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Heat tolerance of automotive lead-acid batteries☆

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ABSTRACT

Starter batteries have to withstand a quite large temperature range. In Europe, the battery temperature can be −30 °C in winter and may even exceed +60 °C in summer. In most modern cars, there is not much space left in the engine compartment to install the battery. So the mean battery temperature may be higher than it was some decades ago. In some car models, the battery is located in the passenger or luggage compartment, where ambient temperatures are more moderate.

Temperature effects are discussed in detail. The consequences of high heat impact into the lead-acid battery may vary for different battery technologies: While grid corrosion is often a dominant factor for flooded lead-acid batteries, water loss may be an additional influence factor for valve-regulated lead-acid batteries. A model was set up that considers external and internal parameters to estimate the water loss of AGM batteries.

Even under hot climate conditions, AGM batteries were found to be highly durable and superior to flooded batteries in many cases. Considering the real battery temperature for adjustment of charging voltage, negative effects can be reduced. Especially in micro-hybrid applications, AGM batteries cope with additional requirements much better than flooded batteries, and show less sensitivity to high temperatures than suspected sometimes.

1. Introduction

The main tasks of automotive lead-acid batteries are to ensure the cranking of the internal combustion engine, to buffer electrical energy in vehicle operation and to supply the electrical system when the engine is off. These functions are covered by SLI batteries (starting, lighting, ignition) [1].

The battery is closely embedded into the electrical system of the vehicle and has to supply the board net under all environmental conditions sufficiently. There are various ageing factors which are leading to a gradual loss of performance [2].

The battery's temperature is one of the most significant parameters for the service life of automotive batteries. Low temperatures may be critical due to freezing of the electrolyte, in particular at low states of charge (SOC). High temperatures may accelerate the ageing of batteries, resulting in premature end of service life. The battery temperature is mainly determined by external factors like climate conditions and battery packaging. As space is limited in the engine compartments of today's cars due to aerodynamic reasons and pedestrian protection measures, batteries are installed either in hot and sometimes crowded underhood locations or in the luggage or passenger compartment.

In conventional applications, the battery is operated in a fairly high SOC, not fully charged, but not intentionally at a SOC below 80% [1,3].

Recently, new automotive applications like micro-hybrid vehicles require additional battery performance—high cycle loads have to be covered, in particular. In systems providing recovery of braking energy, a partial state of charge operating mode (PSOC) is applied, which means that the battery is intentionally not fully charged for extended time periods. High cycling capability, also in PSOC operation mode, is one of the main advantages of AGM batteries (AGM means "absorbent glass mat", one kind of valve-regulated lead-acid (VRLA) battery) [4,5]. Therefore, these batteries are preferred in micro-hybrid applications.

Water loss is one of the parasitical processes which may lead to degradation of battery performance. Both flooded and AGM batteries will lose some water when operated in high-heat environments or charged with high voltages. However, AGM batteries are suspected to be more temperature sensitive than flooded batteries due to their starved electrolyte concept. It is worth taking a closer look at the water loss of AGM in high-heat applications in laboratory, in field tests and by applying modeling tools.

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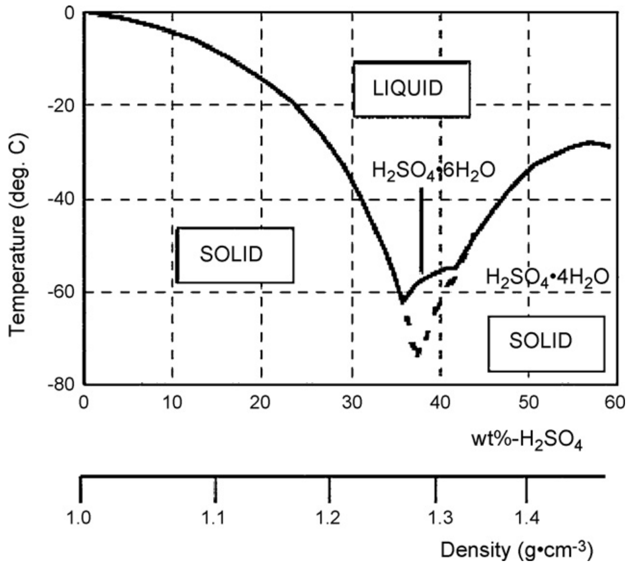

Fig. 1. Solidification curve of H_2SO_4/H_2O system [6].

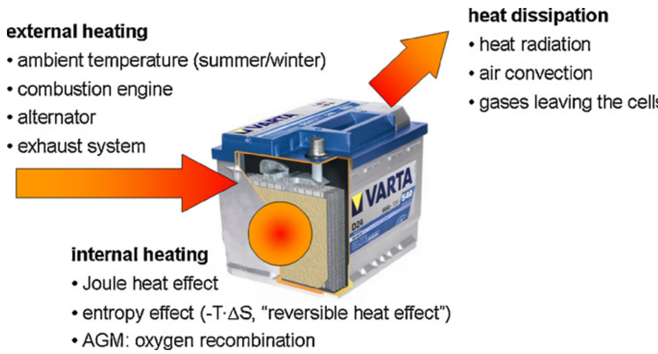

Fig. 2. External and internal heating effects/dynamic equilibrium.

2. Temperature impact on lead-acid batteries

Besides the low reaction rates at low temperatures, the lowest operating temperature for lead-acid batteries is given by the risk of ice formation in the electrolyte. The freezing temperature depends on the local density of the diluted sulfuric acid electrolyte and therefore on the SOC. The critical limit may be reached at low temperature, respectively, within the plates at high-rate discharges (e.g. cold cranking in strong winter), or if the acid density in the upper parts of the container is low due to a large extent of acid stratification. If the electrolyte freezes, the volume expansion of the electrolyte may damage the plates or the battery container irreversibly. Danger of leakage is one of the consequences.

However, even when the battery is fully charged (acid density = 1.28 g cm^{-3}), freezing will occur at about −60 °C [6,7], as shown in Fig. 1.

At high temperatures, the increasing reaction rates (e.g. for grid corrosion and water decomposition) are to be considered. While grid corrosion affects all types of lead-acid batteries similarly, the water decomposition has to be examined in detail.

Due to the design of the batteries, the extent of water decomposition may be different. The top lead alloy of flooded batteries usually comprises some antimony, and for AGM batteries antimony-free top lead is used. In flooded batteries, the antimony may poison the electrolyte with the risk of accelerated hydrogen evolution. Due to absence of antimony in AGM batteries, there is no such effect.

Furthermore, under overcharging conditions, oxygen is generated at the positive plates. While in flooded batteries the gaseous oxygen leaves the cells irreversibly, in AGM batteries the oxygen is partially recovered. Due to the porous glass mat separator, oxygen may diffuse easily to the negative plate and is reduced to water again. So the "oxygen cycle" effectively minimizes the water loss of AGM batteries, provided that there is no excessive hydrogen generation.

For these reasons, the water loss of an AGM battery is significantly lower than that of a flooded design, making AGM batteries advantageous in some high-heat applications.

Besides water decomposition, vaporization of water also contributes to "water loss" and has to be considered at elevated temperatures as well. In AGM batteries, valves are installed to release internal gas pressure from the cells. The opening pressure of these valves is usually in the range of the vapor pressure of diluted sulfuric acid at a temperature of about 60 °C. To prevent the electrolyte from being vaporized in large amounts and from leaving the cells by the valves, the internal temperature of an AGM battery should not exceed 60 °C for extended time periods. On the other hand, flooded batteries do not have any valves installed—water vapor may leave the battery cells without any hindrance. Only at very high ambient air humidity (above 70%), water from outside the battery can be absorbed by the hygroscopic sulfuric acid.

In summary, the internal temperature of any lead-acid battery (flooded and AGM) should not exceed 60 °C for extended time periods frequently to limit vaporization.

2.1. External and internal heating of the battery

As more and more components are installed into the engine compartment of today's passenger cars, the available space for the battery is strictly limited. Additionally, new requirements for pedestrian protection and the efforts to optimize aerodynamics lead to small engine compartments. For these reasons, the battery is often packaged close to hot components, and the ventilation of the engine compartment is hindered. So the mean battery temperature may be higher today than it was some decades ago.

When looking at the battery's internal temperature, one has to consider heating effects from external and internal heat sources (heat input). The most significant impact results from external heating, while effects from internal heating are added on top. Main effects of heat dissipation are heat radiation and air convection. There is always a dynamic equilibrium of heat input and output, determining the battery temperature. An overview is given in Fig. 2.

2.1.1. External effects

Heat emissions from the combustion engine and the alternator are responsible for high temperatures in the engine compartment both while driving the car and afterwards (engine cooling down). These heat sources influence the battery temperature directly, but only temporarily. Long-time external heating is determined by the ambient temperatures and climatic factors, most important in hot summers or in hot climates.

On the other hand, in winter, the battery is also affected by cold climate conditions directly. To get an impression of the influence of climatic conditions on an automotive lead-acid battery, one has to consider the changes of the temperature within a year as well as the temperature changes within 1 day. In some areas of the world, the temperatures at night differ quite strongly from daytime temperatures. The battery will follow these fluctuations with some time delay.

The heating characteristics of an AGM battery can be determined experimentally. In an experiment starting at a battery temperature of 20 °C, an AGM LN5 (95 Ah) battery was put into a thermo cham-

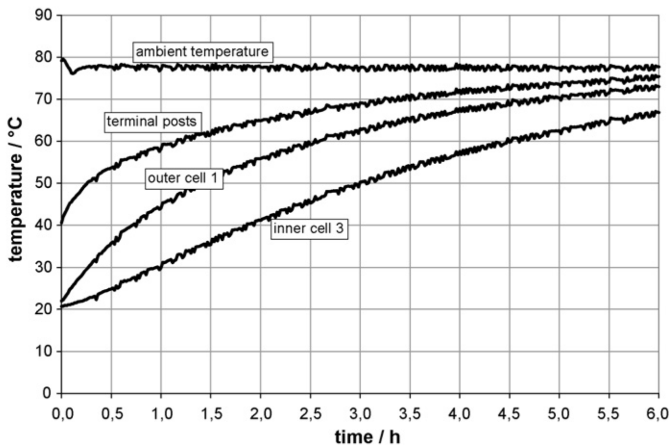

Fig. 3. Heating of an AGM LN5 battery from 20 to 80 °C (first 6 h).

ber of 80 °C. The temperatures were measured at different positions inside and outside the battery. The internal temperature of the battery does not raise homogeneously, the terminal posts and the "outside" cells 1 and 6 heat up faster than the "internal" cells. Starting from 20 °C, during the first 3 h, the temperature of the "inner" cells of the battery increased linearly with a rate of 10 °C h^{-1}. After 3 h, the further increase was not linear anymore and was 6 °C h^{-1} only (Fig. 3). So even at a high ambient temperature of 80 °C, the battery needs 3 h to reach an internal temperature of 50 °C.

2.1.2. Internal effects

Two heat effects are to be considered when charging or discharging a lead-acid battery: the entropy effect (reversible heat effect, $-T\Delta S$) and the Joule effect [5,7]. In most cases, the entropy effect is dominated by the Joule effect from high charging and discharging currents in automotive applications (cf. Table 1). While the Joule effect is helpful for some warming up the battery at low ambient temperatures, the effect may be undesirable at higher ambient temperatures.

Unwanted secondary reactions also contribute to the battery temperature: Water decomposition causes an entropy effect cooling down the battery, and gases leaving the battery cells also dissipate thermal energy, so that a slight decrease of temperature is observed in this case.

In sealed AGM batteries, the charging gases normally do not escape from the cells. In contrast, the recombination of oxygen at the negative plates is one of the effects increasing the internal battery temperature [8].

As shown in Table 1, due to the entropy effect, the usable electrical energy is higher than 100% at low discharging currents. The battery operates as a heat pump and converts thermal energy from the environment to deliver more electrical energy.

At very high currents, the ohmic drop at the cell connectors is to be considered. After applying a discharging current of 1000 A (approx. 200 I_{20}, where I_{20} is the 20-h rate) at room temperature, pictures of an AGM battery were taken with a thermal imaging camera. In Fig. 4, a top view of an AGM LN5 battery (95 Ah) after such a discharge procedure is shown. The hot intercell connectors and terminal posts can be seen as bright spots in the picture.

Table 1
Percentage of discharged energy of a 12 V/18 Ah "Sonnenschein A400" VRLA battery, split into Joule heat effect and reversible heat effect [7].

Discharge current	I_{20}	3.4 I_{20}	10 I_{20}	20 I_{20}	60 I_{20}	100 I_{20}
Joule heat effect	2.7	5.0	8.0	11.5	17.0	25.0
Entropy effect	−4.3	−3.5	−3.6	−3.4	−3.7	−3.8
Sum of heat effects	−1.6	1.6	4.3	8.1	13.2	20.9
Usable electrical energy	101.6	98.4	95.7	91.9	86.8	79.1

I_{20} = 20-h discharge rate.

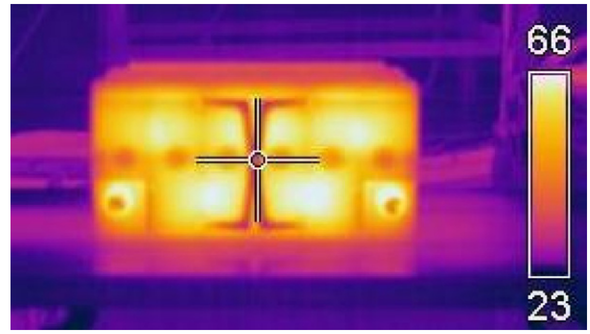

Fig. 4. Infrared picture of an AGM LN5 battery after a high current discharge (temperatures in °C).

Similar thermal imaging investigations of stationary batteries have been published by Giess and co-workers [9,10]

2.2. Battery temperature in automotive applications

The temperature profile of a battery in an automotive application can be quite complex.

An example is the daily course of battery temperature in a vehicle in a commuter duty: The battery will start in the morning with a low temperature close to the ambient temperature. While driving, the battery is heated up by the effects discussed above. When the car is parked somewhere during the day, the ambient temperature (dependent on the season of the year) is heating up or cooling down the battery. Furthermore, due to the lack of cooling from air ventilation from driving, residual heat of the engine affects the battery. While driving back home in the evening, the battery is heated up again. Due to the heat capacity of lead-acid batteries, the internal temperature will change quite slowly (cf. Fig. 3). Therefore, some short driving periods will not change the battery's internal temperature significantly—the temperature will follow the ambient temperature with some time delay.

The battery is heated up most if the car is parked on a hot day just after a long trip in which the battery already has been heated up. In this case, the heat cannot be dissipated sufficiently, and both residual heat from the combustion engine and high ambient temperatures heat up the battery even more.

In automotive applications, the internal battery temperature is not known and difficult to measure. But a battery temperature model can be used to predict the internal temperature of a battery from the temperature measured, e.g. at the terminals. Such a model requires temperatures and currents measured continuously and is parameterized according to the battery type and the location of the battery.

When the battery is installed in the engine compartment, the most important heat sources are the combustion engine and the alternator. Hot air from the cooler may heat up the engine compartment even when the combustion engine is not running. To reduce the heat ingress to the battery, some car manufacturers are using thermal insulations and shields to protect the battery from external heat sources. One of the most effective measures is to shield the battery from direct heat radiation. The mean battery temperature cannot be lowered this way in long term, but temperature peaks can be reduced. However, thermal insulation of automotive batteries may induce other issues as well. Heat dissipation is hindered also, so that the battery temperature may raise upon repetitive vehicle operation. Additionally, in winter, a high effective thermal insula-

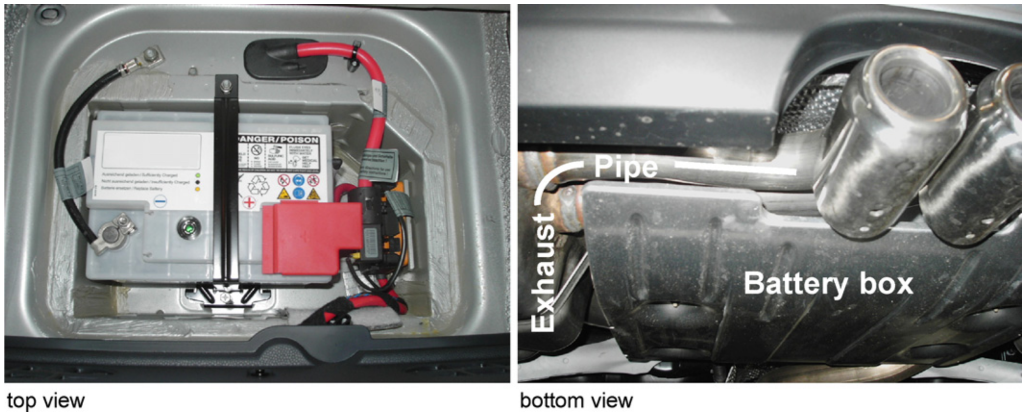

Fig. 5. Battery installed in the luggage compartment—exhaust system close to the battery: left, top view; right, bottom view.

tion may prevent the battery from being warmed from external heat sources, although this is probably desired on cold days.

Usually, the battery has no thermal insulation and is surrounded by an air-flow while driving. If the battery is heated up, the heat can be dissipated by the air-flow. For fuel saving, some car manufacturers use panels at the bottom of the engine compartment, which are hindering dissipation of heat energy as well.

An alternative battery location is the passenger compartment, so that some under hood space can be saved. Usually, here the temperatures are more moderate, and the battery is shielded from the heat radiation of the combustion engine. Most of the cars with the battery installed in the passenger compartment are equipped with an air-conditioning system as well, so the battery will not experience high temperature peaks during vehicle operation. However, this battery location bears a risk of leakage if a flooded battery is installed, and a sealed battery is recommended for this location.

Some car manufacturers install the battery in the luggage compartment, either to save space in the engine compartment or to achieve a better weight distribution in the car. However, this requires longer cabling from the starter and alternator to the battery. Usually, the temperatures in the luggage compartment are more moderate than in the engine compartment, but otherwise even a battery installed here may be exposed to high temperatures. In some car models, the hot exhaust pipes are mounted directly below the luggage compartment, where they are close to the mounting place of the battery which may be heated significantly (Fig. 5) [11].

Recently, a few car models are equipped with an air ventilation system for the SLI battery which is installed in an extra underhood compartment apart from the engine. Air from the passenger compartment is used to temperate the battery. This system insulates the battery from the thermal effects of the engine compartment and uses the moderate temperature conditions of the passenger compartment to keep the battery in a medium temperature range, at least when the vehicle is operated.

Table 2
Effects on the battery temperature.

Category	Effect
Car	• Location of battery/packaging • Heat protection
Environment	• Climatic conditions/climatic region
Operation mode	• Conventional/micro-hybrid vehicle
Usage	• Operation area: urban, suburban, motorway driving • Medium travelling distance • Number of traffic congestions • Frequency of car usage • Parking conditions (garage, direct solar radiation...)

An overview of effects on the battery temperature is given in Table 2.

3. Micro-hybrid applications

The conservation of global resources and the reduction of carbon dioxide emissions are the main goals of today's discussion on the world climate. To save fuel and to reduce carbon dioxide emissions from road traffic, many car manufacturers recently developed some hybrid electric vehicles. The degree of hybridization varies in a wide range. From full-hybrid vehicles, able to drive fully electric on limited distances, over mild-hybrid to micro-hybrid vehicles, using engine start/stop functions only, there are a lot of possibilities to install additional electrical components into a standard combustion engine driven car. Full-hybrid vehicles are regarded as most fuel efficient, but they are quite expensive because of additional costs of the electric drivetrain and the high-voltage battery.

Micro-hybrid vehicles seem to be today's preferred solution in the European market. Car manufacturers reduce the fleet fuel consumption of their cars to meet legal requirements (e.g. maximum carbon dioxide emissions of 120 g km^{-1} in EU as of 2015). Due to the fairly low additional costs for the electrical components needed for micro-hybrid systems, such functions may be installed in nearly all cars of a manufacturer's product range.

So the reduction of total carbon dioxide emissions may be higher with many cars saving only some percents of fuel (micro-hybrid) than it was if only some cars save some more percents (full hybrid).

3.1. Elements of micro-hybrid systems

Micro-hybrid systems comprise at least an engine start/stop function. Additionally, some more functions like passive boost and regeneration of braking energy may be installed.

1) The engine start/stop system is able to stop and to restart the engine automatically at short stop phases (traffic light, railway crossings, etc.). The amount of fuel saved by engine start/stop is the amount of fuel used for idling otherwise, i.e. 1–5% on average, dependent on the driving profile. The battery has to supply the electrical system in stop phases and has to crank the engine again afterwards.
2) "Passive boost" means the reduction of battery charging voltage while accelerating the car. If the alternator is de-energized, less mechanical energy is needed—more energy of the drivetrain is available for propulsion. Again, the battery has to bridge the electrical power for this period.
3) Additionally, regeneration of braking energy is able to save some more fuel. When the car is de-accelerated, a part of the braking

energy is used to recharge the battery. To increase the efficiency of this function, the alternator voltage is raised to higher voltage levels up to 15 V. The battery has to cope with these high voltages and has to accept higher charging currents.

4) Other systems regulate the battery voltage dependent on the SOC and the driving situation. Such voltage control systems lower the charging voltage when the battery's SOC is high enough, and raise the voltage in braking phases or if the SOC is low. Additionally, in idling phases, the charging voltage may be lowered as much as the board net is supplied by the battery completely. As the combustion engine is not switched off, there is no restart load for the battery.

For all these functions, except for engine start/stop, the alternator voltage has to be controlled. An adjustable alternator is capable of controlling the output voltage according to an electronic input signal, e.g. from the vehicles bus system. A battery monitoring system determines the SOC of the battery [1,3,11].

Micro-hybrid functions may be combined with electrical components replacing mechanical components. For example, compressors for air conditioning and power steering may be switched off while not in use, if they are driven electrically, reducing fuel consumption.

The batteries for these applications have to be more cycle-proof because of the higher capacity turnover from bridging during stop phases and engine restarts. Usually, the battery technology used in micro-hybrid cars is lead-acid (AGM), with little additional costs for a cycle-proof battery and keeping the standard 14 V on-board electrical system.

3.2. Simulation of a micro-hybrid application

For a few years now, some micro-hybrid cars are available on the worldwide markets. Some of these cars available in Europe have been tested in consideration of the electrical system and the lead-acid battery installed. One has to distinguish two types of micro-hybrid cars: The first group with an engine start/stop system only and the second group with both engine start/stop and regeneration of braking energy.

In all of these cars, the cycle load on the battery is higher compared to standard applications. In the second group, the battery has to withstand longer time periods kept in a partial SOC, additionally. In all cases, the battery has to be recharged while driving after a stop phase and therefore the recharging time is longer and the charging current is higher (dependent on the alternator) compared to conventional cars. The heat impact on the battery may be slightly higher therefore.

Experiment: A fairly severe micro-hybrid application was simulated to obtain the internal battery temperature while cycling. An AGM LN3 battery (70 Ah) is heated by internal effects during continuous cycling operation, while the ambient temperature is held constant in a thermo chamber with ventilation. Due to high charge and discharge currents, the capacity turnover is relatively high (20× nominal capacity in one week).

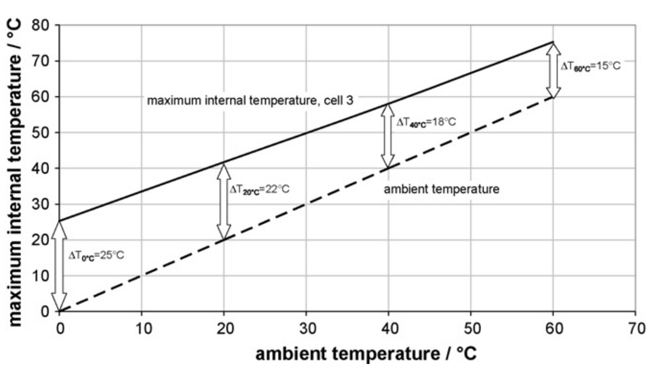

Fig. 6. Experimental simulation of a micro-hybrid application: difference of maximum internal temperature and ambient temperature.

Test result: the difference of the battery's internal and external temperature depends on the ambient temperature. At an ambient temperature of 0 °C, the battery reached a temperature maximum of 25 °C after 5 h of uninterrupted operation. This difference decreased with increasing ambient temperatures and was 15 °C at an ambient temperature of 60 °C (Fig. 6).

This experiment considers an extreme case for the battery internal heat ingress. In real life, the throughput of charge is much lower and the cycling time is shorter and more often interrupted by rest periods.

4. Battery requirements

Battery requirements change over the time. As more electrical devices are installed into cars, the energy demand is growing. New functions like micro-hybrid systems may even make higher demands on batteries.

4.1. "Traditional" requirements for SLI batteries

1) Cranking: deliver high discharge currents for the engine cranking, approximately 300–1000 A for a short time of less than 1 up to 5 s, with a voltage above 7.5 V, also at low temperatures down to −18 °C or down to −30 °C (depending on OEM requirements).
2) Quiescent currents: supply small currents of about 20 mA for several weeks and ensure engine cranking afterwards.
3) Power supply: currents of about 10–30 A (radio, lights, electronic equipment, etc.) in engine-off phases for a medium duration of several minutes to hours.
4) Buffering: buffer voltage fluctuations in the electrical system (ripples, transients of electric loads and alternator).
5) Recharge: sufficient charge acceptance, also at lower temperatures.
6) Maintenance: maintenance-free during the whole service life of several years.
7) Operating conditions: at high and low temperatures, at high and low SOC, under the influence of vibrations, etc.
8) Weight and volume: minimized, but standardized size.
9) Cost: low-priced, but on a high safety and quality level.
10) Environment: environmental friendly in production and operation, allow for a complete recycling after the end of service life.

Additional requirements since the 1990s:

11) Cycling capability: more cycle loads from more electric devices like optional comfort features, to be supplied also in idling and engine-off phases.
12) Deep discharges: withstand deep discharges without deterioration of the cells.
13) Battery storage: logistics and warehousing require long storage times (several weeks to months) until batteries are installed.

To cover these additional requirements, cycle-proof batteries are preferred. For example, AGM batteries are predominantly used in luxury and upper-class vehicles, taxi and truck applications, where high power is demanded [1,11].

Additional to this, in engine start/stop and micro-hybrid systems, AGM batteries have been used for a few years now.

4.2. Additional battery requirements for micro-hybrid vehicles

Recently, due to new battery applications like micro-hybrid vehicles, there are even more and higher requirements to be fulfilled by the battery.

Table 3
Comparison of conventional and micro-hybrid applications.

	Conventional	Micro-hybrid
Engine cranking	Also at low temperatures	Many more cranking events, also at low SOC/low temperatures
Power supply while engine off	Rarely, usually very low currents (≈10 mA)	Cover entire load in stop phases, much more often (some 10 A)
Recharging	Only after cranking	Quick recharge, high charging currents to be accepted
Cycling capability	Limited, only occasionally	High cycling capability and high DoD capability
Extended time periods without recharging	Rarely (e.g. airport parking)	Partial SOC operation regularly, risk of sulfation

1) Higher cycle loads: In engine-off phases, the battery has to cover the entire electrical load of the on-board system. The engine start/stop function leads to more engine-off phases compared to a standard car's usage profile. In extended stop phases, the depth of discharge may become quite high, in particular if a lot of electric consumers remain activated. Additionally, not only start/stop, but also passive boost functions require the battery to supply the electrical system. A cycle-proof battery like AGM copes best with the requirements of micro-hybrid vehicles.
2) High recharging currents: An efficient recovery of braking energy requires a battery accepting high charging currents within short time periods to collect quite large amounts of energy. In consequence, the battery may heat up faster due to high charging currents (Joule heat effects) exceeding the previous range.
3) Incomplete recharging: In vehicles with recovery of braking energy, the battery is held at a medium SOC to be able to accept energy while braking. So the battery is intentionally not fully charged during long time periods. But even in standard cars, the battery may be not fully charged: A poor load balance (more discharge by electric loads than recharge by the alternator) and a low idle-running speed (low alternator voltage) may cause the battery not being fully charged for an extended period of time. In consequence, if the battery is kept at a lower SOC for a long time, the fine lead sulfate of the partially discharged plates will recrystallize to more coarse crystals (sulfation) [12]. The charge acceptance will be lower afterwards. By regularly recharging to high SOC, sulfation may be avoided.

An additional effect is to be observed with flooded batteries: If flooded batteries are cycled but not charged sufficiently, a stratification of electrolyte may occur. When these batteries are kept in a partial state of charge for a longer time, the acid stratification will be converted into a "mass stratification": Due to different electrochemical potentials in high- and low-concentration sulfuric acid, the upper and lower parts of the partially discharged plates will be discharged and recharged, respectively, to reach an equilibrium. This effect is not reversible in vehicle. VRLA batteries do not show acid stratification and do not suffer from this effect described above so that AGM batteries are considered to be the preferred solution for this application (cf. Table 3).

5. Ageing of lead-acid batteries, failure modes

Several ageing processes, often not independent from each other, lead to gradual loss of performance of lead-acid batteries [2,13]. Some main ageing processes affect both flooded and AGM batteries similarly [7], while others are specific for AGM or flooded, respectively:

1) Disintegration of the positive active material (mainly after high cycle loads at the end of service life of batteries), leading to the failure mode of mass shedding. High temperatures may accelerate mass degradation.
2) Loss of inner surface of negative sponge lead electrode (to be prevented by expanding additives in the negative active mass)—resulting in a degradation of high-rate capability.
3) Corrosion of positive grid and conducting elements (dependent on the alloy)—leading to higher internal resistance.
4) Sulfation (recrystallization of lead sulfate).
5) Water loss due to overcharging or evaporation.In AGM batteries, some additional ageing effects may take place:
6) Oxidation of negative active material by oxygen intake from the air (to be prevented by valves and a tightly sealed battery container design).
7) Corrosion of negative bus-bar and plate lugs due to the loss of "cathodic corrosion protection" as a consequence of the top lead not covered by electrolyte.
8) Increase of internal resistance from water loss.In flooded batteries, one significant ageing effect can be observed:
9) Stratification of electrolyte.

Some of these effects are influenced by the operating temperature of the battery and will be discussed in the next section of this paper.

5.1. Heat as an ageing factor for battery's lifetime

Heat is one of the most important influencing factors for battery's lifetime. According to the Arrhenius equation, the reaction rate is approximately doubled when temperature is increased by 8–10 K [7]. So all chemical reactions—desired or undesired—will be faster at high heat. One of these undesired reactions is the self-discharge reaction, for example. On the other hand, mass transport processes are not accelerated in this way, so not all battery characteristics are changed by the given factor. Diffusion of lead ions within the pores of the plates is linearly dependent on the temperature, for example.

Some important ageing factors are as follows.

1. In flooded as well as in valve-regulated lead-acid batteries (VRLA), one of the most significant undesired reactions is the corrosion of the lead alloy of the grids of positive plates. This reaction is able to deteriorate lead grids completely and is running even in batteries on standstill. The metallic lead of the positive grid is oxidized to lead oxide or lead sulfate under the influence of the high positive electrode potential [7]. Usually this process is relatively slow because a corrosion layer is formed which mainly prevents the metal from further corrosion [14].
2. Gassing due to decomposition of electrolyte: All lead-acid batteries will lose some water by electrolysis when (over-) charged at high temperatures. Today's grid materials mainly are lead–calcium alloys. In former days when lead–antimony alloys were used, this problem was even worse because antimony was oxidized and diffused to the electrolyte. If antimony ions reach the negative electrode, they lower the hydrogen overvoltage so that hydrogen generation is facilitated significantly also at low charging voltages. The negative plate is "poisoned" with antimony in this case.
3. Water evaporation is another effect accelerated by temperature. Even without an external charging voltage, the battery will lose

Table 4
Heat capacities of LN3 batteries (70 Ah, 278 mm × 175 mm × 190 mm).

Battery type	Battery weight (kg)	Heat capacity (absolute) ($kJ\,K^{-1}$)	Heat capacity (related to weight) ($kJ\,K^{-1}\,kg^{-1}$)
Flooded LN3	19.0	18.6	0.98
AGM LN3	20.7	17.8	0.86

some water. The higher the electrolyte temperature is, the higher the water loss from evaporation will be. In contrast to flooded batteries exhibiting an excess reservoir of sulfuric acid, VRLA batteries are starved in electrolyte. In this case, there is a general risk from losing some water, because the internal resistance of the AGM battery may increase.

For the comparison of heat tolerances of flooded and AGM batteries, it is important to know their heat capacity, which is mainly determined by the amount of electrolyte (sulfuric acid and water) in the battery. The percentage of heat capacity determined by sulfuric acid is 75–85% in flooded batteries and 64–75% in AGM batteries [7]. As the AGM battery contains less electrolyte compared to a equal-sized flooded battery, its heat capacity is smaller. In the literature, values of 0.94–1.2 $kJ\,K^{-1}\,kg^{-1}$ for flooded and 0.75–1.0 $kJ\,K^{-1}\,kg^{-1}$ for VRLA batteries can be found [7].

Typical values of LN3 batteries are given in Table 4. The AGM battery exhibits a heat capacity about 12% lower compared to the flooded design related to the total weight, while the difference of absolute values is only 4.5%.

Therefore, an AGM battery will heat up or cool down only slightly faster than a flooded battery if battery size and ambient conditions are comparable.

One has to consider that lead-acid batteries in automotive applications usually are not exposed to high temperatures during all their service life continuously. In most cases, the high-temperature excursions are quite rare, compared to the entire service life. Therefore, it is not meaningful to define a hard temperature limit for the battery—to estimate the heat impact, the integrated temperature profile has to be considered.

If the battery system consists of two separate battery blocks, e.g. in 24 V board nets of European trucks and buses, the temperature difference of the two batteries may be important. If this difference is high or even if the individual cells of one battery are not on the same temperature level, all chemical reaction rates will be different as well—according to the local temperature. So the performance of the individual battery cells within one battery block varies. As the weakest cell generally limits the battery's discharge characteristics, this imbalance is disadvantageous. In consequence, even the polarity of the weakest cell of the battery may be reversed, if there is an unequal distribution of heat within the battery block.

6. Water-loss model for AGM batteries

Overcharging of AGM batteries causes some water loss, in particular at high overcharging voltages and high battery temperatures [2].

A model was set up to estimate the water loss of an AGM battery under overcharging conditions [15]. The model calculates the actual water-loss rate from given input parameters:

i. battery temperature,
ii. charging voltage and
iii. battery age, where battery age is specified as the accumulated water loss.

The model is based on overcharging experiments at prismatic AGM batteries of different sizes. Water-loss experiments were carried out at various temperatures under controlled laboratory conditions, and the weight losses were measured. All data were applied to a parameterized empirical model. After full parameterization, the model was tested at new batteries both in laboratory and in real-battery applications in the field.

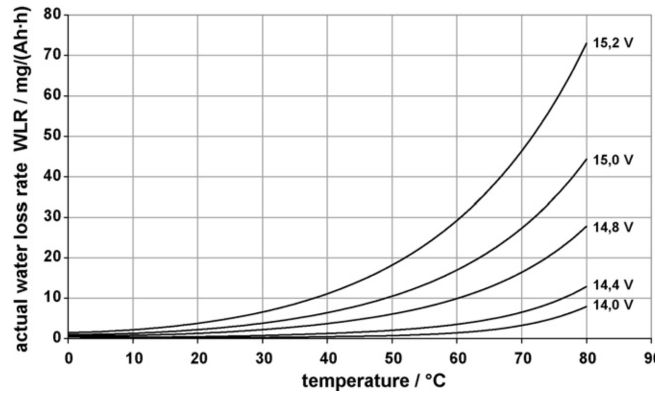

Fig. 7. Water-loss rates of AGM batteries, calculated with the water-loss model—exponential dependency on temperature and charging voltage.

The model has proven to give a good estimation of the actual water-loss rate, measured in $mg\,Ah^{-1}\,h^{-1}$. The water-loss rate is referred to the nominal capacity of the battery to consider the battery size.

The total water loss consists of two main parts:

a) water loss generated while charging/recharging/overcharging the battery and
b) water loss generated during rest periods (without charging).

Both parts depend on temperature, but part (a) is dependent on other factors, in addition. The water-loss rate (WLR, weight loss in $mg\,Ah^{-1}\,h^{-1}$) is calculated as:

$$\mathrm{WLR} = x_{\mathrm{H_2O}}\ x_{\mathrm{U}}\ x_T\ x_{\mathrm{WL}}\ x_{\mathrm{ABC}} + f(T) \quad (1)$$

where $x_{\mathrm{H_2O}}$ is a factor for the basic level of water loss (in units of $mg\,Ah^{-1}\,h^{-1}$), x_{U} is a voltage-dependent term, x_T is a temperature-dependent term, x_{WL} is considering the accumulated water loss. The term x_{ABC} represents further model extensions. Finally, $f(T)$

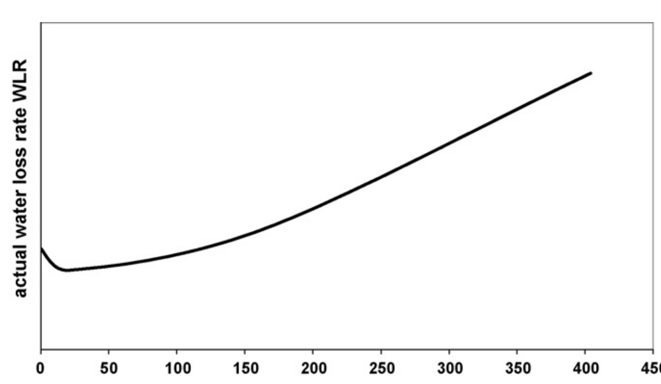

Fig. 8. Water loss of AGM batteries vs. battery age/accumulated water loss.

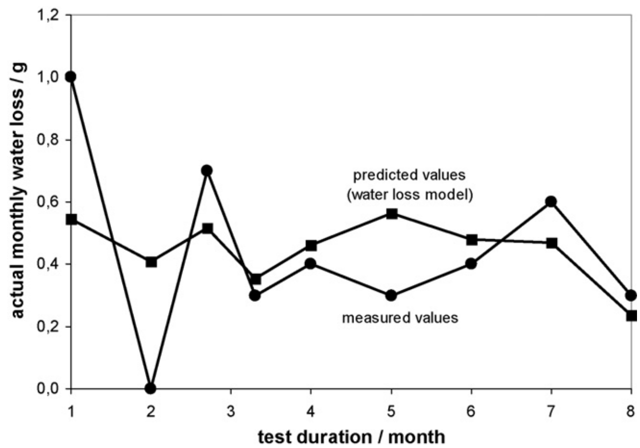

Fig. 9. Comparison of experimental water loss and model prediction. N.B.: balance 0.1 g scale, battery approx. 20 kg.

describes a polynomial function of temperature considering the water loss caused by evaporation.

Water loss of AGM batteries depends exponentially on temperature and charging voltage (Fig. 7).

Interestingly, the battery age, described as accumulated water loss, term x_{WL} of equation (1), turned out to be an important factor. Water loss is drafted vs. the accumulated water loss in Fig. 8. At the start of service life, a slightly higher weight loss is observed. This is due to degradation of organic components being oxidized to carbon dioxide which is released from the battery. The CO_2 can be identified by precipitation of barium carbonate from an aqueous solution of barium hydroxide when analyzing the charging gases of the battery at this initial time period. Afterwards, the actual water-loss rate is continuously increasing with higher accumulated water loss.

Generally speaking, the water-loss rate of an AGM battery increases within service life. These findings seem to be not in agreement with the common knowledge that water loss of AGM batteries decreases when the oxygen cycle starts working highly efficiently. Maybe the experimental conditions have not been the same. All our experiments have been carried out in a thermo chamber at temperatures up to 60 °C. Under these conditions, the batteries are heated nearly uniformly, which means that all parts of the battery, including the lid and the valves, were on the same high temperature level. In contrast to experiments carried out in a cooler environment or in a water bath, the electrolyte cannot be condensed at the inside of the lid. So at high internal battery temperatures, not only the water loss from electrolysis but also the water loss from vaporization is higher. In our experiments, the battery will heat up with increasing efficiency of oxygen cycle and will lose more water by vaporization. The lid and the valves are not the coldest parts of the battery, as they are in experiments carried out in a water bath.

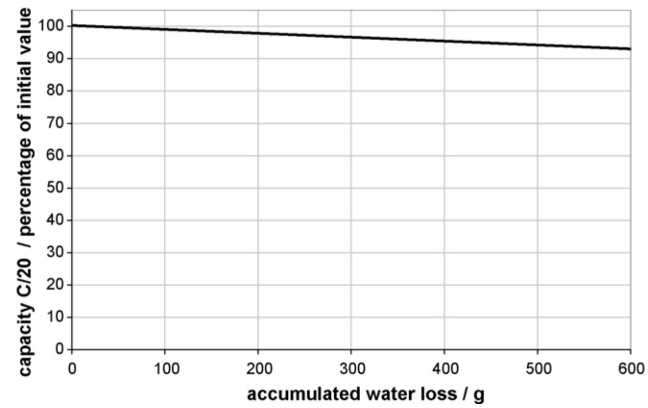

Fig. 11. Dependency of AGM batteries' capacity C/20 on the accumulated water loss.

The reason for temperature increase with higher accumulated water loss is probably the loss of water in the glass mat separator, inducing a higher recombination current, observed in experiments at higher accumulated water losses. There is always a balance between heat generation and heat dissipation also at elevated temperatures. Therefore, the battery environment determines the battery temperature.

However, in all experiments carried out in our laboratory, an equilibrium was reached. In some experiments, the recombination current turned into a high, but stable level. A thermal runaway phenomenon has not been observed [8]. Batteries exhibiting a high recombination current and a high actual water-loss rate at elevated battery temperatures, reproducibly show significantly reduced recombination currents and low actual water-loss rates again after cooling down to lower temperatures afterwards.

The water-loss model does not include the CO_2 evolution of the initial period, which is only a minor effect in total, but it includes the effect of increased actual water-loss rate with accumulated water loss, specified by the term x_{WL} in equation (1).

In the experiments, the weight of the batteries was periodically determined before and after a test step, so that the data fed into the water-loss model are mass loss data, strictly speaking. However, even the initial mass loss can be described as water loss, because the oxidation of organic substances to CO_2 in the initial phase of battery service life also consumes some water as an oxygen source.

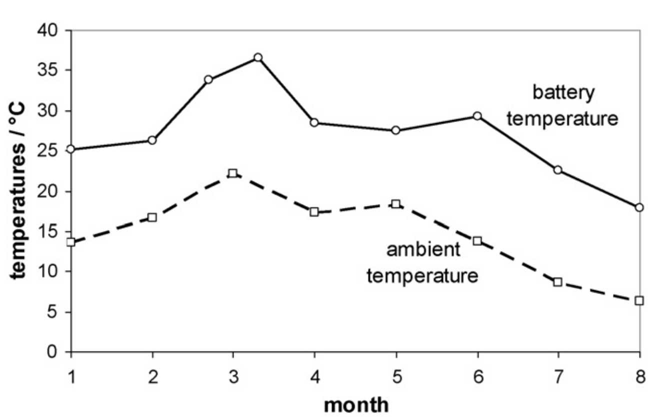

Fig. 10. Temperature data from a water-loss experiment (average temperature per month).

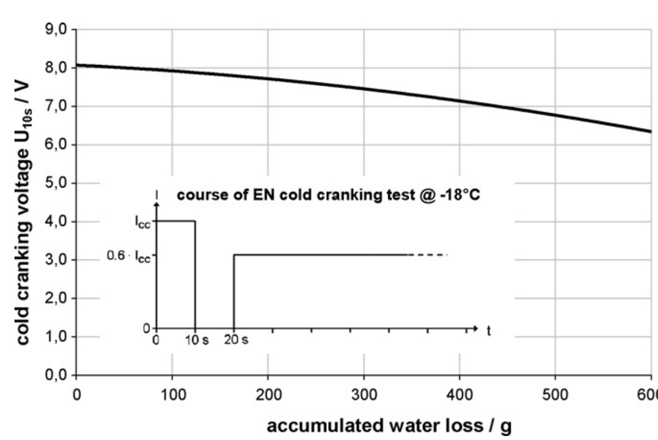

Fig. 12. Dependency of AGM batteries' cold cranking voltage U10 s on the accumulated water loss. Insert: current profile.

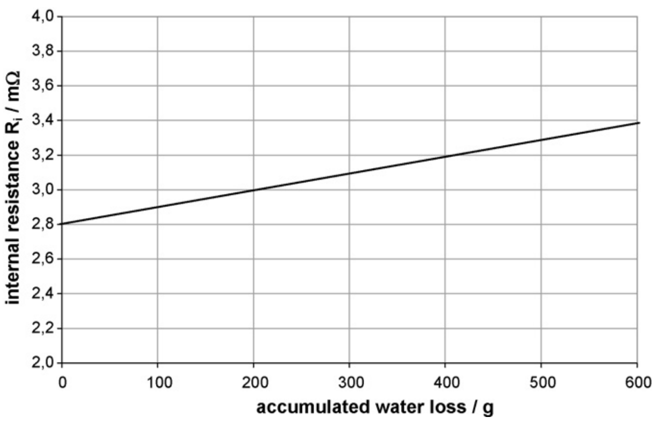

Fig. 13. Dependency of an AGM battery's internal resistance on the accumulated water loss.

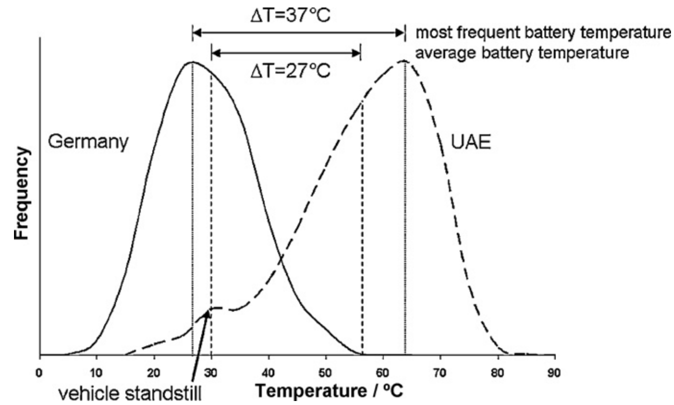

Fig. 14. Temperature histogram of field tests in Hannover, Germany, and the United Arab Emirates.

6.1. Comparison of experimental and calculated water-loss rates

To validate the model and to get more information on the water loss of AGM batteries in real-life applications, a test program was started. Some cars have been equipped with prismatic AGM batteries and data loggers for battery voltage and temperature. Some batteries were installed in the engine compartment, some others in the luggage compartment.

The cars were operated in a commuter duty, at several weekends also on long-distance trips. Every 4 weeks, the batteries were weighed and the measured data were fed into the water-loss model. Within 8 months of test, the calculated and the measured values for the water loss have been compared. The result of one of the test series is shown in Fig. 9.

The key issue was to obtain exact battery weight data from measurements on the balance. Main deviations are caused by weighing inaccuracies when looking for weight changes of less than 1 g at objects of a total weight of about 20 kg. Most frequent charging voltage was 14.5 V, average battery temperature was 27 °C. In Fig. 10, the ambient and battery temperatures are shown. The average battery temperature roughly follows the average ambient temperature.

Test results:

1. The battery temperature is mainly determined by the ambient temperature with some offset (dependent on the driving profile).
2. Water loss of AGM batteries is negligible low under real-life conditions in central European climate.
3. The model prediction is in the correct order of magnitude.
4. The actual water-loss rate under these climatic conditions is not determined by the average temperature significantly.

A battery located in the luggage compartment showed a water loss of less than 2 g in 1 year. With installation in the engine compartment, the water loss was found to be less than 5 g per year (measured data for 8 months extrapolated to 12 months).

6.2. Consequences of water loss for AGM batteries on electrical performance

The dependency of the battery's 20-h capacity (C/20) on water loss is shown in Fig. 11 (example, AGM LN5 design). The capacity is scarcely influenced by water loss. Even with a non-realistic high water loss of 300 g, the battery's capacity is still 95% of initial value, and even after a water loss of 600 g the C/20 value is approximately 90%.

The dependency of the cold cranking voltage U10 s at −18 °C (according to European specification "EN 50342-1") is shown in Fig. 12. The load voltage after 10 s of discharge with the given cold cranking current (CCA) is affected by the water loss significantly. But even at a high water loss of 350 g, the "EN 50342-1" specification limit (valid for fresh batteries) of 7.5 V is still met.

Culpin and Peters published similar results at low- and high-rate discharges of VRLA batteries [16].

The internal resistance of AGM batteries is directly influenced by the water loss. A linear increase was observed. If water loss is the only deterioration factor, an increased internal resistance of 20% is observed at AGM LN5 batteries with an excessive water loss of 600 g (Fig. 13).

For example, several 2-year-old prismatic AGM test batteries from our laboratory with a fairly high water loss of 300–370 g (after overcharging experiments, calculated residual filling degrees of glass mat separator = 81–84%) were examined. In accordance to the diagrams 11–13, all tested parameters were found to match or even to be above EN specification limits for fresh batteries (Table 5).

Calculations and measurements carried out so far suggest that water loss of AGM batteries is not a critical factor limiting the lifetime of AGM batteries in most cases. Under central European climatic conditions, the batteries will lose some water while in operation, but the total amount of water loss usually will be less than 30 g per year (taxi operation), in most cases (commuter, private use) less than 5 g per year. Very high water losses of hundreds of grams have not been found in real-life applications and had to be prepared under laboratory conditions. Batteries with a low water loss (below 100 g) or even fairly high water loss (200–300 g) are still

Table 5
AGM LN5 batteries with fairly high water losses still meet European standard "EN 50342-1" requirements.

	Total water loss (g)	Capacity C/20 (%)	cc voltage U10 s (V)	Internal resistance (mΩ)[a]
Fresh battery	0	>100	>7.7	2.8
Battery 1	300	103	≈7.6	3.1
Battery 2	370	102	≈7.5	3.2

cc voltage = cold cranking voltage U10 s according to EN 50342-1.
[a] Averaged.

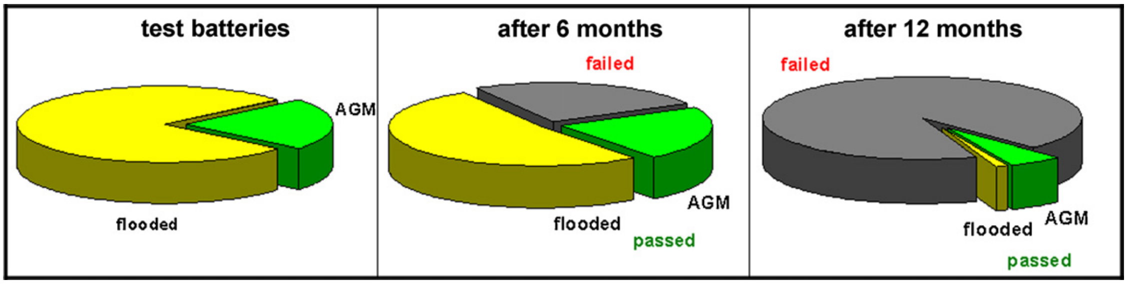

Fig. 15. Results of taxi fleet test in the United Arab Emirates.

highly powerful in automotive applications and even fulfill specification limits valid for fresh batteries in some cases, as shown in the diagrams above. The capacity at low currents (C/20) is scarcely influenced, and the degree of deterioration of high current performance (cold cranking test) is acceptable, if water loss is the only degradation factor.

In all experiments with high charging voltages at high temperatures, some additional impact of corrosion should be considered. Corrosion effects were veiled due to the high water losses prepared within short durations in the experiments shown.

All experiments carried out so far suggest that there is no hard limit for battery failure due to water loss. Deteriorations resulting from water loss were found to proceed continuously, not stepwise.

Usually, such high water losses prepared for these tests cannot be found in real-life applications.

7. Field tests in different climatic regions

To get more information on the durability of batteries in high-heat applications under real-life conditions, some taxi fleet tests in different regions and different climate zones of the world have been carried out. In taxi operations, the batteries have to fulfill quite high requirements as extended operating up to 24 h a day, cycle load much higher than in standard applications. Quite often, taxis are equipped with large diesel engines to be started also at low temperatures (in Europe, at least). Additionally, taxis often operate in urban areas and experience traffic congestions quite often.

Two of these test series are presented here.

7.1. Hannover, Germany

In Hannover, a taxi fleet was equipped with both flooded and AGM batteries in 1998. All batteries in this test were installed in the luggage compartment.

Results: The prismatic AGM batteries achieved a more than 2.5 times higher lifetime compared to flooded standard batteries. Due to the high cycle load in continuous taxi operation, flooded batteries reached the end of service life after 6–11 months. AGM batteries were able to fulfill the requirements for 27–29 months on average. The average driving distance covered by one AGM battery was 176,000 km. Furthermore, AGM batteries showed a low water loss of less than 40 g in 3 years, which is equivalent to a water loss value of about 0.44 g Ah^{-1} in 3 years. The weight loss in the first year was 25 g on average, assuming that only a part of this weight loss can be ascribed to the loss of water (CO_2 evolution, see above).

7.2. United Arab Emirates

In the United Arab Emirates (UAE), a taxi fleet test under high-heat conditions with flooded and prismatic AGM batteries started in 2006. All batteries in this test were installed in the engine compartment.

Fig. 14 shows a battery temperature histogram of fleet tests in Hannover, Germany, and the UAE. The most frequent battery temperatures are 64 °C in UAE and 27 °C in Germany, so the difference is 37 °C. The hot and dry climate in UAE is characterized by a large temperature difference between day and night time, in contrast to the moderate climate in Germany. Therefore, the average battery temperatures are different from the most frequent battery temperatures. The average battery temperatures are 57 °C in UAE and 30 °C in Germany, so the difference is 27 °C. The temperature histogram of UAE shows a second peak at 30 °C, which is assigned to vehicle standstill at nighttime (lower ambient temperatures).

Results: After half a year under these severe conditions, a quarter of the batteries failed—none of these batteries was an AGM battery (Fig. 15). The test ended after 1 year with only 7% of all batteries still working. More than 80% of these remaining batteries were AGM batteries. This 1-year test exemplifies the relative robustness of AGM batteries against high-heat impact. Even under these climate conditions with underhood battery packaging, no thermal runaway effect was observed.

7.3. Comparison of field test data and prediction of water-loss model

In another taxi fleet test in Hannover in 2006, AGM batteries have been investigated after 6–18 months of service life.

The measured water loss per year was 26 g on average. The water-loss model predicted a water loss of 28 g per year, based on following assumptions:

- operation time of 8 h per day, 300 days per year,
- charging voltage was assumed to be in accordance with the charging voltage recommendation for AGM batteries and
- ambient temperatures are based on the climate graph of Hannover.

Comparing the two water-loss values, the model estimates the water loss correctly.

8. Conclusions

Thermal effects have to be considered in automotive battery applications. In micro-hybrid vehicles, lead-acid batteries have to withstand higher cycle loads and deeper discharges. AGM batteries seem to be the best solution for these applications: They are cycle-proof, spill-proof and do not show acid stratification, which is one of the main issues of flooded batteries. The high durability of AGM batteries even in high-heat applications has been proven both in simulations and in experiments. In taxi fleet tests, AGM batteries have shown to be superior to flooded ones even under severe high-heat climate conditions in the UAE.

Under moderate climate conditions, the water loss is low and not an observed failure mode. The C/20 capacity of AGM batteries is scarcely influenced by water loss, and cold cranking voltage U10 s still meets the specification limit up to fairly high water losses (e.g. 300 g for AGM LN5). The increase of internal resistance is observed to be linear and is less than 20% even at excessive water losses (e.g. 600 g for AGM LN5), but only achievable under laboratory conditions.

Considering the real battery temperature for adjustment of charging voltage, water loss can be reduced significantly.

Although water loss is an undesirable effect of lead-acid batteries (with both AGM and flooded), the deterioration effect caused by water loss is acceptable or even negligible in most cases in real-life applications, as it is shown in this paper.

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