Modeling of the cranking and charging processes of conventional valve regulated lead acid (VRLA) batteries in micro-hybrid applications

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HIGHLIGHTS

- The stop—start cycling of a conventional VRLA battery was modeled.
- The effect of stop—start cycling on electrode sulfation aging was analyzed.
- Cranking pulses produce high overpotentials at the negative/separator interface.
- Parametric studies were done to analyze their effects on sulfation over cycling.

ABSTRACT

The cranking and charging processes of a VRLA battery during stop—start cycling in micro-hybrid applications were simulated by one dimensional mathematical modeling, to study the formation and distribution of lead sulfate across the cell and analyze the resulting effect on battery aging. The battery focused on in this study represents a conventional VRLA battery without any carbon additives in the electrodes or carbon-based electrodes. The modeling results were validated against experimental data and used to analyze the "sulfation" of negative electrodes — the common failure mode of lead acid batteries under high-rate partial state of charge (HRPSoC) cycling. The analyses were based on two aging mechanisms proposed in previous studies and the predictions showed consistency with the previous teardown observations that the sulfate formed at the negative interface is more difficult to be converted back than anywhere else in the electrodes. The impact of cranking pulses during stop—start cycling on current density and the corresponding sulfate layer production was estimated. The effects of some critical design parameters on sulfate formation, distribution and aging over cycling were investigated, which provided guidelines for developing models and designing of VRLA batteries in micro-hybrid applications.

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1. Introduction

The U.S. Environmental Protection Agency (EPA) and National Highway Traffic Safety Administration (NHTSA) recently announced a joint final rulemaking on standards to reduce greenhouse gases and to improve fuel economy for light-duty vehicles in the United States for model years 2017—2025. The final standards are projected to reduce carbon dioxide emissions from 250 g mile^{-1} in 2016 to 163 g mile^{-1} in model year 2025, which is equivalent to improving the fleet average fuel economy from 35.5 miles gallon^{-1} to 54.5 miles gallon^{-1}. As the regulation becomes more and more stringent, the auto industry will employ every technology available to meet these standards. Micro-hybrid vehicles with "stop—start" and "regenerative braking" features are a potential solution under intense development today. Lead acid batteries in such applications experience extended discharging, high-rate cranking and follow-on charging processes more frequently than those used in conventional vehicles without "stop start". Under such high-rate partial state of charge (HRPSoC) operations, negative electrode sulfation is always considered as the major failure mode of batteries [1—3]. Presently two major mechanisms of sulfation formation have been proposed and accepted, which constitute the basis of our analyses in this paper.

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The first one was from Lam et al. [2], who identified high-rate discharge as the key factor responsible for the build-up of lead-sulfate layers in negative electrodes after a teardown analysis of batteries operated under HRPSoC duties. It was shown that a compact layer of sulfate was left on the surface of the negative electrode in a cell after charging, which means hard sulfation at the negative electrode was caused by the quick precipitation of Pb^{2+} during the high-rate discharge process. In our study, this process is referred to as the quick-precipitation mechanism. The second mechanism was developed by Yamaguchi et al. [4], who observed the formation of larger sulfate particles with flatter surfaces after the battery has been dormant for a long time under incomplete charge. This was explained by the sulfate re-crystallization mechanism, which was verified by experimental results in other studies [5,6].

With knowledge of these two mechanisms, one can anticipate that in stop–start cycling, frequent high-rate discharge may lead to the accumulation of a hard sulfation layer at the negative electrodes; Also, the short charge intervals between stop–start events can leave batteries incompletely charged, where small sulfate particles would re-crystallize into hard particles that are difficult to be converted back. Although there are current development proposed to accommodate the HRPSoC duties by using carbon additives or by using new carbon-based electrodes [7], this paper focuses on the conventional VRLA batteries without any carbon additives or carbon-based electrodes. The modeling approach should be adjusted if carbon additives or carbon-based electrodes are considered, which can be conducted in our future studies.

Presently, physico-chemical modeling of the above-mentioned two aging processes based on fundamental laws is very limited. Thele et al. [8] developed an impedance-based battery model with "hardening crystals" aging mechanism (same concept as the re-crystallization mechanism) integrated, wherein the modeling results showed improvement of SOC prediction compared to those without consideration of crystal hardening effect. The "hardening crystals" modeling approach was also extended to explain and predict the limit of charge acceptance during charging processes in their later work [9]. However, all of their work was based on electric equivalent circuit models and thus the crystal hardening effect was represented by a resistor in parallel with a capacitor, which did not fundamentally model the physical process, and consequently was incapable of predicting the details (e.g. spatial distribution or easiest locations) of crystal hardening across the battery electrodes.

The objective of this paper is three-fold: 1) To understand the internal physical process of the formation and distribution of lead sulfate that affects both the aging process inside a conventional VRLA battery during frequent cranking and follow-up charging through computer modeling; 2) To quantitatively estimate the effect of high-rate cranking pulses on lead sulfate formation and accumulation on electrodes; and 3) To study the effects of critical design parameters on lead-sulfate distribution and consequential sulfation accumulation, providing guidelines of battery design and development for micro-hybrid applications.

2. Mathematical model

The mathematical model used in this study was originally developed by Wang et al. [10–12] and integrated with electric double layer effect in their follow-up work [13]. This model was developed from first-principle conservation laws, such as charge, mass and species conservations. This model, therefore, is intrinsically capable of revealing the details of internal physical and chemical processes inside lead acid batteries during charge and discharge. In our study, this model has been simplified by removing gassing side reactions and thermal evolution. This is because the
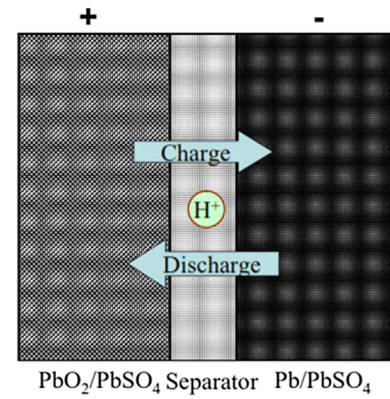

Fig. 1. Schematic of a VRLA cell.

voltage limit of our charging system on board is usually 14.3 V/6 cells, which we believe does not trigger much gassing reactions; also, all of our simulation focus on the transient processes and thus the temperature variation would not be pronounced enough to affect the results. Therefore it would not be worthwhile to add complexity without seeing significant impact on the results. Inheriting from the original work, the model itself is a performance model and does not mathematically model the hard sulfation process, but the simulation results generated in this study are analyzed based on the two aging mechanisms proposed and validated by other studies [1,4–6], providing the details of physical processes inside the battery to help better understand and prevent battery sulfation aging in stop–start applications.

A schematic of the VRLA cell, shown in Fig. 1, displays the cell region modeled. The battery modeled here is a conventional VRLA battery, thus the cell only comprises of conventional sponge lead dioxide and lead paste without any carbon additives as the electrodes and absorbent glass mat as the separator. Electrolyte is stored and stabilized in the separator. The Pb alloy grids work as the current collectors for both electrodes.

All the model governing equations are summarized in Table 1. The physical meaning of all modeling parameters can be found in Table 2. The battery specifications are listed in Table 3. The definitions of coefficients and source terms related to the positive

Table 1
Summary of governing equations.

Kinetic rate equations	$i = i_{o,ref}\left(\dfrac{C^H}{C^H_{ref}}\right)^{\gamma}\left[\exp\left(\dfrac{\alpha_a F}{RT}\eta\right) - \exp\left(-\dfrac{\alpha_c F}{RT}\eta\right)\right]$	(1)
Conservation of charge	$\nabla\cdot\left(\kappa^{eff}\nabla\phi_e\right) + \nabla\cdot\left[\kappa^{eff}_D\nabla\left(\ln c^H\right)\right] = -ai - aC_{dl}\dfrac{\partial(\phi_s - \phi_e)}{\partial t}$	(2)
	$\nabla\cdot\left(\sigma^{eff}\nabla\phi_s\right) = ai + aC_{dl}\dfrac{\partial(\phi_s - \phi_e)}{\partial t}$	(3)
Conservation of mass	$\dfrac{\partial\varepsilon_e}{\partial t} = S^V_e$	(4)
	$\dfrac{\partial\varepsilon_s}{\partial t} = S^V_s$	(5)
Conservation of species	$\dfrac{\partial(\varepsilon_e c^H)}{\partial t} = \nabla\cdot\left(D^H_{eff}\nabla c^H\right) + S^H$	(6)