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Optimum battery design for applications in photovoltaic systems — theoretical considerations

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Abstract

In comparison to standard applications, lifetimes of lead–acid batteries in photovoltaic (PV) systems are shorter than one might expect. This investigation aims to identify reasons for the accelerated ageing. A detailed mathematical model of current, potential and acid distribution within the electrodes during normal operation is developed and used.

Results show that the rather small currents in PV applications (on an average between I_{50} and I_{100}) and the limited charging time cause problems, which are of minor relevance for standard applications. Small currents in conjunction with acid stratification cause a significant undercharging of the lower part of the electrodes, which again causes accelerated sulphation. Further, the number of sulphate crystals decreases with decreasing discharge current used for a full charge of the battery. This reduces the overall surface of the sulphate crystals and results in higher polarisation during the charging. The time taken for a battery cell to be completely charged is dominated by the positive electrode because it shows a high polarisation well before the electrode is completely charged. Simulations show that the charging time could be reduced if positive electrodes with less inner surface were to be used in batteries for PV systems. It is worth mentioning that the requirements for power are rather small in PV systems.

This paper focuses on the qualitative results of the simulations and their interpretation. No models are explained in detail.

Keywords: Lead–acid battery; Remote area power supply; Acid stratification; Charging characteristics; Morphology of positive active mass; Modelling

1. Introduction

PV applications represent a fast growing market for lead–acid batteries. As shown in many investigations (e.g. [1–4]) operation conditions of batteries in PV systems are completely different from standard applications for lead–acid batteries. Requirements for power density are rather small, because currents above I_5 to I_{10} occur very seldom. Average currents are between I_{50} and I_{100} [3]. On the other hand, the time available for battery charging is limited due to the limited number of sunshine hours per day. Therefore, complete charging of the batteries also occurs very seldom [4], while long periods in medium or low states of charges are typical.

Lifetimes of batteries in PV applications are shorter than extrapolated from standard applications. Therefore, it is the goal of the investigations referred to in this paper to figure out the reasons for accelerated ageing. The basis of the work described here is a detailed mathematical model of the battery. Many different models for different aspects and purposes were developed by various authors (e.g. [5–15]) in the past. But when looking at the models in detail and at the results calculated on the basis of these models, it turns out, that most of them are focused on discharge behaviour. The models were developed to understand and to optimise the discharging conditions of the batteries. Charging was not the focus of the researchers, because, in most standard applications, there is unlimited power and normally enough time available for complete charging of the battery.

In PV systems the situation is completely different. Discharging requirements in PV systems are no challenge for lead–acid batteries. But charging power and time are restricted and charging and discharging cycles interfere with each other. Therefore, it is necessary to use models which describe charge and discharge processes in detail. By the way, the problem of charging is also becoming more and more important for classical SLI applications, because of the high electrical energy consumption by the auxiliaries in cars. To figure out what happens during battery operation, it is

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necessary to simulate real operating conditions. This means, simulations over long periods of time with changing currents (charging and discharging) and integration of the battery model into an overall system simulation. The latter is necessary to evaluate the specific charging conditions in PV systems and the interaction with the charge regulators and charging strategies commonly used.

2. Simulation models

The model which allows an investigation of the ageing process consists of three parts. The following will give only a brief qualitative description of these parts.

2.1. Acid stratification and vertical current distribution within the electrodes

A model presented in [16,17], was used to calculate the extent of acid stratification in flooded lead–acid batteries. This was coupled with a model of vertical current distribution within the electrodes. Using this model we are able to show that small currents, in conjunction with acid stratification, lead to a significant undercharging of the lower part of the electrodes. This effect becomes more and more pronounced the smaller are the battery currents. When acid stratification occurs, the upper part of the electrodes is charged preferentially and the lower part is discharged preferentially. This results in differences in the local state of charge between the upper and the lower part of up to 30%. During the limited charging time, the upper part can reach a very high state of charge while the lower part is far from completely charged. This means, that the lower part of the electrode is cycled in lower states of charge than it appears from the average state of charge of the electrode. Further, the lower part is cycled without a full charge for extended periods.

These findings are confirmed by two sets of experimental results. On the one hand, it was possible to show experimentally the effect of inhomogeneous current distribution and state of charge within the electrode as a function of the charge/discharge currents [17]. On the other hand, almost all physico-chemical analysis of lead–acid batteries from PV systems at the end of their lifetime show a high degree of sulphation in the lower part of the electrodes [2,18].

2.2. Size of sulphate crystals

We assume that the basic electrochemical reaction in lead–acid batteries during discharge is a reaction via the liquid phase (solution-precipitation reaction) and is not a solid state reaction. During discharging, PbO_2 is converted to $PbSO_4$ in the positive electrode, and Pb is converted to $PbSO_4$ in the negative electrode. The discharge current creates Pb^{2+} ions, which dissolve in the electrolyte. Together with ${SO_4}^{2-}$ ions they form $PbSO_4$ molecules.

The overall volume of $PbSO_4$ in the electrode is determined by the state of charge. But the number, and therefore the size and the overall surface, of $PbSO_4$ crystals depends on the discharge currents and the cycling regime. The surface area of the $PbSO_4$ crystals influences the polarisation during charging. The dissolution rate of $PbSO_4$ depends only on the surface of the $PbSO_4$ crystals, the solubility of the Pb^{2+} ions in the electrolyte and the difference between the actual concentration and the equilibrium concentration of the Pb^{2+} ions. Therefore, the number and size of $PbSO_4$ crystals have an impact on the overall voltage of the battery. This influences efficiencies, and especially the charging time, during constant voltage charging. Therefore, it is of great importance to create a large number of small sulphate crystals to assure a low overvoltage during the charging process.

The theory on the nucleation of $PbSO_4$ crystals in lead–acid batteries is described by Kappus [19] as follows.

Nucleation of crystals occurs only under high supersaturation of the electrolyte with Pb^{2+} ions. This occurs only at the beginning of a discharge after a complete charging when no $PbSO_4$ is available anymore. Otherwise only existing $PbSO_4$ crystals will grow and the supersaturation will be too low to create new nuclei. Several experimental results (e.g. [20,21]) show high evidence for this reaction mechanism.

The electrode acts during discharge as a continuos Pb^{2+} ion source. At the beginning of the discharge, after a complete and perfect charging of the electrode, no $PbSO_4$ is present. The ion source increases the Pb^{2+} supersaturation steadily. The supersaturation during the discharge leads to a transient polarisation which can be measured as the "Spannungssack" [22,23]. With increasing supersaturation the nucleation rate increases exponentially. New nuclei act as a sink for the $PbSO_4$ molecules. Therefore, after a certain number of nuclei are build, the concentration of Pb^{2+} in the electrolyte decreases rapidly resulting in the increasing voltage at the end of the "Spannungssack" and growing sulphate crystals.

When the supersaturation diminishes (i.e. when "Spannungssack" is no longer observed), the number of crystals remains unchanged until the battery is fully charged again (i.e. all $PbSO_4$ is transferred to PbO_2). Further discharge will lead to an enlargement of the existing crystals, not the creation of new crystals. New crystallites are only formed in conditions of high supersaturation.

The prediction from the theory is as follows: if the battery is discharged with a high discharge current directly after a full charge, then (a) a large number of small crystals is generated (confirmed by experiments, e.g. [24,25]), and (b) this large number remains unchanged, independent of the value of the following discharge currents.

2.3. Morphology of the positive active mass

From experiments it is known, that the positive electrode shows during charging high polarisation well before it is

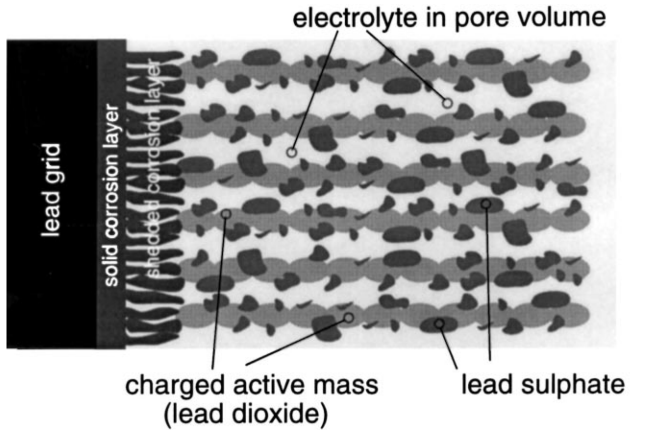

Fig. 1. One-dimensional electrode model as basis for the models on the morphology of the active mass.

fully charged. A significant increase can be observed at states of charge between 80 and 90%. The negative electrode only shows the high polarisation close to full state of charge. This results also in the well known difference in the charging efficiency of the electrodes. Regarding the morphology of the electrodes this is hard to understand. The positive electrode has an internal surface area which is approximately a factor of 10 larger than the corresponding surface of the negative electrode. This should result in lower polarisation. But detailed modelling of the charging process showed that the difference in the internal surface area is the reason for the difference in the electrode behaviour as observed in reality.

The following explanation is based on a simple one-dimensional electrode geometry as shown in Fig. 1. Many simulations of electrodes show that the active material is preferentially discharged at the boundary between the active material and the electrolyte. The local depth of discharge is lowest close to the grid. The difference between the depth of discharge close to the grid and close to the free electrolyte depends on the discharge current: the higher is the discharge current, the higher the differences in the local states of charge. Nevertheless, this difference is more pronounced in the positive electrode than in the negative electrode. This is due to complex interaction between specific resistance of active materials and the electrolyte on the one hand, and the surface areas for the electrochemical reaction on the other hand. A lower internal surface area causes a more homogenous distribution of the discharge process within the active material.

The simulations show that the positive electrode shows high polarisation much earlier than the negative electrode, because of the distribution within the active material. In fact, parts of the active material are converted completely to charged active material at an early stage. Therefore, the charging current concentrates more and more to smaller areas, which still need charging. This effect increases the specific current for the charging reaction and results in an increased polarisation of the electrode. The charging process in the negative electrode is much more homogenous due to the lower internal surface area and therefore no early polarisation occurs.

3. Optimisation of battery design and battery operation

With the help of the models it is possible to investigate the behaviour of the battery with respect to different parameters. This includes design parameters and operation parameters.

For the three effects described above parameter variations were performed. The results imply possible optimisations of the electrode design or the active mass morphology. In a more simple manner they give clues to measures for an optimised operation strategy, or the use of peripherals, for an extension of battery life.

3.1. Avoiding unevenly vertical current distribution in cells with acid stratification

For flooded lead–acid batteries the problem of inhomogeneous current distribution can be avoided simply by an electrolyte agitation system. These systems are well known and available on the market. Users often avoid these systems because of extra investment costs even though they could benefit from reduced lifetime costs.

If no agitation system is installed, acid stratification will occur. The acid stratification itself is not a primary problem for the battery. It is the unevenly distributed current among the upper and the lower part of the electrode. Calculations show that this effect can be reduced, if the specific grid resistance increases steadily from the top of the electrode to the bottom or by reducing the amount of active material from top to bottom. This reduces the inhomogenity of the current distribution during discharging while an acid stratification exists. As a consequence, the lower part of the electrode stays at higher states of charge and has a higher possibility to be fully charged. The use of the active mass and the state of charge of the electrode becomes more homogeneous. This will prevent the electrode from an early failure, because accelerated sulphation of the lower part of the electrode can be avoided.

Certainly, a higher resistance of the grid increases the overall resistance of the cell. But this is not a major problem in PV applications because the average currents are very small. Detailed calculations of the resistance profile of the grid are necessary to find the optimum design. All other design parameters of the cell, like thickness of active masses, distance between electrodes, nominal volume and density of the electrolyte and the preferred applications for the modified batteries, need to be taken into account.

3.2. Increasing the number of sulphate crystals

Experiments show that after discharging the battery with constant currents between $3 \times I_{10}$ and $0.1 \times I_{10}$, the voltage during recharge (in all cases with $2 \times I_{10}$) depends on the previous discharge current. In accordance with the Kappus theory [19], the voltage during recharge is higher if the previous discharge occurred at a lower current.

Experiments were conducted to see if these structural changes can be assigned to the first minutes of the discharge process after full charge. The experiment was set up with a 40 Ah flooded lead–acid battery with flat plates as follows.

1. After completing the recharge of the battery by an IUI_a charge regime (namely $I = 2 \times I_{10}$, $U = 2, 5$ V per cell, $I_a = 0.2 \times I_{10}$, recharge of 24.5 Ah after discharge of 20 Ah), the battery was discharged immediately for 2% of the C_{10} capacity by a current with amplitudes between $0.2 \times I_{10}$ and $10 \times I_{10}$.
2. Then the discharge was continued in all tests with $0.5 \times I_{10}$ for another 48% of the C_{10} capacity. This results in a 50% discharge of the battery.
3. After a rest period of 6 h, the battery was recharged, in all cases with constant current $2 \times I_{10}$.

All tests were performed at constant battery temperature of 20 ± 0.5°C in a water bath.

To evaluate the results, the voltage during the recharge with $2 \times I_{10}$ was recorded and plotted. These results are shown in Fig. 2. The figure shows, that the voltage during charging increases with decreasing amplitude of the initial discharge impulse. It can be seen, that the time of constant current charging can be extended significantly by the initial discharge impulse.

There are several open questions which need to be investigated.

- How strongly does the effect depend on the ratio between α-PbO_2 and the β-PbO_2 in the positive electrode?
- To what extent must the battery be recharged before the first discharge pulse shows benefits?
- What proportion of the capacity and what amplitude is needed during the first discharge pulse to get a benefit from this?
- Does the first discharge impulse only effect the sulphate structure in the positive electrode or in the negative electrode as well?

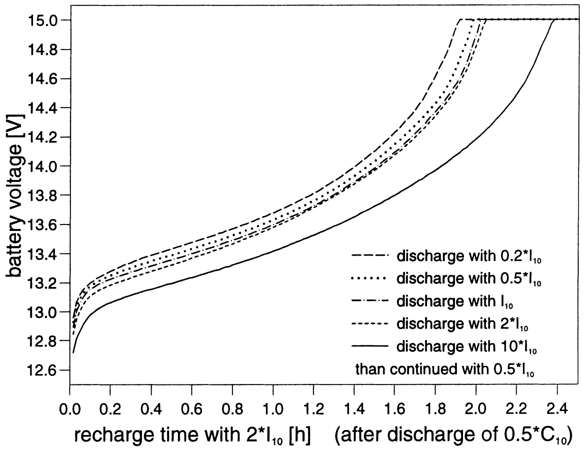

Fig. 2. Voltage during recharge after the battery was discharged to 50% DOD by a 2% discharge impulse with amplitudes between $0.2 \times I_{10}$ and $10 \times I_{10}$ followed by a 48% discharge with $0.5 \times I_{10}$.

Nevertheless, if a discharge impulse after a full charging of the battery enlarges the number of sulphate crystals through nucleation, two benefits for the battery operation are generated: prolonged charging times at constant current until the voltage limit is reached and a higher resistance against sulphation. Prolonged charging times at constant current allow batteries in PV systems to reach a higher state of charge within a day. A function for an initial discharge impulse can be integrated into charge controllers for batteries.

In standard applications high discharging currents are usually available due to the nature of the load. Additionally, the influence on the recharge behaviour on the overall performance is of minor importance, because usually an unlimited power source for recharging is available.

3.3. *Decreasing of the inner surface of the positive electrode*

The results discussed above showed, that an apparent advantage (high internal surface area of the positive active mass) can turn into a disadvantage. While the higher internal surface area allows higher discharge power and therefore increases the power density of the battery, it decreases the ability for fast recharge. Simulations show that a reduced internal surface area in the positive electrode leads to a faster recharge in the case of charging with a voltage limit. This is of great importance in PV systems, because of the limited charging time. By the way, gassing of the positive electrode is reduced because the polarisation of the electrode is less pronounced.

A reduced internal surface are of the positive electrode will reduce the available capacity at small currents slightly but the charging performance and therefore the lifetime expectation is increased.

4. Conclusion

Detailed simulations of lead–acid batteries under typical operation conditions in PV systems resulted in some suggestions for a better battery design and better operation strategy for PV systems. These ideas are in contradiction to requirements on the battery design and operation in other applications for lead–acid batteries. The ideas presented show that due to the varying conditions in PV systems it is very important to recognise that other features in battery development, like the impact of small currents and restricted charging conditions, need to be taken into account.

No special requirements for high power is needed in PV systems. The batteries act as an energy storage where maximum currents are between I_{10} and I_5 and average currents are between I_{50} and I_{100}. Therefore, a low resistance for high discharge performance is of minor importance.

The second fact is, that charging of the battery in PV systems is much more crucial than discharging. Energy and time for recharging are limited in PV systems. Therefore, it is very important to optimise battery design and operation in such a way that the limited resources can be used in an optimum way. This increases the performance of the overall system and allows a better battery operation, resulting in longer battery lifetimes.

All measures for an optimised battery operation in PV systems discussed in this paper need further theoretical and experimental investigations. But they do show that detailed theoretical investigations open new insights and may open ways to improved battery design.

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