

Charging performance of automotive batteries—An underestimated factor influencing lifetime and reliable battery operation

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Abstract

Dynamic charge acceptance and charge acceptance under constant voltage charging conditions are for two reasons essential for lead-acid battery operation: energy efficiency in applications with limited charging time (e.g. PV systems or regenerative braking in vehicles) and avoidance of accelerated ageing due to sulphation. Laboratory tests often use charge regimes which are beneficial for the battery life, but which differ significantly from the operating conditions in the field.

Lead-acid batteries in applications with limited charging time and partial-state-of-charge operation are rarely fully charged due to their limited charge acceptance. Therefore, they suffer from sulphation and early capacity loss. However, when appropriate charging strategies are applied most of the lost capacity and thus performance for the user may be recovered.

The paper presents several aspects of charging regimes and charge acceptance. Theoretical and experimental investigations show that temperature is the most critical parameter. Full charging within short times can be achieved only at elevated temperatures. A strong dependency of the charge acceptance during charging pulses on the pre-treatment of the battery can be observed, which is not yet fully understood. But these effects have a significant impact on the fuel efficiency of micro-hybrid electric vehicles.

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1. Introduction

In various applications with partial-state-of-charge operation (PSOC) and – at maximum – sporadic full recharge, lead-acid batteries suffer from rapid capacity loss and shorter lifetime compared with the real potential of the lead-acid technology. Sulphation is the dominating ageing mechanism under such conditions [1,2]. Various investigations have shown that batteries in the field are often regarded as at the end of their lifetime, while sufficient charging could recover a significant portion of the capacity (e.g. [3–5]).

Two typical PSOC battery applications are autonomous power supply systems based on volatile renewable energies such as photovoltaics or wind power generators, as well as automotive batteries in modern cars. Both applications have limited time slices for charging and the charging processes are very often interrupted by discharging periods. Charging times for automotive batteries are limited by the driving time during one trip, which is on average well below 30 min and very seldom as long as 3 h or more. However, the European Standard defines the standard charge for flooded starter batteries as 16 V constant voltage over 24 h [6] to achieve full charging, though both voltage and duration are not realistic under real-world vehicle operating conditions. In photovoltaic systems charging times are limited at maximum to the duration of daytime. In both applications, power generation and power consumption show large variability. Hence, charging and discharging periods change frequently.

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In automotive applications, batteries are currently facing a new challenge: Micro-hybrid operation with start/stop of the internal combustion engine and regenerative braking by the alternator or starter-generator cause charging pulses in the range 1–2 C rate and several seconds [7,8]. To minimise fuel consumption the battery's charge acceptance under such dynamic conditions is crucial.

During discharge lead-sulphate crystals are formed and these crystals tend to grow with each partial cycle. Only during a full charge the sulphate is reconverted completely into charged active mass (lead or lead-dioxide for the negative or the positive electrode). However, after prolonged PSOC operation the sulphate crystals grow to a limit where they can be hardly reconverted which then results in permanent sulphation appearing to the battery user as a capacity and power loss.

Dissolution of lead-sulphate crystals is a chemical process and therefore it depends on the temperature, time, crystal surface and the concentration of ions in the electrolyte. These parameters have an impact on the charge acceptance. Adequate charging strategies take these parameters into account and assure that the battery is getting charged as much as possible within the limited available time.

If a battery fails, it is typically stated that the battery has a short lifetime or is insufficient for the application. In many cases, this is only one side of the story. Insufficient charging due to non-adequate charging strategies or due to limited available charging power, energy or time is a core reason for early performance decline of lead-acid batteries. State-of-the-art automotive power supply system design methods ensure battery service life by appropriate system sizing.

This paper presents several examples for reactivated capacity by appropriate charging strategies. Furthermore different aspects of dynamic charge acceptance will be discussed that demonstrate the strong effect of charging regimes. The discussion among battery manufacturers, power supply system designers and component suppliers must be intensified to achieve the full potential of lead-acid battery technology to remain competitive with other battery technologies. Today, as performance tests focus on discharging and partial state of charge operation, charging is done typically with an excessive charging regime resulting in a full recovery of the capacity every time.

2. Results from charge acceptance tests on gel batteries

In the following, two examples for the recovery of capacity by appropriate charging regimes are shown.

The first example is a field test which has been performed with a gel type, flat plate battery in a PV system located in Germany. The system was operated as a PV-battery-load system without an additional power generator and with a conventional charge controller. The charging voltage during normal operation was limited to 2.35 V per cell. More details on this system can be found in [3].

A capacity test was performed every 6 months. For the capacity test first a so-called "solar charging" regime was used,

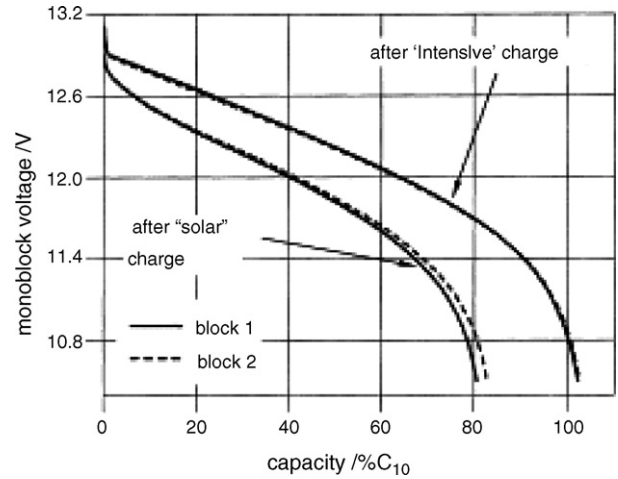


Fig. 1. Comparison of discharge curves after a cccv charging with 5 h cc at I_{10} and cv at 2.35 V per cell and 5 h ("solar charge") and after cccvcc charging with cc at I_{10} , cv at 2.45 V until current $<0.1I_{10}$ and cc at $0.1I_{10}$ until recharge of 112% of C_{10} during the complete cccvcc charging (figure from [3]).

which consists in cccv¹ charging with a maximum current of I_{10} and a constant voltage charging period at 2.35 V for 5 h. The duration of 5 h reflects the best charge conditions which a battery in such a system can achieve under Central European weather conditions. Fig. 1 shows the capacity test for two blocks, which were tested individually after 1 year in service. The available capacity was 80% of the nominal capacity. By definition, this is the end of life criterion for a stationary battery.

However, after this first test an "intensive" cccvcc² charging with constant current at I_{10} , constant voltage at 2.35 V per cell and the additional constant current at $0.1I_{10}$ without voltage limit was performed. The constant current charging at low rate was performed until 112% of the nominal capacity is recharged to the battery within the complete charging cycle.

The capacity after this "112% intensive charging" was back to 100% of the nominal capacity. A similar behaviour was observed every 6 months. An increase of 20% in capacity was very normal. Various authors (e.g. [9,10]) have presented the beneficial effect of constant current charging steps with low rates but without voltage limit for VRLA batteries.

This example shows very clearly that the available capacity for the user taking into account the available charging times and charging conditions can be significantly less than what the battery would be able to deliver under optimum charging conditions. The example also shows where the problems among battery users and battery manufacturers are: The battery user sees a battery at 80% capacity in its application; the battery manufacturer sees a battery at 100% of the nominal capacity when using the appropriate charging regime. But how are battery capacity and battery lifetime defined properly?

¹ Constant current charging until voltage limit is reached, constant voltage charging at this voltage limit until end-of-charge criterion.

² Constant current, constant voltage, constant current; second constant current charging at low current rates with a time or Ah limit.

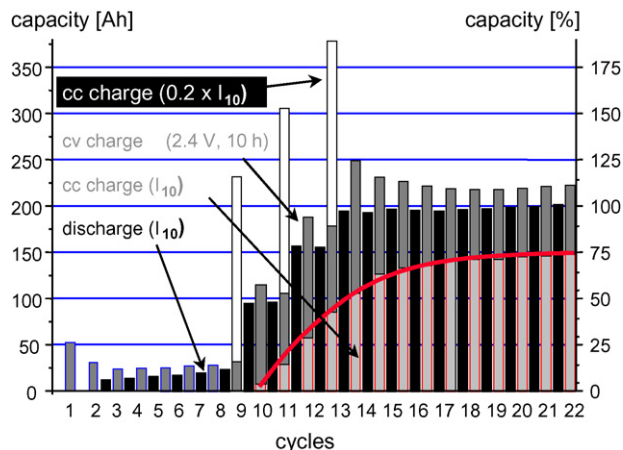


Fig. 2. Example for the recovery of the capacity for a 5 years old tubular plate, gel lead-acid battery (OPzV) by using appropriate charging regimes.

The second example is a more academic, nevertheless it shows very clearly the impact of charging regimes and the potential for the recovery of capacity by appropriate charging regimes. The results are shown in Fig. 2. The experimental set-up was as follows.

An OPzV battery (tubular plate, gel electrolyte) with a nominal capacity of 200 Ah was stored under open circuit conditions in a laboratory for a period of 5 years (average temperature approx. 20 °C) without any charging. In fact, the cell was left over from the installation of a high voltage battery, remained unused, and was forgotten. Before the battery was removed, a series of capacity tests after different charging regime was performed. Fig. 2 shows the results of the test. In the figure the discharged (black bars) and the charged Ah (grey and white bars) are shown next to each other for a series of 22 cycles in total.

Discharging was performed with I_{10} down to 1.7 V per cell. Regular recharging was done with a cccv charging whereas I_{10} was offered during the cc charging and the cv charging was done at 2.4 V per cell for a periods of 10 h. The cc period was limited only by reaching the voltage limit of 2.4 V per cell.

The initial discharge after 5 years under open-circuit conditions resulted in zero Ah. During the following charging period according to the above mentioned charging regime approx. 50 Ah were charged into the battery (cycle 1) but again resulting in zero Ah discharge capacity (cycle 2). After the second charging a capacity of some 10 Ah (5% of the nominal capacity) was available. The discharge/charge regime was repeated 7 times and the battery capacity then returned to a value close to 25 Ah (12.5% of the nominal capacity). Until this point in time the battery had seen an accumulated charging time of 70 h at 2.4 V.

For the following cycle the charging regime was changed to a cccvcc charging regime, where the cccv part was identical to the above mentioned charging regime. The additional cc charging was performed with $0.2I_{10}$ for a period of 50 h, hence the nominal capacity was charged to the battery without a voltage limit and with a small current. The voltage went up to 2.6–2.7 V during the cc charging period. The available capacity after this

extensive charging was close to 100 Ah (50% of nominal capacity). Using the conventional charging regime as before resulted in the same discharge capacity. In cycle 10 again the intensive cccvcc charging was done and the capacity returned to more than 75% of the nominal capacity and after repeating the intensive charging in cycle 12 the capacity went back to almost 100% of the nominal capacity.

Ten more cycles with the conventional cccv charging regime confirmed that the discharge capacity was stable around 100% of the nominal capacity. The light grey bars show also that at the end 75% of the capacity is recharged in the cc charging period.

Even though nobody should leave a lead-acid battery in the shelf for 5 years under open-circuit conditions, this result, which was obtained just by chance and unplanned, shows very clearly that a battery which suffers from strong sulphation can be recovered to a very high extent. In the literature several examples can be found which show a string capacity decline during cycling, which is recovered after an intensive charging, e.g. [4]. For sure, any capacity loss due to effects such as corrosion would be irreversible.

Not only in these examples, the additional cc charging at limited current in the range 0.1 – $0.2I_{10}$ without any voltage limit proved to be very beneficial for the recovery of lead-sulphate, especially in gel batteries, but also in AGM and flooded batteries.

3. Charge acceptance of automotive batteries

The following experiments were performed in the last 2 years on commercial automotive batteries from different major internationally operating battery manufacturers, mostly flooded batteries. All experiments confirm that the charging regime as it occurs in the vehicles cannot reconvert all sulphate crystals completely. Sulphation cannot be completely removed at typical operational temperatures of 25 °C and therefore the available capacity of the batteries is significantly reduced.

3.1. Charge acceptance during standard constant voltage charging

A flooded battery (rated capacity $C_{20} = 80$ Ah) was treated with an accelerated corrosion test at 75 °C for 6 weeks. After the ageing test the battery was put into operation with a test profile for battery management systems (10 days test with varying state of charge and current profiles). At a certain point in the test the battery was charged according to an EN charging regime at elevated temperature (40 °C, max. voltage 2.6 V per cell, 24 h) and the capacity was measured still at a battery temperature of 40 °C. Then the battery was cooled down to 25 °C and an EN charge was performed again (25 °C, max. voltage 2.667 V per cell, 24 h) with a subsequent capacity test. The currents during constant voltage charging at the end of the 24 h charging are shown in Fig. 3.

The currents at the end of the 24 h charging were 0.55 A at 25 °C and 0.25 A at 40 °C. Assuming that gassing doubles with

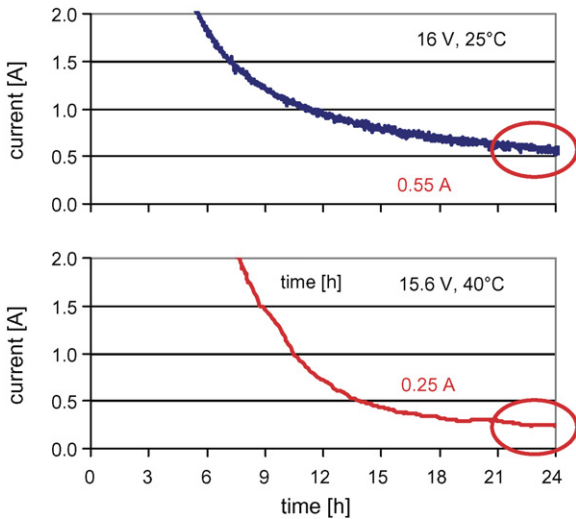


Fig. 3. Measured current during a 24 h charging with 40 °C and 2.6 V per cell and at 25 °C and 2.667 V per cell.

each 10 K temperature increase and gassing triples with 100 mV per cell voltage increase, the gassing current would be a factor 1.4 higher for the test at 40 °C taking into account the difference in cell voltage. The results of the capacity tests with I_{20} were 90.5 Ah at 40 °C after charging at 40 °C, and 4.8 Ah at 25 °C after charging at 25 °C. Taking into account a temperature dependent increase of the capacity of $0.006\% \text{ K}^{-1}$, the 90.5 Ah at 40 °C are equivalent to 82.4 Ah at 25 °C, and the battery charged at 40 °C still yields 9.5% more capacity with respect to the rated capacity. The test procedure was defined in way that allows to exclude factors such as acid stratification, ageing or pre-treatment as reasons for the differences in charge acceptance.

3.2. Charge acceptance of automotive batteries in the field

To analyse the charge acceptance of SLI batteries in normal vehicles more than 200 batteries was taken from vehicles selected randomly in workshops specialised on vehicle maintenance. Vehicles with diesel and gasoline engine, small and medium sized, and batteries with capacities between 43 and 70 Ah, 2–5 years old, operated in central Europe and in Southern Europe were selected randomly. None of the customers reported any battery problems at the time of battery removal. All batteries were of the flooded type. For all batteries the state of charge at the time of removal from the vehicles was measured and the capacities were determined after performing an operational full charge (cccv with 3 h at constant voltage at 2.45 V per cell, 25 °C) and after performing an EN charge (24 h at 2.667 V per cell, 25 °C).

Fig. 4 shows a result of the tests as a bar graph of the capacity obtained after an operational charge to the capacity after an EN charge. In some cases the capacity measured after operational charging was higher than after EN charging. These were typically batteries with a low remaining capacity compared with rated capacity that suffered from accelerated ageing from the first capacity test after operational charge.

On average the capacity achieved after operational charge is 14% less than the capacity after EN charge. In addition it is

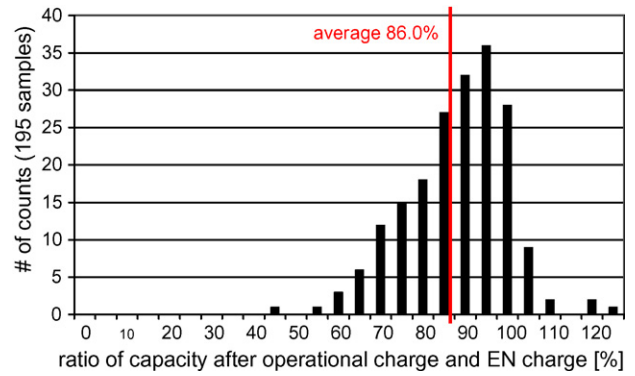


Fig. 4. Ratio of capacity after operational charge and after EN charge (both at 25 °C) for standard SLI batteries from vehicles in the field (various rated capacities, vehicle types, battery ages). A few batteries with capacities below 50% of rated capacity were not taken into account for the analysis.

necessary to take into account the results presented in Fig. 3. The EN charge at 25 °C is not sufficient to reconvert all sulphate crystals which are in principle reversible. Adding the results means that after an operational charge still 20–25% of reversible sulphate is present, which is not available for the user. Additional experiments, which are not presented here in detail, showed that acid stratification is not the main reason for the limited charge acceptance. Even batteries of the same type with mechanical stirred electrolyte suffer from the reported effects.

3.3. Charge acceptance depending on the short-term cycling history

Even though temperature and state of charge are fixed, the charge acceptance of a certain battery can vary significantly with the battery’s history. Fig. 5 shows the dynamic charge acceptance of a flooded SLI battery for standard vehicle applications.

A fully charged battery was set to 90% SOC. The SOC was adjusted in two different ways, called hereafter as “after charge” and “after discharge”:

- full charging of the battery, discharging 10% of rated capacity with I_{20} , operation point 90% SOC, referred as “after discharge”;

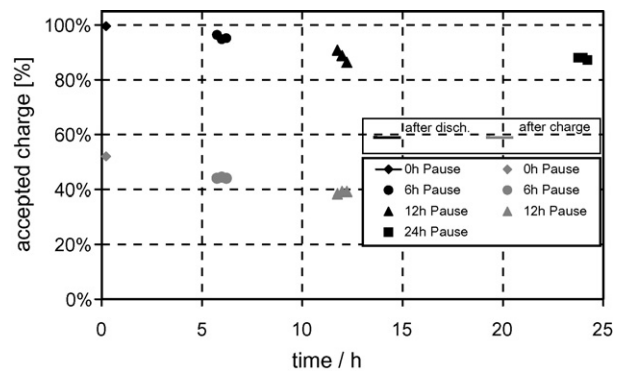


Fig. 5. Charge acceptance tests on a flooded lead-acid battery (standard automotive type, 90 Ah) with 10 s charging pulses at 1 C rate at 90% SOC after different rest periods following the adjustment of the SOC and different cycle regimes to achieve the projected SOC.

- full charging of the battery, discharging of 50% of the rated capacity, recharging 40% of rated capacity, operation point 90% SOC, referred as “after charge”.

The battery had been prepared individually for the tests with different rest periods, thus nothing happened for to the battery e.g. for 12 h before the pulse was performed. Then charging pulses of 10 s duration with 1 C rate were applied. The voltage during each pulse was limited to 14.7 V. The figure shows the charge acceptance relative to the maximum amount of charge which could have been charged at 1 C rate within 10 s for three consecutive pulses using different rest periods after the SOC was adjusted.

Two aspects are of relevance:

1. The charge acceptance decreases with the increasing duration of rest periods. Something changes in the battery under open circuit conditions, which leads to a change in charge acceptance. Thele et al. [11] have proposed a model to take this effect into account for electrical performance modelling. The concept has been described as “hardening crystals”. The assumption is that the crystal structure is changing with time. Crystals or parts of crystals of high solubility change their structure with time into crystals of lower solubility. This could be either a change in the crystal structure or a recrystallisation process resulting in a reduction of the number of crystals and therefore a reduction in active surface area. However, this is only a consideration based on the electrical measurement results. The microscopic processes are not fully understood.
2. The charge acceptance depends considerably on the way how the state of charge was adjusted. Setting the state of charge by discharging the fully charged battery results in a dynamic charge acceptance twice as high compared with the same SOC reached by charging from a lower state of charge. Temperature, SOC, and current rates are identical, but the internal structure is significantly different.

The above results show that charge acceptance is a very complex topic and the processes which affect charge acceptance are not fully understood yet. The charge acceptance is changing

during rest periods but the battery’s history which resulted in a certain state of charge has a much greater impact. For any performance rating of lead-acid batteries with regard to charge acceptance it is therefore essential to define and to document the operating conditions in detail. Results from laboratory experiments can be transferred into real world applications only if the test cycle corresponds closely to the real world operating conditions.

3.4. Charge acceptance of sulphated batteries after microcycle operation

Another test investigates the charge acceptance of batteries after an accelerated microcycle ageing profile at partial state of charge. The microcycle ageing simulates the impact of the start/stop operation of a vehicle, where the internal combustion engine is shut down whenever no acceleration is needed. During the shut down periods the battery is discharged by the full electrical load in the vehicle and as soon as the motor is restarted the battery is recharged again. Significant capacity loss was reported in the literature during microcycle operation including the recovery of the capacity through intensive charging regimes [9]. Lam et al. [5] showed the impact of high rate partial state-of-charge operation on the capacity of a VRLA battery, identifying insufficient reconversion into lead in the negative electrode resulting in sulphation as the main reason for capacity loss.

For the tests presented in Figs. 6 and 7 15,000 microcycles were performed with 1% DOD per cycle with 1 C rate for the flooded batteries and 10,000 microcycles with 2% DOD as well with 1 C rate for the AGM batteries. Thus the capacity throughput was 150 resp. 200 times the nominal capacity. Except some rest periods nothing else than the microcycles were applied to the battery.

Before microcycling started the initial capacity of the batteries was measured. Two capacity tests were performed for this purpose with EN charges. After microcycling the batteries were charged with certain charging strategies. Different charging strategies, which differ in the maximum charging voltage, the temperature during charging and the duration of the charging, were tested. The presented results are only examples which represent the most probable case in today’s vehicles (strategy

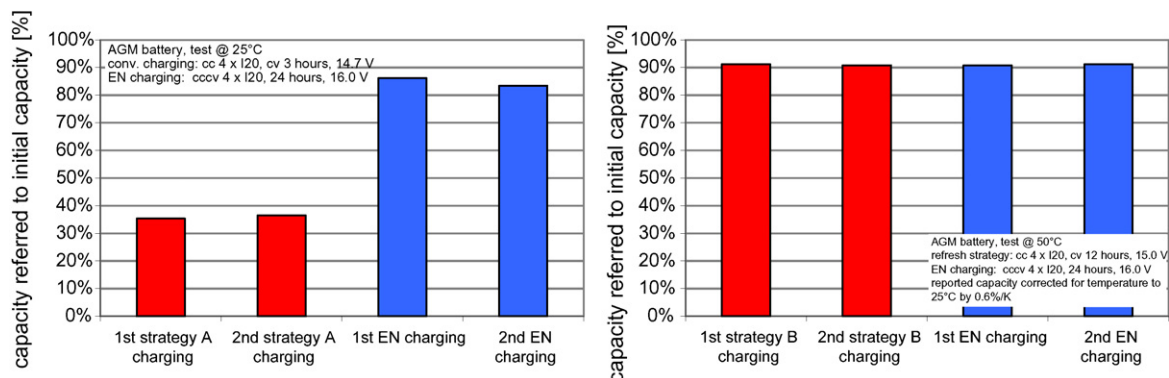


Fig. 6. Results of capacity tests within a test procedure for the determination of the charge acceptance for batteries aged by microcycles for an AGM battery with charging strategies A and B. Test procedure described in the text.

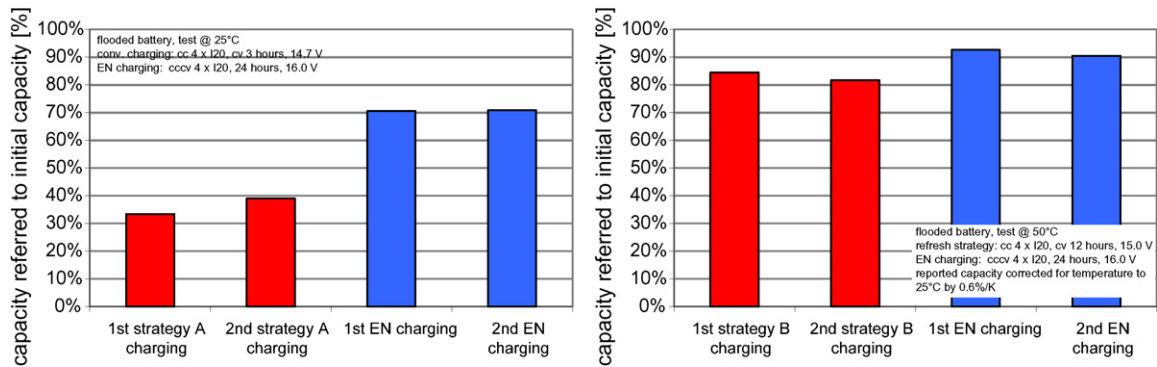


Fig. 7. Results of capacity tests within a test procedure for the determination of the charge acceptance for batteries aged by microcycles for a flooded SLI battery (antimony free, standard product) with charging strategies A and B. Test procedure described in the text.

A) and a strategy which goes to all limits to see, what might be possible (strategy B).

- *Strategy A or “operational charge”*: constant current ($4I_{20}$), constant voltage (14.7 V, duration 3 h), battery temperature 25 °C (measured at outer battery case wall).
- *Strategy B*: constant current ($4I_{20}$), constant voltage (15.0 V, duration 12 h), battery temperature 50 °C (measured at outer battery case wall).

The specific charging strategy was repeatedly applied after the capacity test had been performed with $4I_{20}$. The capacity tests were performed at the same temperature as the previous charging. After these two charge/discharge cycles the battery was charged with an EN charge. For the battery where strategy A was applied a 24 h charging at $U_{\max} = 16$ V and 25 °C was performed. For the battery with strategy B the 24 h charging occurred at 15.4 V and 50 °C. Again a capacity test was performed as after charging with strategies A resp. B. This procedure was also repeated twice.

Finally, four capacity values are available which are presented in Figs. 6 and 7. All capacities are normalised to the initial capacity measured at 25 °C and $4I_{20}$ before the microcycling commenced.

The left hand graphs show the results obtained with charging strategy A for the AGM battery in Fig. 6 and the flooded battery in Fig. 7. The right hand graphs in both figures show the results for charging strategy B and the following EN charges.

For both battery technologies the available capacity which can be achieved after an “operational charge” falls below 40% of the initial capacity. It is necessary to mention that the batteries were previously treated with a microcycle regime at states of charge below 80% in an extreme way that caused severe sulphation. A repetition of the charge/discharge cycle with strategy A gave little additional capacity recovery. When applying the EN charging the capacity approx. doubled for both battery technologies. But the AGM battery returned after this treatment at 25 °C to approx. 85% of the initial capacity whereas the flooded battery remained at approx. 70% of the initial capacity.

The right hand graphs in both figures show that strategy B is much more efficient in recovering the capacity. This is surely not surprising: temperature and voltage are higher, charging time is

prolonged. But it is interesting to see that strategy B already recovered the maximum capacity with the first charge/discharge cycle which was also achieved with the following EN chargings. All four tests ended with almost identical capacities.

For the flooded battery (Fig. 7) the capacity recovery with strategy B also worked also very well, however, the EN charges increased the available capacity by approx. 10%.

Please keep in mind that the microcycle ageing used in these tests is equivalent with 200 nominal capacity turnovers for the AGM and 150 nominal capacity turnovers for the flooded batteries. Figs. 6 and 7 show that the irreversible capacity loss is less than 10% in both cases, which is a promising result with respect to microcycle operation in vehicle applications.

The message from these tests is as follows:

- AGM and flooded batteries show more than 90% of their initial capacity after PSOC microcycle operation with 200 resp. 150 capacity turnovers, when properly charged.
- Standard charging regimes as available in some applications can result in a severe capacity decline, when combined with aggressive PSOC microcycling.
- By charging at elevated temperature the capacity of AGM batteries is recovered immediately.
- For flooded batteries even EN charging (repeated twice, 24 h each at 16 V) does not recover the available capacity. This is in line with the results discussed in Figs. 3 and 4. Charging at 50 °C brings 20% additional capacity.

4. Theoretical impact of temperature and potential on sulphate dissolution

To understand the experimental results, it is worth to have a closer look at the charge/discharge processes in a lead-acid battery. They can be expressed in a first order approximation as a combination of an electrochemical, a physical and a chemical process. Fig. 8 schematically shows the underlying reaction at the negative electrode (Pb electrode), which has been presented by various authors. In the context of charge acceptance only the charging branch (lower part of the figure) is of relevance. A charging current induces two electrons into the active mass and these electrons are compensated by the reduction of a Pb^{2+} ion which comes from the electrolyte. This causes a reduction

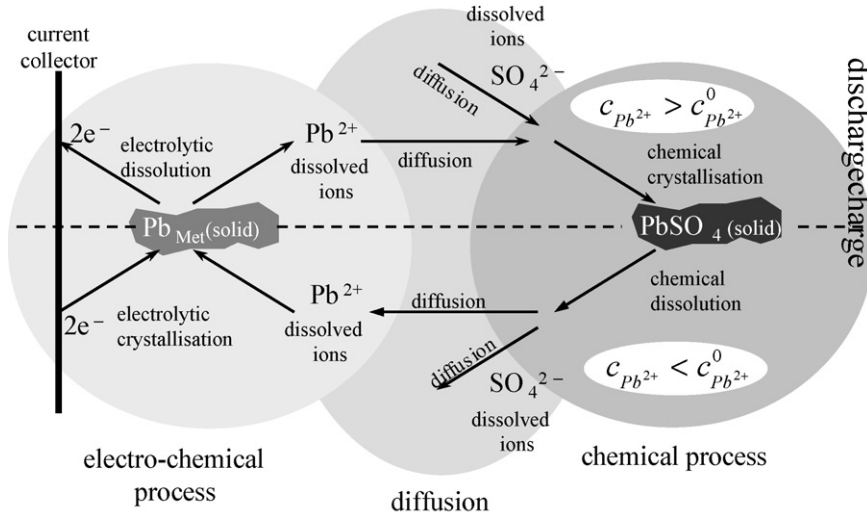


Fig. 8. Schematic representation of the charge/discharge processes in the lead-acid battery using the negative electrode as an example and assuming and dissolution/crystallisation process as the reaction channel.

of the Pb^{2+} ion concentration in the electrolyte and therefore a dissolution of $PbSO_4$ crystals, which is a purely chemical process and thus driven by the difference in the concentration in the electrolyte and the equilibrium concentration of the Pb^{2+} ions in the electrolyte.

Thus, close to full charge when the available lead sulphate is becoming scarce the dissolution of the lead-sulphate becomes the limiting step in the reaction process. To understand the limitations of charging processes we have to analyse the dependencies of the dissolution rate of the sulphate crystals on temperature and potential.

Eq. (1) describes the dissolution rate s (mol s^{-1}) as a function of the molar volume v_m of the species and the size distribution function $f(r, t)$ of the crystals. The integration goes from the smallest crystals with radius r^* which are stable from a thermodynamic point of view to the largest crystals [12,13].

$$s = \frac{4\pi}{3} \frac{1}{v_m} \frac{d}{dt} \int_{r^*}^{\infty} r^3 f(r, t) dr \quad (1)$$

Assuming that all lead-sulphate crystals have the same size (assuming spherical crystals) and the overall crystal volume is V_{PbSO_4} the size distribution function simplifies to $f(r, t) = N(t) = V_{PbSO_4}(t)/((4/3)\pi r(t)^3)$. The change in the radius of a crystal due to chemical dissolution is given by the following equation:

$$\frac{\partial r}{\partial t} = \frac{v_m D(c_{Pb^{2+}} - c_{Pb^{2+}}^0)}{r} \quad (2)$$

where $c_{Pb^{2+}}^0$ is the equilibrium concentration of Pb^{2+} and $c_{Pb^{2+}}$ is the actual Pb^{2+} concentration. Putting together Eqs. (1) and (2) under the assumption of similar radius of all lead-sulphate crystals results in a dissolution rate as given by Eq. (3) for a certain point in time

$$s = \frac{V_{PbSO_4} D(c_{Pb^{2+}} - c_{Pb^{2+}}^0)}{r^2} \quad (3)$$

From Eq. (3) the following conclusions can be deduced for the dissolution rate at a given state of charge ($V_{PbSO_4} = \text{const.}$, linear change with SOC):

1. The dissolution rate increases with increasing diffusion constant. The diffusion constant is a function of the material, the temperature (mainly linear in the temperature) and the concentration of the sulphuric acid.
2. The dissolution rate is inversely proportional to the square of the crystal radius. Hence, the smaller the crystals at a given state of charge, the higher the dissolution rate.
3. The dissolution rate is proportional to the difference in concentration of the Pb^{2+} ions in the electrolyte and their equilibrium concentration. During charging the concentration of the ions in the electrolyte is always smaller than the equilibrium concentration. The ion concentration in the electrolyte is given by $\partial c_{Pb^{2+}}/\partial t = q - s$, where s is the dissolution rate from Eq. (3) and $q = -I/nF$ is the production rate of ions due to the electrochemical process (Fig. 8) and therefore directly proportional to the current. The current I is positive during charging. The equilibrium concentration is mainly directly proportional to the temperature and depends also on the acid concentration.

To understand the effect of charging voltage on the dissolution of sulphate crystals, it is necessary to analyse the overvoltages in a battery cell. The overvoltage is summed up from the Ohmic voltage drop, the diffusion overvoltage due to gradients in the concentration of any ions in the electrolyte and the reaction overvoltage which is described by the Butler–Volmer equation. Close to full charging a major contribution comes from the diffusion overvoltage which is associated with the concentration of the Pb^{2+} ions (Eq. (4))

$$U_{\text{diff}} = -\frac{RT}{nF} \ln \left[\frac{c_{Pb^{2+}}}{c_{Pb^{2+}}^0} \right] \quad (4)$$

The concentration of the Pb^{2+} ions is approaching zero, because the charging current takes all ions from the electrolyte which are available. Therefore the diffusion overvoltage and finally the battery voltage are increasing strongly. Inversely speaking, an increase in charging voltage will reduce the Pb^{2+} ion concentration. However, inserting Eq. (4) in Eq. (3) results in Eq. (5)

$$s = \frac{V_{\text{PbSO}_4} D c_{\text{Pb}^{2+}}^0 (e^{-(nF/RT)U_{\text{diff}}} - 1)}{r^2} \quad (5)$$

This equation shows that an increase in the overvoltage cannot significantly increase the dissolution rate if $U_{\text{diff}} \gg RT/nF = 12.8 \text{ mV}$.

Thus, the increase of the voltage beyond certain limits will not accelerate charging of the active masses anymore. Assuming in a first order approximation an Arrhenius dependency for both, the diffusion constant D and the equilibrium concentration $c_{\text{Pb}^{2+}}^0$, on the temperature T (doubling with an increase of temperature by 10 K), the dissolution rate can be expressed as

$$s = \frac{V_{\text{PbSO}_4} \cdot D^{25^\circ\text{C}} \cdot 2^{(T-25^\circ\text{C})/10\text{K}} \cdot c_{\text{Pb}^{2+}}^{25^\circ\text{C}} \cdot 2^{(T-25^\circ\text{C})/10\text{K}} \cdot (e^{-(nF/R\cdot T)U_{\text{diff}}} - 1)}{r^2} \quad (6)$$

while still assuming a certain state of charge and a given radius of the sulphate crystals. The dissolution rate doubles with 5 K temperature increase. Even though this is only a first order approximation and neglects other aspects such as uneven current distribution within the electrode or concentration gradients in the electrolyte, the experimental results presented above are fully in line with these theoretical considerations.

5. Discussion

It is not the scope of this paper to describe the reasons for the varying and in many cases very low charge acceptance or to define the ultimate charging strategy. The scope of the paper is to increase the awareness with regard to the charging strategies and the charge acceptance as the key factors for the performance of batteries in partial-state-of-charge operation and for the achievable lifetime in such applications. Experimental results demonstrate that lead-acid batteries often suffer from insufficient charging. This problem occurs in all field applications with irregular cycling regimes and limited time for charging. It is not restricted to flooded batteries but can be observed as well for VRLA batteries. Sufficient charging can recover the capacity of the batteries to a very high degree. Sulphation can be dissolved to a high extent. Capacity recoveries of more than 50% of the rated capacity have been observed for flooded, AGM and gel batteries.

In a paper published in 1998 [14], Nelson discussed the question, whether VRLA batteries require different charging strategies to compensate for the lower charge acceptance of VRLA batteries versus flooded batteries. Even though he did not discuss SLI batteries in particular, he showed results of significantly higher charge acceptance for flooded batteries compared with the VRLA batteries. Our measurements show that for the SLI batteries used nowadays in the market this cannot be

seen anymore. One explanation could be the shift to antimony-free grids for the flooded batteries resulting in the low charge acceptance.

Laboratory tests often do not show the problems with charging, as charging regimes in the lab are typically designed in a way that allows full charging. Therefore it would make sense to define electrical performance or durability tests that employ realistic “field” charging regimes. The dynamic charge acceptance is one key to longer battery service life and hence should be addressed in battery specifications and benchmarkings. Furthermore, improved system efficiency is crucial in various applications.

Future battery designs should take this into consideration:

- Charge acceptance during pulse charging (e.g. regenerative braking) and constant voltage charging should become a key design parameter.
- The focus should be on assuring a high sulphate crystal surface, which can be achieved only if the crystals remain small.

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- The negative electrode is the key for an improved charge acceptance. Measurements show the high polarisation of the negative electrode during charging pulses [15].

An optimal charging strategy to avoid or revert sulphation of modern lead/acid batteries with low water consumption would include a period of recharge with low current (e.g. $0.1\text{--}0.2I_{10}$) without voltage limit and with sufficient overcharge factors or charging times. Periodical refreshing should be done with at least 110% of the nominal capacity. This has been reported in various papers.

Still, if charging times are limited, a beneficial effect after extended periods of PSOC microcycling operation can be achieved by charging at elevated temperatures without temperature correction of the charging voltage. Elevated temperature supports the dissolution of sulphate crystals. If the charging voltage is reduced at increasing temperatures, no benefits can be taken from the temperature. Intelligent charging strategies should be implemented making use of high ambient temperatures in the summer. A beneficial balance for the voltage control must be found between the need for periodical refresh chargings and the minimisation of water loss and corrosion. Also, charging strategies with pulses should be revisited with regard to their ability to increase the temperature right at the point where sulphate dissolution must take place. Surely such charging periods must be limited to several hours a month and cannot take place if the battery temperature is too high and the battery might end up with a thermal runaway.

While battery manufacturers should develop the batteries further to increase charge acceptance, battery operators need to implement advanced operating strategies. The results show again that lead-acid batteries can achieve sufficient lifetime and

performance in microcycle and PSOC applications if both prerequisites are fulfilled.

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