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Modeling of the charge acceptance of lead–acid batteries

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Abstract

This paper presents a model for flooded and VRLA batteries that is parameterized by impedance spectroscopy and includes the overcharging effects to allow charge-acceptance simulations (e.g. for regenerative-braking drive-cycle profiles). The full dynamic behavior and the short-term charge/discharge history is taken into account. This is achieved by a detailed modeling of the sulfate crystal growth and modeling of the internal gas recombination cycle. The model is applicable in the full realistic temperature and current range of automotive applications.

For model validation, several load profiles (covering the dynamics and the current range appearing in electrically assisted or hybrid cars) are examined and the charge-acceptance limiting effects are elaborately discussed. The validation measurements have been performed for different types of lead–acid batteries (flooded and VRLA). The model is therefore an important tool for the development of automotive power nets, but it also allows to analyze different charging strategies and energy gains which can be achieved during regenerative-braking.

Keywords: Frequency domain; Model; Overcharging; Charge acceptance; Lead–acid; VRLA

1. Introduction

Insufficient charge acceptance is one of the major concerns for lead–acid batteries in applications with limited charging times or a need for a high dynamic charge acceptance. Many authors have reported these battery problems and they were recently summed up in [20]. Most battery models fail to simulate charging processes at high rates or close to full charging accurately. Therefore, this paper focuses on the depletion of Pb^{2+} ions as the primary limiting process during dynamic charging. An adequate modeling approach of this effect is proposed (Section 4) which supplements a comprehensive impedance-based model for lead–acid batteries, which we have presented earlier [8,24,25].

Since the charge acceptance occurs as part of the general operation of a battery, a full model is necessary to describe processes such as charge-transfer reactions, gassing reactions and electrolyte-transport processes. Short descriptions with corresponding references to the theory and the model topologies are given in Section 3.2.

2. Depletion of Pb^{2+} ions during overcharge

This effect is modeled by submodels (for each electrode) in the latest model version [25] and has been identified to be the main limiting process during charging at high current rates or high states of charge under dynamic operation. The decrease of the Pb^{2+} ion concentration is caused by the generation of Pb and PbO_2 from Pb^{2+} ions in the negative and the positive electrode, respectively. A liquid phase dissolution/crystallization process is assumed. The dissolution process of the $PbSO_4$ crystals limits Pb^{2+} ion delivery. This causes a significant overvoltage and the charge acceptance of the battery is limited if maximum charging voltage limits are used, which is in fact the case in most applications. During operation at moderate current rates and low states of charge, the dissolution rate of $PbSO_4$ crystals is high and, consequently, it is not recognized as a limiting process. A theory for homogeneous nucleation and the subsequent growth of $PbSO_4$ crystals has been proposed by Kappus [13] and has been

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developed further for simulation models by Sauer [19]. This algorithm is part of the model presented in this paper.

The processes of crystal solution and the transport of Pb^{2+} ions have also been identified by other researchers as important charge-acceptance limiting processes. Petkova and Pavlov [17] investigated the influences of different charge modes on the negative electrode and considers thereby that lower acid concentrations inside the pores lead to a higher solubility of the $PbSO_4$ crystals. Also for this reason, a third charging step with moderate constant current rate is recommended by Petkova for fully charging of the NAM. Takehara [22] imputes the limited charge acceptance of the negative electrode to the limited mass transfer of Pb^{2+} ions and a consequential depletion. However, charging of the positive electrode is reported to be mainly limited by charge transfer. This is inline with our observations which are discussed in Section 6. The modeling approach of the Pb^{2+} ions depletion is presented in Section 4.

2.1. Process of "Hardening Crystals"

A further process needs to be recognized which becomes obvious during extended experimental tests with lead–acid batteries. If a battery undergoes shallow cycles around a fixed state of charge, the charge acceptance increases with increased cycling time. This leads to the assumption that the newly formed sulfate crystals can be dissolved during charging easier than sulfate crystals that have been formed earlier. To cope with this effect, an additional modeling approach of "Hardening Crystals" has been introduced. Hereby, crystals that have been formed recently have a higher dissolution rate than older crystals. Fig. 1 illustrates the effect by considering charging and discharging steps with rest periods in between.

The duration of each step is 10 s and the discharging current is doubled after eight repetitions (-7, -14, $-28I_{20}$). The charging steps are unlimited in current rate but voltage limited at 2.45 V. Hence, the controlled current during charging can be evaluated as a measure of charge acceptance. Having the discharge current doubled (e.g. from $-14I_{20}$ to $-28I_{20}$, Fig. 1 (right hand)), the accepted current rate during charging increases stepwise in each case. Neither a significant change of SOC (which is smaller than 0.4% of C_N) nor a significantly pronounced acid concentration gradient (the open-circuit voltages are nearly the same after each rest period, Fig. 1 (right hand)) can explain the observed behavior. Moreover, the observations cannot be imputed to significantly more discharged double-layer capacities since the measured capacity values are too small (or the measured overpotentials after rest periods should differ much more, respectively). Consequently, the solubility of the $PbSO_4$ crystals after the different discharging periods seems to vary.

Equal observations are published numerously by Yamaguchi and co-workers [24,16]. By Electro-Chemical Atomic Force Microscopy technique (EC-AFM) he observed a changing morphology of the crystal distribution in a range of minutes during open-circuit standing. The resulting influences on the charge acceptance have been investigated and proven particularly for the negative electrode. He also proposed a model which is quite similar to the "Hardening Crystals" modeling approach which is described in detail in Section 4.2.

3. Lead–acid battery modeling

3.1. General information on electrical-circuit models

As batteries are non-linear and highly dependent on divers parameters like temperature, state of charge (SOC) and short-term history [6], the implementation of battery models is very difficult and a simple modeling with high precision is consequently nearly impossible. However, fast computing and small parameterization effort are mainly needed. A good compromise can be achieved by employing equivalent electrical-circuit models which allow high computing speed and the representation of the physico-chemical processes by electrical components as inductors, capacitors and resistors.

Such modeling approaches have been presented recently by several groups. Barsoukov et al. and Buller [2,7] demonstrated the applicability of this approach to several battery technologies by using non-linear components. Hejabi et al. [12] models the kinetic behavior of the positive lead acid electrode. For

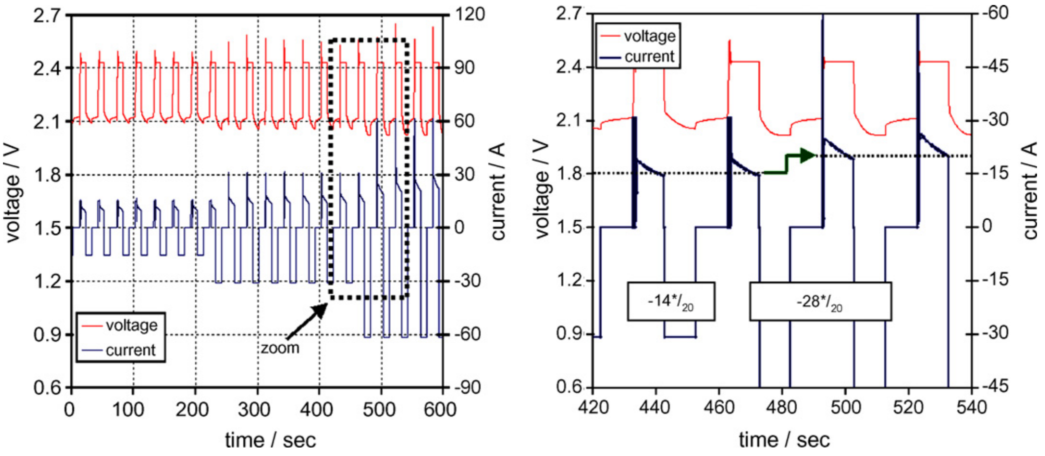

Fig. 1. Illustration of voltage and current data during alternating current steps (recorded at 25 °C and 90% SOC); stepwise increase of charge acceptance becomes obvious after the discharge current is doubled.