



Empirical sulfation model for valve-regulated lead-acid batteries under cycling operation[☆]

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HIGHLIGHTS

- The Internal resistance of a VRLA battery increases during cycling.
- Increase can be linked to sulfation and depends on operating condition.
- High discharge currents and charge voltages result in less increase.
- Behavior can be modeled by an empirical root function.

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ABSTRACT

An empirical sulfation model for valve-regulated lead-acid (VRLA) batteries is presented. The model is based on measurements of the internal resistance during cycling in different state of charge (SOC) ranges. Further influence factors like voltage, current and depth of discharge (DOD) are varied and their effect on the gradient of the internal resistance is investigated. The behavior of the internal resistance correlates to the charge acceptance which is related to the sulfation of the battery. The model is tested by separate measurements.

1. Introduction

Stationary energy storage is becoming an important factor for the integration of renewable energy sources into the existing power grid. Using lead-acid batteries as the storage device of choice is still attractive due to their low price, easy handling, high recyclability and thus low environmental impact. The only drawback is the low cycle life compared to other technologies when it comes to applications where high DODs are necessary. In this case sulfation is the dominating aging mechanism of lead-acid batteries. Due to the lack of complete full charges and partial state of charge operation (PSOC) sulfate crystals can not be dissolved properly and grow over time. This leads to decreasing charge acceptance, poor efficiency and accelerated battery failure. Thus avoiding irreversible sulfation becomes one of the key factors in the operation management of stationary lead-acid systems with frequent cycling.

In literature these aspects have been discussed with more focus on automotive starter batteries. Models have been developed by Refs. [1] and [2] that describe the sulfate crystal size and radii distribution. Also the influence of charge/discharge history has been modeled by introducing the concept of “hardening crystals” [3]. The concept

indicates that previously formed crystals can be dissolved easier than crystals that formed earlier. Unfortunately these models are only validated on automotive specific test profiles e.g. shallow cycles around a fixed SOC with high current or long rest periods without battery operation [4]. So the results of this research are only partially transferable to solar/deep cycle batteries.

In recent research carbon is utilized as an additive in the negative active mass. This results in better efficiency, charge acceptance and cycle life [5,6]. But again the focus lies more on automotive than stationary applications.

Prior to this study, aging experiments on OPzV batteries for solar applications were performed. These batteries were cycled under fixed voltage limits in different SOC-ranges with only one full charge per month. During cycling the internal resistance R_i was determined using the current change after each micro cycle. The idea was to link increasing battery resistance with overall aging of the battery. The Method for determining R_i is explained in section 2.2.

These experiments showed that battery resistance increases from micro cycle to micro cycle. Along with the increase in resistance the Ampere hour (Ah) throughput from cycle to cycle decreases and therefore charge acceptance decreases. The results of one cycle period

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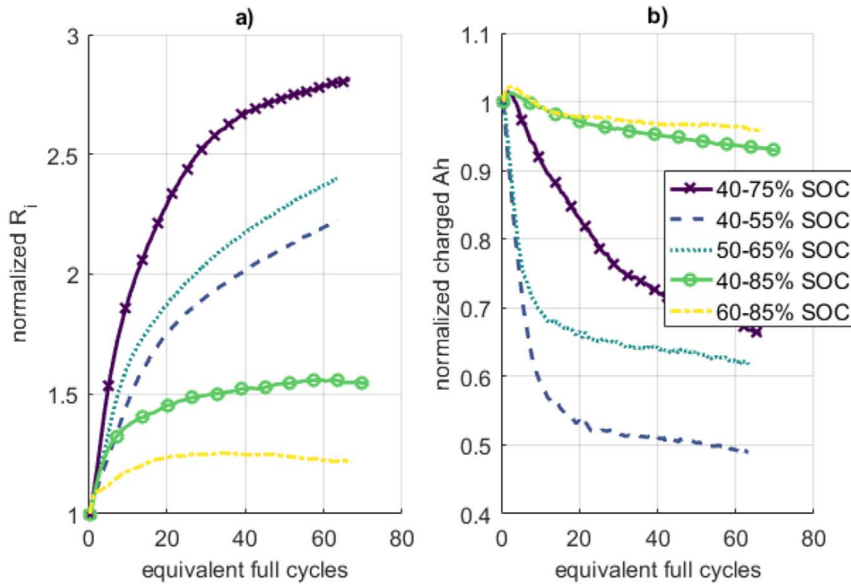


Fig. 1. Increasing resistance a) and decreasing charge acceptance b) for OPzV batteries during cycling. Values are normalized to the first micro-cycle.

can be seen if Fig. 1. The values for R_i and charge acceptance are normalized to the value of the first micro cycle so they can be compared to each other. Absolute values differ because of the different SOC-ranges and other effects, see section 2.1. After a full charge (constant current (cc) to 2.4 V and constant voltage (cv) for 24 h) these aging effects were reversed and the parameters returned to their initial values. For such a short period long time aging effects like corrosion can be neglected and the observed behavior can be linked to the reversible sulfation of the battery. Fig. 1 also shows that the increase of R_i depends on the SOC-range and its gradient seems to be inversely proportional to the charge acceptance. This leads to the following questions for the present study:

1. Which impact factors during battery operation influence short term resistance growth and charge acceptance?
2. How do they influence short term resistance growth and charge acceptance?
3. How can such a behavior be modeled?

2. Reaction kinetics and R_i

This section gives a short overview about the reaction kinetics of lead-acid batteries. The purpose is to show which parameters are influenced by sulfation and can thus be responsible for the observed increase of the internal resistance during cycling. Also methods for determining R_i with respect to electrode kinetics are discussed.

2.1. Reaction kinetics

The cell voltage E_{cell} of lead-acid batteries is given by

$$E_{\text{cell}} = E^0 + \eta \quad (1)$$

with E^0 being the equilibrium voltage and η the overpotential. The overpotential is the sum of different effects

$$\eta = \eta_{\text{act}} + \eta_{\text{con}} + \eta_{\text{crys}} + \eta_{\text{ohm}} \quad (2)$$

- activation overpotential η_{act}
- concentration overpotential η_{con}
- crystallization overpotential η_{crys}
- resistive overpotential η_{ohm} .

All of these contribute to the internal resistance of the battery in

different ways. Since temperature is affecting all of the overpotentials and thus R_i , its influence is not mentioned specifically when dealing with the different equations.

The activation overpotential is caused by the main reactions taking place at the positive and negative electrode. These reactions represent the transition from charge transport by electrons to the transport by ions. This current flow is defined by the Butler-Volmer-Equation

$$i(\eta_{\text{act}}) = i_0 \left(e^{\frac{\alpha n F}{R T} \eta_{\text{act}}} - e^{-\frac{(1-\alpha) n F}{R T} \eta_{\text{act}}} \right), \quad (3)$$

with symmetry factor α , valency n , gas constant R , temperature T , Faraday constant F and i_0 as the exchange current density. For high current densities i , the potential η_{act} is shifted far enough from E^0 and the reverse reaction can be neglected [7]. Eq. (3) then simplifies to the form of a Tafel equation

$$\eta_{\text{act}} = \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(i) - \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(i_0). \quad (4)$$

The equation shows the logarithmic relationship between η_{act} and current density. So as the battery current increases the activation overpotential increases and therefore R_i . In the case of $\alpha \neq 0.5$, the current-voltage behavior comprises different gradients for charging and discharging and this directly affects R_i . The exchange current density i_0 is influenced by the active surface area and therefore has an impact on R_i . The active surface area decreases during discharge since the PbSO_4 layer is formed on the electrodes. The effect is reversed during charging. Only if sulfation progresses over time undissolved crystals remain and the active surface area decreases.

As soon as the charge transfer reaction occurs, the concentration of the reactants near the electrode surface changes due to the limited mobility of the reaction products. This process can be described by the concentration or diffusion overpotential

$$\eta_{\text{con}} = \frac{R \cdot T}{n \cdot F} \ln \frac{c_{\text{ox}}/c_{\text{ox}}^0}{c_{\text{red}}/c_{\text{red}}^0}, \quad (5)$$

with $c_{\text{ox,red}}$ the involved reducing agents (red) and oxidizers (ox) and $c_{\text{ox,red}}^0$ being the concentration at equilibrium potential. For lead-acid batteries the reactants are Pb^{2+} and the electrolyte H_2SO_4 . During discharge enough H_2SO_4 is available and thus the impact of η_{con} is very small and can be neglected [7]. The crystallization overpotential η_{crys} describes the energy needed to form new sulfate crystals. This effect occurs most notably at beginning of discharge as the “coup de fouet” [2,8]. It generates a rise in Pb^{2+} ion-concentration and can thus be

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