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Advantages in energy efficiency of flooded lead-acid batteries when using partial state of charge operation

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HIGHLIGHTS

- Increase of the energy efficiency of flooded lead acid traction batteries.
- Management strategy which includes operation in a partial state of charge.
- Sulfation of the negative plates could be identified as the main failure mode.
- Evidence for the buildup of 'hard' sulfate using XRD and SEM.

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ABSTRACT

Today lead acid batteries are the most commonly used energy storage technology in material handling systems. Evaluation methods for the energy efficiency of forklifts, traction batteries and chargers have gained in relevance in this field. Generally, representative cycles are used to determine the energy efficiency in order to avoid multiple long lasting cycle live tests. At first glance this seems to be the adequate approach. However, for electrochemical storage systems with significant side reactions - like lead acid batteries - this procedure leads, to significantly lower values for energy efficiencies than in real life applications. While these battery systems need some overcharging to reach fully charged state, an overcharge is not necessary at every charge/discharge cycle.

We report on results obtained with flooded lead acid batteries demonstrating that with a management strategy which includes operation in a partial state of charge, energy efficiencies of about 0.87 can be reached with minimal impact on lifetime. The usage of a typical representative cycle leads to an efficiency value of 0.77 with active electrolyte circulation respectively 0.70 without.

We were able to identify the so called 'hard sulfation' of the negative plates as the major failure mode of insufficiently charged batteries.

1. Introduction

The use of vehicles with electric drive in the material handling sector has gained an increasingly market acceptance in the past decades. In the particular case of the European market flooded lead acid batteries with tubular plate technology (PzS) have successfully fulfilled the special requirements for industrial vehicles, like forklift and off-road trucks. A particular advantage of the lead acid battery for forklift trucks used in different material handling applications is their counterbalance capability; paradoxically a consequence of their relatively low gravimetric energy when compared with lithium ion batteries.

In the past, the battery deployment was optimized to reach long operational times, high cycle life, and short charge times. Today energy efficiency has become an important requirement. In general, the energy efficiency of an electrochemical cell is defined by

$$\eta = \frac{E^{\mathrm{Dchg}}}{E^{\mathrm{Chg}}} \tag{1}$$

as the ratio between the useful electrical energy, e.g. the discharged energy

$$E^{\mathrm{Dchg}} = \int_{I<0} U(t)\cdot I(t)\, dt\ , \tag{2}$$

and the consumed electrical energy, e.g. the charged energy

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$$E^{\mathrm{Chg}} = \int_{I>0} U(t)\cdot I(t)\,dt\ . \tag{3}$$

From a general point of view, the evaluation of the energy efficiency of a battery is only useful at the end of battery lifetime. Thus, the overall energy efficiency is given by

$$\eta = \frac{\sum_{i=1}^{N} E_i^{\mathrm{Dchg}}}{\sum_{i=1}^{N} E_i^{\mathrm{Chg}}}\ , \tag{4}$$

where N is the total number of discharge/charge cycles at end of life, E_i^{Dchg} is the energy discharged in each discharge/charge cycle i, and E_i^{Chg} is the energy charged.

In order to avoid long lasting life-cycle tests, it is common, like in DIN EN 16796-1:2017-01, to use a representative cycle starting and ending with a fully charged battery (State of Charge = FULL [8]) to determine the batteries' energy efficiency. If we assumed that the energy efficiency does not change over the whole lifetime of a battery, this appears to be the best approach. However, it will be shown in what follows that for storage systems with relevant side reactions like water decomposition this procedure can lead to underestimated energy efficiencies.

The difference in amount of energy between the charged and discharged battery has two major sources:

1. Polarization losses: Every cell current in charge or discharge direction leads to a voltage drop which is proportional to the value and the direction of the current. This voltage drop can be formally described with a single resistive term R_i containing the ohmic resistances and the kinetic effects. According to this the terminal voltage of an electrochemical cell would be

   $$U(\mathrm{SOC},I) = U_0(\mathrm{SOC}) + R_i(\mathrm{SOC},I)\cdot I\ , \tag{5}$$

   where U_0 is the equilibrium voltage and SOC is the State of charge coefficient.

2. Overcharge: The coulombic efficiency of the lead acid battery is smaller than 1; e.g. to reach a fully charged state a coulombic charge factor (CF) greater than one is needed. A CF between 1.15 and 1.2 is usual for PzS batteries and through the implementation of an active electrolyte circulation the CF ratio can further be reduced to a value in the range of 1.05–1.1.

   The CF of a discharge/charge cycle is defined by

$$CF = \frac{Q_{\mathrm{Chg}}}{Q_{\mathrm{DChg}}} \tag{6}$$

where Q_{Chg} the amount of charged Ah and Q_{DChg} the amount of Ah of the previous discharge.

An increase in the charging efficiency due to the reduction of polarization losses by means of improvements in cell design, active mass additives, as well as the use of lower currents, optimal depth of discharges, and lower CFs would in principle impact on the energy efficiency for a representative cycle, see Fig. 1 (a). However, this measures do not take into account that it is unnecessary to overcharge the battery at every cycle. This is particularly true in the case of the operation of forklift fleets, where opportunity charging within the working week in combination with an equalization charge at the weekend is one of the preferred strategies.

The advantage concerning the efficiency of this operation mode in the, so called, partial state of charge (PSOC) will become clear with the following approximation:

A PSOC operation with n charges with $E^{\mathrm{Chg}}(\mathrm{CF} \approx 1)$ followed by one full charge with $E^{\mathrm{Chg}}(\mathrm{CF} \gg 1)$ and constant discharges of E^{DChg} inserted in equation (1) results in

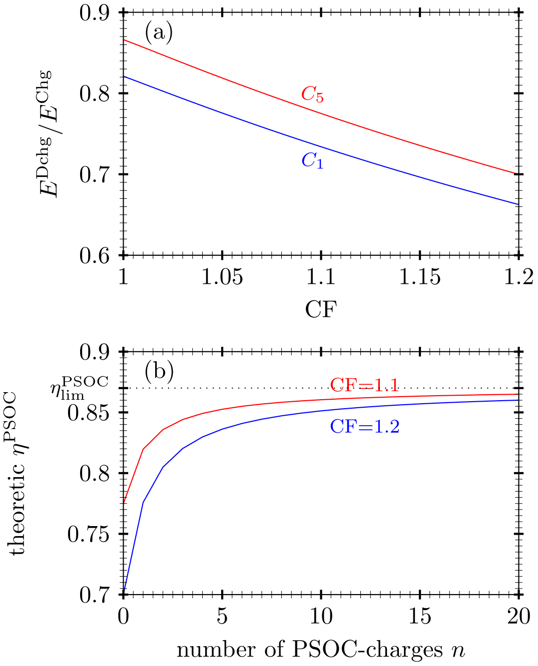

Fig. 1. (a) Calculated ratio between discharged energy and charged energy within a constant current capacity test with 113 A (C_1) and 36 A (C_5) of a 3PzS180 battery. Charged with cc 36 A (20 A/100 Ah), cv 2.4 V/c, cc 9 A (5 A/100 Ah). (b) Theoretically reachable energy efficiencies depending on the number of PSOC-cycles for two different charge factors used in the periodic full charges according to equation (7).

$$\eta^{\mathrm{PSOC}} = \frac{(n+1)E^{\mathrm{DChg}}}{n\cdot E^{\mathrm{Chg}}(\mathrm{CF} \approx 1) + E^{\mathrm{Chg}}(\mathrm{CF} \gg 1)}\ . \tag{7}$$

From equation (7) it becomes apparent that an increasing number of PSOC cycles n leads to an increasing energy efficiency limited to

$$\eta_{\mathrm{lim}}^{\mathrm{PSOC}} := \lim_{n\to\infty} \eta^{\mathrm{PSOC}} = \frac{E^{\mathrm{DChg}}}{E^{\mathrm{Chg}}(\mathrm{CF} \approx 1)}\ . \tag{8}$$

As can be seen in Fig. 1 (a), the advantage in terms of efficiency from CF 1.2 to 1.0 is nearly 17%. The theoretically reachable energy efficiencies in PSOC-operation calculated with equation (7) based on the C_5 values of Fig. 1 (a) are shown in Fig. 1 (b). After ten PSOC-cycles the difference between the efficiency limit derived from equation (8) and the calculated energy efficiency is already smaller then 2%. This shows that the management strategies based on PSOC operation are an important lever for significantly improving the energy efficiency.

The disadvantage of an arbitrary PSOC operation is that with an increasing number of cycles under insufficient charging, detrimental effects like the irreversible sulfation of (mainly) the negative plates.

One of the drawbacks is acid stratification, which leads to massive build up of lead sulfate crystals at the bottom region of the plates. The stratification phenomenon is inherent to vented lead acid system, i.e. it can be minimized but cannot be eliminated. It leads to highly increased acid concentrations in the bottom region of the jars and subsequently to the build up of irreducible lead sulfate crystals - at high sulfuric acid concentrations lead sulfate exhibits very low solubility.

To avoid irreversible sulfation effects due to acid stratification the PSOC cycling tests were carried with an electrolyte circulation pump during charging phases [7] with the consequently removal of acid density gradients within the cell.

Nevertheless the progressive capacity losses as consequence of continues aggregation of sulfate crystals due to the full charge lacking in PSOC cycling cannot be completely avoided.

The effects of sulfation occurring within partial state of charge operation has already been described for photovoltaic lead acid storage