lifespan of the battery as shown (Fig.7).

Die Ladung wiederaufladbarer Energiespeicher hat nicht nur den Zweck die entnommene Ladungsmenge wieder einzulagern, sondern auch Alterungsmechanismen aufzuheben oder wenigstens zu minimieren. Mit anderen Worten, die Ladetechnik hat einen entscheidenden Einfluss auf die Lebensdauer des Energiespeichers, wie (Abb.7) zeigt. For example, a continuously excessive charging voltage leads to gassing and

Alloy	PbSb		PbCa	
	Standard	Low	Standard	Low
Mass-%	4 – 7	0.3 – 3	0.09 – 0.13	0.02 – 0.08
Additives	As, Sn, Cu	Se, Te, S,	Al, 0.3-1.5 Sn, 0.01-0.04 Ag	
Type	+/- Electrode, hybrid form only -		+/- Electrode, hybrid form only +	
Maintenance interval	4-6 weeks (aged) [Bo02]	3-5 years in U-const operation [Be03]	-	-
Pos. effects	very good cycle stability, toughness, casting ability and mechanical stability; low Sb: also good cycle stability, antimony poisoning very scarce at < 2%Sb ⇒ maintenance-free, mechanical stability, casting ability and toughness, due to grain-refining additives such as Se, Te, S, Cu		much higher H <sub>2</sub> over voltage compared with PbSb, ⇒ extremely low water consumption, extremely low self-discharge. maintenance-free during the whole operational life; Low-PbCa: low corrosion; Sn improves: corrosion behaviour, mechanical stability, charge acceptance; Sn causes additional high H <sub>2</sub> and O <sub>2</sub> over voltage as well as lower self discharging and thereby water consumption, reduces the growth of PbSO <sub>4</sub> crystals [Bu97]; Ag reduces the corrosion rate and grid growth of the positive electrode during high temperatures [Pr02]	
Neg. effects	due to antimony poisoning ⇒ increased hydrogen generation, higher self discharging of the negative electrode, higher water consumption during the complete operating time with ever shorter service intervals		higher corrosion rates, grid growth especially during cyclic operation, very bad cyclic properties (PCL effect) and limited charge acceptance above all with U-const charging [Ra04], [Ki03], [Sa06]; low Ca: low Ca content: poor mechanical stability and casting ability. Expanded metal technology; Ag: reduced O <sub>2</sub> over voltage [Bu97]	

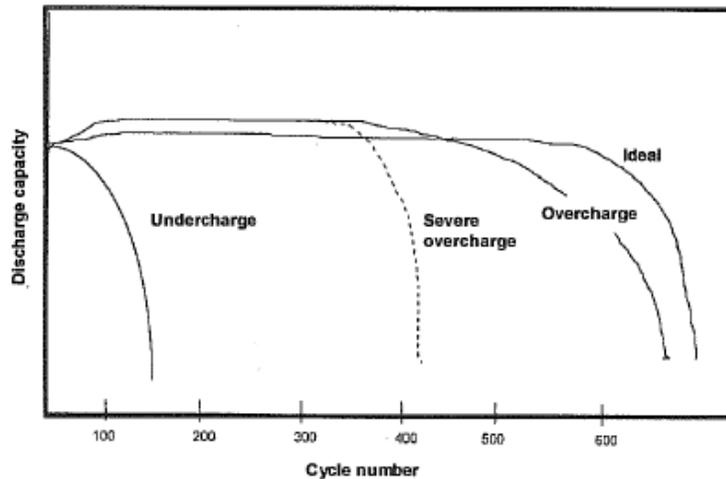
**Table 2:** Alloys used in starter batteries and their properties

hence to loss of water and also anode corrosion. If however the voltage is too low, then there is the threat of sulphation and an associated loss of capacity. As can be seen in the ram too lower charging in lead batteries with PbCa grid technology is more detrimental than over charging.

In the previous sections is has been shown that changes in the operating strategy, grid technology and grid production methods accelerates the ageing process due to:

1. Sulphation
2. Acid stratification
3. PCL-effect
4. short circuit

As a result these can lead to premature battery failures. The deciding point to mention at this juncture is that apart from short circuiting, all the ageing processes mentioned are to a greater extent reversible, as long as an appropriate charging strategy is followed.



**Figure 7:** Achievable number of cycles for lead batteries with PbCa grids dependent on the charging method [Ra04]

Field tests also prove that severely sulphating lead batteries can be restored to 100% using a suitable charging characteristic. In many cases it is actually possible to increase the capacity of lead batteries severely aged due to sulphation, so that they can assume their former tasks [Sa06],[Ca04]. However, currently there is no generally valid and approved procedure, which dependant on the available current, voltage and temperature parameters

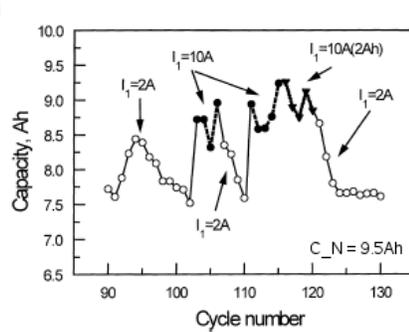
- measures the degree of sulphation i.e. the proportion of not easily soluble lead sulphate crystals with respect to the total solution.
- completely restore the active mass of sulphated lead batteries.

To date the most promising method is based on the IU1a charging characteristic, whose second constant current charging (typically  $0.02C_{20}$ ) which is time or ampere-hour limiting but not voltage limiting. A charging factor of 1.5 - 2 are not uncommon and these during a number of cycles. Thereby charging voltages of 2.75V/cell are achieved, that are lie beyond the maximum allowed on-board network voltage of 15.5V [BMW03]. Even the specified EN charging rate (16V , 24h at 25°C) devised for the capacity test in the DIN-EN 50342-1 standard from November 2006 [EN06] is not sufficient to convert all the lead sulphate crystals back into the active mass [Sa06], and it certainly isn't possible using the charging methods of most of the currently available commercial battery chargers. Therefore, neither of the charging methods can be applied in vehicles. The conversion of lead sulphate crystals in the active mass is among others dependant on the charging voltage and the temperature. High temperatures and high charging voltages improve the reduction of the lead sulphate crystals. However, simply increasing the temperature does not result hardly any advantage [Sa06].

The acid stratification is a reversible ageing mechanism [Ca04], however only as long as no irreversible sulphation has been created. In the traction area they can be reversed using the often utilized forced electrolyte mixing or through controlled gassing (e.g. 10 - 20% over-charging).

In the following instance the PCL effect is reversible<sup>4</sup>. Based on morphologic research of the interlayer grid PAM and the PAM itself, Pavlov was able to show in [Pa01] that high charging currents =  $1.5CN$  with lead batteries using PbCa grid technology reversed both PCL1 and also PCL2, whereas low charging currents, in the range of  $CN/5$ , lead to massive capacity loss after only a few cycles (. 8). The relevance of higher charging currents is only significant with PbCa grid technology, i.e. higher charging currents in lead batteries with PbCa grid technology deliver the same good cycle-characteristics as PbSb grids.

<sup>4</sup>Hereby the scope of optimisation due to the technological procedure was disregarded, as these are not influenced by the user



**Figure 8:** Influence of the charging current on the capacity development of a lead battery with PbCa technology [Pa01]

## 5 Conclusions and Outlook

To achieve significantly higher lifecycles for starter batteries with antimony-free PbCa grids an intelligent charging strategy should be considered taking into account the following points:

1. The formation of not easily dissoluble lead sulphate crystals should be avoided. Additionally, a refresh charge should be carried out at suitable intervals dependant on cyclic load, discharge level or standing time. Because here the associated charging voltage significantly exceeds the maximum permissible on-board network voltage, it would appear sensible to carry out this refresh charge using an external charger, which compared to conventional chargers delivers an output voltage of up to 18V. Of course during this process the battery should be disconnected. To prevent loss of data in the on-board equipment (clock, date, radio settings, etc.) during refresh charging, a charger with a low powered secondary output (ca. 30W) should be used to provide a backup.
2. The refresh charge burdens the starter battery with respect to the water consumption and corrosion. Hence the refresh intervals should also be chosen with respect to both of these ageing mechanisms.
3. There are two reasons why it is necessary to choose a charger with high performance. Firstly a charging cycle with high current repairs the PCL effect and the associated loss of capacity and secondly the warming of the battery leads to a more effective reduction in lead sulphate crystals, so that after the refresh charge a higher capacity is available.
4. The charger used should at least be capable of an initial high power in the order of 22,5CN Watt for 5 minutes. A higher initial power reduces the initial time.
5. Considering the fact that starter batteries with PbCa technology have a much better temperature stability, it would appear sensible during the hot summer months to go without the temperature compensation of the charging voltage, thereby profiting from the positive effect that higher temperatures have on the reduction of lead sulphate crystals.
6. Acid stratification should be avoided in starter batteries. Refresh charging nullifies this ageing effect completely.
7. The charger should be capable of identifying defective cells - for example internal short-circuits - during the charging process and to discontinue the process with a corresponding message. Due to sec. 3 an internal short-circuit could occur during the charging process.

The preceding conclusions show that there are still many things to be specified and therefore there is enough margin for optimisation available. For the development of suitable charging techniques it is inevitable that you will have to get to grips with the physicochemical processes which take place during battery

charging and discharging. Only after the mechanisms are determined can the physical value be found, which influence the sought after effect (e.g. the reduction of lead sulphate crystals). The mechanisms of acid stratification or sulphation are still today not fully understood. In any case this proves the present plethora of publication regarding this subject.

Some modern vehicles are equipped with an elaborate energy management, which not least is due to the introduction of an intelligent battery sensor, making it possible to monitor the permanent charging status (=SOC), ageing status (=SOH) and cold cranking capability (=SOF). In vehicles that are already equipped with an intelligent battery sensor, the implementation of the above mentioned requirements is considerably easier, then the battery sensor already measures the relevant battery and operational data. Hence, with the help of this data the refresh intervals can be more easily determined as the previous history of the battery is known. A possible symbiosis for the automobile and charger manufacturers could therefore be that the BMS determines the point in time for a refresh, after that the relevant data for the refresh charge could be sent to the external charger, based on this the charging parameters are then determined. By this method the charging time is optimised and the inevitable gassing and corrosion due to the refresh charge are minimised.

## Copyright-Directions

All rights regarding this article is solely the author. The reproduction, whether in part or as a whole, is only allowed with written permission of the author. Direct your inquiries with your address and reason for the reproduction to: sales@deutronic.com.

## References

[ADAC06] ADAC-Pannenstatistik 2006,

[www.adac.de/Auto\\_Motorrad/pannenstatistik\\_maengelforum/pannenstatistik\\_2006/Batterien/default.asp?ComponentID=179505&SourcePageID=17958](http://www.adac.de/Auto_Motorrad/pannenstatistik_maengelforum/pannenstatistik_2006/Batterien/default.asp?ComponentID=179505&SourcePageID=17958)

[ADAC05] ADAC-Pannenstatistik 2005, Stand 04/06,

[www.adac.de/images/Pannenstatistik\%202005\\_tcm8-145338.pdf](http://www.adac.de/images/Pannenstatistik\%202005_tcm8-145338.pdf)

[Be86] D. Berndt: *Bleiakkumulatoren*, VARTA, 1986

[Be99] D. Berndt: *Lead Oxides* in J.O. Besenhard(Ed.): Handbook of Battery Materials , 1999

[Be03] D. Berndt: *Grundlagen elektrochemischer Energiespeicher*, aus H.-A. Kiehne: Batterien, Expert-Verlag 2003

[Boe99] W. B"ohnstedt: *Separators* in J.O. Besenhard(Ed.): Handbook of Battery Materials , 1999

[Bo02] Robert Bosch GmbH: *Batterien und Bordnetze f"ur Kraftfahrzeuge*, 2002

[BMW03] BMW-Group: *Qualtit"atsvorschrift f"ur Batterieladeger"ate und Fremdstromversorgungen*, 2003

[Bu97] N. Bui et.al.: *The Tin effect in lead -calcium alloy*, Journal of Power Sources 67 ( 1997) 61-67

[Ca04] H. A. Catherino et.al.: *Sulfation in lead-acid batteries*, Journal of Power Sources 129 (2004) 113-120

[Cl04] T.J. Clough: *Antimon positive grids*,, Battery Man Magazine, 2004

[Eh05] C. Ehret et.al.: *Ehrfahrungen und Entwicklungslinien von BM und Diagnosesystemen Energiepeicher f"ur Bordnetze und Antriebssysteme*, HDT, 2006

- [Fa06] R. M. Fabis, *Beitrag zum Energiemanagement in Kfz-Bordnetzen* Dissertation, 2006
- [Fo99] S. Fouache et.al.: *Effect of calcium, tin and silver contents in the positive grids of automotive batteries with respect to the grid manufacturing process*, J. of Power Sources 78 (1999) 12-32
- [EN06] Deutsche Norm DIN-EN 50342-1: *Blei-Akkumulatoren-Starterbatterien — Teil 1: Allgemeine Anforderungen und Prüfungen*, November 2006
- [Ap93] L. Apateanu et.al. *Electrolyte stratification in lead acid batteries: Effect of grid antimony and relationship to capacity loss* J.Power Sources 46 (1993) 239-250
- [Ho96] A.F. Hollenkamp *When is capacity loss in lead/acid batteries "premature"?*, Journal of Power Sources 59 (1996) 87-98
- [Ki03] H.A. Kiehne et.al., *Batterien — Grundlagen und Theorie, aktueller technischer Stand und Entwicklungstendenzen*, Expert-Verlag, 2003
- [Ko97] M. Kosai et.al. *Effect of antimony on premature capacity loss of lead-acid batteries* Journal of Power Sources 67 (1997) 43-48
- [Pa93] D. Pavlov: *Premature capacity loss PCL of the positive lead acid battery plate: a new concept to describe the phenomenon* Journal of Power Sources 42 (1993) 345-363
- [Pa01] D. Pavlov: *Influence of grid alloy and fast charge on battery cycle life and structure of PAM of lead acid batteries* Journal of Power Sources 93 (2001) 234-257
- [Pr02] R.D. Prengaman et.al. *Manufacturing and operational issues with lead-acid batteries* Journal of Power Sources 107 (2002) 280-300
- [Pr06] R.D. Prengaman *New low-antimony alloy for straps and cycling service in lead-acid batteries* Journal of Power Sources 158 (2006) 1110-1116
- [Ra04] D.A.J. Rand, P.T. Moseley et.al.: *Valve Regulated Lead Acid Batteries*, ELSEVIER, 2004
- [Ru04] P. Ruetschi: *Aging mechanisms and service life of lead-acid-batteries*, Journal of Power Sources 127 2004 33-44
- [Sa06] D.U. Sauer et.al.: *Charging performance of automotive batteries*, 10th ELBC, Athen, 2006
- [Gu07] Y. Guo et.al.: *Effects of electrolyte stratification of flooded lead acid batteries*, ECS 154 (2007) A1-A6
- [Sp04] D.U. C. Wüst.: *Schlamm im Stromtank*, Zeitschrift: Der Spiegel, 2004
- [Th06] M. Thele et.al.: *Impedance-based overcharging and gassing model for VRLA/AGM batteries*, 10.ELBC Athen, 2006
- [Th07] M. Thele et.al.: *Modeling of the charge acceptance of lead acid batteries*, Journal of Power Sources 168 (2007) 31-39
- [Wa05] R. Wagner et.al., *Einsatz von Bleibatterien in Kraftfahrzeugen* Energiepeicher für Bordnetze und Antriebssysteme, HDT, 2006
- [Ya00] Y. Yamaguchi et.al.: *In situ analysis of electrochemical reactions at a lead surface in sulfuric acid*, Journal of Power Sources 85 2000 22-28
- [Ya01] Y. Yamaguchi et.al.: *Study of charge acceptance for the lead-acid battery through in-situ EC-AFM observation — influence of open-circuit standing on negative electrode*, Journal of Power Sources 102 2001 155-161