



Identification and remediation of sulfation in lead-acid batteries using cell voltage and pressure sensing

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HIGHLIGHTS

- ▶ Real-time aging diagnostic tools were developed for lead-acid batteries using cell voltage and pressure sensing.
- ▶ Different aging mechanisms dominated the capacity loss in different cells within a dead 12 V VRLA battery.
- ▶ Sulfation was the predominant aging mechanism in the weakest cell but water loss reduced the capacity of several other cells.
- ▶ A controlled-pressure charging algorithm was designed and applied to reverse sulfation in the weakest cell.
- ▶ Desulfation increased the sulfated cell capacity by 41% and the battery capacity by 25%.

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ABSTRACT

The operating environment, manufacturing variability, and use can cause different degradation mechanisms to dominate capacity loss inside valve regulated lead-acid (VRLA) batteries. If an aging mechanism for each cell can be identified in real-time, cell usage can be adjusted by the battery management system to optimize the performance and service life of the energy storage system. In this paper, the cell voltage and pressure of new and dead VRLA batteries are monitored during testing to determine the cause of death of the cells. The new cells have fairly uniform performance with limited signs of degradation while the cells in the dead battery have widely ranging performance, especially at the end of discharge and charge. Based on the measurement data, it appears that one cell died from sulfation and another three died of dehydration. The battery capacity is mainly dictated by the sulfated cell. A desulfation charging control scheme with pressure feedback is designed to break up hard sulfate and recover capacity while minimizing water loss by using low current charging. The capacity of the cell is recovered by 41% with minimal water loss, demonstrating the effectiveness of the desulfation charge controller.

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1. Introduction

Lead-acid is the most widely used chemistry for batteries in stationary and hybrid applications, with the majority consisting of a valve-regulated lead-acid (VRLA) design. The most common damage mechanisms for a VRLA battery include [1–9]:

- Positive electrode corrosion
- Irreversible hard sulfation
- Water loss/dry-out
- Positive electrode softening and shedding
- Electrolyte stratification

- Internal short-circuit
- Mechanical damage (current connector failure, case damage, etc.)
- Others (passive lead oxide film, thermal runaway, etc.)

They are often not independent from each other and multiple mechanisms can occur in one cell. VRLA batteries are designed to minimize these effects as much as possible but the operating environment, cell-to-cell and battery-to-battery manufacturing variations, and use can cause different degradation mechanisms to dominate capacity loss and/or impedance rise. With the ability to determine in real time the predominant degradation for each cell, battery management system (BMS) can predict the cell SOH accurately, adjust cell use accordingly and balance cells with respect to their health conditions so as to extend service life of the battery pack.

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For system/control engineers, a practically optimal BMS design will have a very accurate yet computationally cheap baseline model, as few as possible sensors, and sophisticated controllers. The controllers use the model and the sensor measurements (e.g., current, voltage, temperature, etc.) to calculate/estimate the other states (e.g., state of charge, state of health), predict the future performance based on the external power demand (e.g., how much power and how long the pack can provide it, how much life will be left and when maintenance will be needed) so that the BMS can adjust the cells use, protect the cells from thermal runaway and other safety issues, balance the cells according to not only SOC but also SOH, maintain their service lives, and optimize the overall pack performance.

There are several challenges here. First, to have accurate estimation of SOC/SOH requires an underlying model including the predominant aging mechanisms but usually such a comprehensive model is complicated and computationally so expensive that it cannot be handled by a small on-board microprocessor. Second, more sensors make it easier for system engineers to design high performance controllers. Given the limited space within the pack and the large number of cells, it is typically not practical to have the detailed measurements that can be made in a laboratory setting. Third, in industrial applications, many manufacturing parameters such as acid concentration, saturation, and grid composition, needed for controllers design are not available due to IP agreements or contracts which drives engineers to add extra on-board sensing or use estimators based models.

To perform real-time aging diagnosis in vehicles/locomotives, nondestructive techniques with as few sensors as possible are favored because switching out an aged cell from a pack and examining it using laboratory tools/methods costs a lot of labor and system downtime and can only be performed at very low frequency. Many studies that investigate aging in VRLAs use destructive techniques to identify degradation mechanisms. Studying a dissected battery using a scanning electron microscope and chemical analysis provides a physical understanding of aging processes, such as hard lead sulfate formation [10–12] or corrosion layer growth [13,14]. Although these invasive techniques provide detailed information about the SOH of the battery, they can only be used posthumously. With nondestructive monitoring techniques, on the other hand, the BMS can diagnosis aging and implement unique charging strategies to extend service life.

Nondestructive techniques are also essential for accurate SOH estimation in real time. Most nondestructive techniques for on-line SOC/SOH estimation are model-based [15–18] and require accurate model fitting. The techniques developed so far, however, do not specify the degradation mechanisms that cause battery aging or use models which require a priori knowledge of major degradation. Trying to include every possible failure mode in the model can result in computationally-expensive models that on-board BMS cannot handle. Analyzing data from nondestructive tests may offer an alternative to a model-based approach for SOH estimation. Nondestructive tests that require only current and voltage data include: full charge/discharge cycling, pulse train, and Electrochemical Impedance Spectroscopy (EIS). In particular, EIS is influenced by SOC [19] and the shape of the impedance curve is often related to degradation mechanisms, such as gassing at a single electrode [20].

In this study, individual cell voltage and pressure measurements are available and the current can be controlled to completely charge/discharge, pulse train, and sinusoidally charge/discharge for EIS. These are considered to be nondestructive measurements because the access terminals and pressure ports could be integrated relatively easily into the battery. Voltage and pressure sensors are attached during the autopsy to make the desired measurements.

The results of this autopsy can then be used to revive the battery, adjust the BMS utilization, or direct recycling efforts.

The ability to not only identify degraded cells within a VRLA battery but also to restore their capacity could dramatically prolong battery life. Typical VRLA batteries have multiple cells connected in series. As the battery ages, the cell capacities diverge and the cell with the lowest capacity limits the overall battery capacity. A BMS that identifies sulfated cells and has the ability to desulfate those cells could increase the overall capacity of an aged battery.

Negative plate sulfation is one of the most prominent aging mechanisms for VRLA batteries and is especially common in hybrid vehicle applications [21,22]. Gibson et al. conclude that high rate charging and discharging at partial states of charge leads to the progressive accumulation of lead sulfate on the negative plates of VRLA batteries. Gibson et al. [10], Yamaguchi et al. [11], and Takehara [12] have thoroughly studied and developed an understanding of the structure and recrystallization of hard crystalline lead sulfate. Lead dioxide and lead are discharged in sulfuric acid to form lead sulfate and water. The reaction reverses during charge, lead sulfate being decomposed to produce lead dioxide and lead. Both reactions take place via dissolution–precipitation processes. During discharge, electrons are transferred to form lead ions then dissolved into the solution and supersaturation of Pb^{2+} may be achieved. After the nuclei are formed, $PbSO_4$ precipitates and the size of the $PbSO_4$ crystals depends on the concentration of sulfuric acid and the current density. During charge, lead sulfate dissolves into Pb^{2+} and SO_4^{2-} . Then electron transfer occurs on the electrode grid and the ions are oxidized/reduced to PbO_2 and Pb . This process is greatly affected by the current density, the diffusion rate, the crystal size and the solubility of $PbSO_4$. In addition, the reaction area changes by several orders of magnitude during the reactions. The lead sulfate crystals formed through electrochemical process have rough surfaces with high porosity and activity. Therefore, the lead ions may dissolve from the crystals and re-crystallize back, a process known as Ostwald ripening. Crystals formed in recrystallization have finer surfaces with higher density and lower activity. Hence, these lead sulfate crystals have less reaction area and are much more difficult to be converted back during charge. Approaches to reducing sulfation include high-frequency pulse charging [23,24], using carbon additives [25,26] and expander components [8,27,28] and replacing the negative electrode with carbon [21,29,30].

Desulfation can restore some of the capacity lost to sulfation. Most commercial battery chargers/desulfators conduct desulfation using a technique known as “pulse conditioning”, which consists of applying short, high-current pulses to a cell [31–34]. Lam et al. found pulsed charging to be a promising approach towards enhancing the cycle life of $Pb-Sb$ and $Pb-Ca-Sn$ cells [35] that Keyser et al. proposed to use high finishing currents and current-interrupt charging algorithm to minimize sulfation and gassing during cycling [36]. Hydrogen and oxygen production associated with the electrolysis of water molecules at high states of charge, however, can lead to water loss, another aging mechanism that decreases cell capacity. Desulfation techniques must minimize water loss to effectively recover lost capacity.

Electrolyte stratification is another common failure mode for lead-acid batteries. It is considered to be most severe in flooded batteries, much less prominent in AGM batteries and not significant at all in gelled batteries due to the immobilized electrolyte [37–39]. Electrolyte stratification causes a vertical distribution of acid and promotes the formation of irreversible lead sulfate in the lower parts of the electrodes [40,41]. Electrolyte stratification can be mitigated by overcharging and gassing [9,39,40,42].

The goal of this work is to develop real-time aging diagnostic techniques that can be integrated into battery management

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