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Original Research Article

Lead-acid battery response to various formation levels – Part B: Internal resistance

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ABSTRACT

In Part A of this study, eight lead-acid battery cells were formed to different levels to investigate their performance in conventional and off-grid solar photovoltaic applications. In Part B of the study (this article) the objective is to investigate the internal resistance of the cells as a function of finished formation level. Cells were formed to levels corresponding to 0.7, 1.4, 1.9, 2.3, 2.8, 4.2, 5.6, and 7.0 times their theoretical capacity, and cycled 10 times using a deep-cycle algorithm. A correlation between formation level and internal resistance is shown. Higher formation levels resulted in lower internal resistance values for both discharging and charging processes, although they differed in magnitude. It is also shown that internal resistance values of the under-formed cells start converging with the remaining cells after 4 cycles as they complete their formation process. It is recommended that manufacturers of under-formed cells suggest higher voltage setpoints during the constant-voltage phase of the charge. This would overcome the high internal resistance limitations of these aforementioned cells, thus allowing for faster formation completion, while increasing their energy efficiency in deep-cycling operation.

Introduction

As introduced in Part A of this study, the initiative to develop rural electricity services using off-grid solar photovoltaic systems provides new sale opportunities for lead-acid battery manufacturers. The lead-acid battery (LAB) is presently the most widely used energy storage medium for off-grid systems due to comparatively low cost, its wide availability, and its maturity [1,2]. Part A investigated the LAB characteristics of amp-hour (Ah) capacity, voltage, and temperature as a function of formation level using a constant-current formation algorithm [3]. In Part B of this study (this article), we will investigate the LAB characteristics of internal resistance (IR) as a function of formation level.

Background and motivation

The IR components of a battery can be modeled by an equivalent electric circuit, as shown in Fig. 1. In the diagram, the current conducting elements, such as the tabs, grids, active material, and electrolyte, are modeled with the series resistor, R_o (i.e., ohmic resistance), while the charge transfer reactions are modeled with the parallel resistor, R_{ct}. A charged electrode immersed in electrolyte will inherently feature an electrical double layer (EDL) at the interface. This phenomenon is explained in detail in [4]. The electrostatic charge and discharge of the EDL plays an important role in the charge/discharge mechanisms of the battery and is typically modeled as the parallel capacitor, C_{dl}. Diffusive mass transfer effects are usually included in the model as well, and are typically represented by the Warburg impedance, Z_W, which is a constant-phase-element [4]. While the electrical response of the ohmic resistance is essentially instantaneous, both the EDL and the diffusion effects will have significant time constants in their electrical responses to stimuli. Time constants for the EDL, while current dependent, are typically on the order of seconds, while time constants for diffusion are typically on the order of minutes to hours [5].

By considering the equivalent electrical circuit in Fig. 1, it can be seen that an open-circuit battery in equilibrium will have a total voltage V_{bat} equal to the electromotive force V_{EMF}, which is equal to 2.041 V + (RT/nF) ln $(a^2_{H_2SO_4}/a^2_{H_2O})$, where R is the ideal gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature in K, n is the number of moles of electrons exchanged in the electrochemical reaction (i.e., 2 for a LAB), F is the is the Faraday constant (96,485 C mol^{-1}), and where $a_{H_2SO_4}$ and a_{H_2O} are the activity coefficients of sulfuric acid and water, respectively [6]. When a current is applied to the battery, the corresponding voltage change is a result of the electronic dynamics in the metallic components (i.e., voltage across

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List of Nomenclature and Symbols

Acronyms

a.c.	alternating current
CC	constant-current
CV	constant-voltage
d.c.	direct current
EDL	electrical double layer
HFR	high-frequency resistance
IR	internal resistance
LAB	lead-acid battery
SG	specific gravity
SoC	state of charge

R_o) as well as the ionic dynamics at the reaction layer (i.e., voltage across the $C_{dl} - R_{ct} - Z_W$ sub-circuit). The total battery voltage V_{bat} is therefore increased or decreased from V_{EMF} depending on the direction of the current flow. More complex equivalent circuit models can also include inductive effects (which are important at high frequencies), components for both positive and negative plates, geometric capacitance, self-discharge resistance, and additional resistor–capacitor sub-circuits, as additional time constants improve the accuracy of the model. Examples of more complex models can be found in [7–11].

With respect to the aforementioned ohmic resistance of the LAB (R_o in Fig. 1), its three major components (i.e., the electrode, the electrolyte, and the separators) have the greatest influence. Wagner [12] states that in order to achieve ideal battery performance and to reduce the effect of inhomogeneous current distribution across the plates, the overall resistance of the electrode must be minimized. This parameter can be controlled by the grid structure and material of the plates, and by the composition of the active material [12,13]. Lead-antinomy alloys, which are used in a wide range of lead-acid battery applications such as stationary power storage and automobiles, are strong, creep resistant, and can easily be cast into the desired shape [14]. While these benefits result in easier handling of the material for the remainder of the manufacturing process, lead-antimony alloys are 3–10% less conductive (i. e., higher resistance) than comparable calcium or tin alloys, thus resulting in reduced performance [14]. Regarding the composition of the active material, considerable work has been done regarding the addition of carbon additives in the paste of the negative active material to improve the electrical conductivity at partial state-of-charge operation [15–18]. For instance, Fernandez et al. [17] demonstrated that the addition of a carbon additive to the negative active material of a LAB evenly distributes the generation of $PbSO_4$ throughout the thickness of the plate during cycling, which is otherwise deposited on the surface of the plate, inhibiting the acid diffusion to the reaction pores, as well as creating a high ohmic resistance barrier.

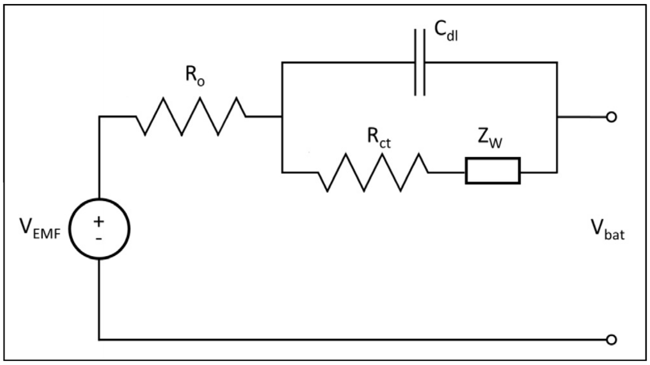

Fig. 1. Simple equivalent electric circuit for a battery.

The resistivity of the electrolyte, influenced by its concentration and temperature, plays a significant role regarding the IR of a LAB and consequently on its power capability [19]. Pavlov [19] has shown that electrolyte specific gravity (SG) values ranging between 1.100 (fully discharged LAB) and 1.275 (fully charged LAB) [20] have the lowest resistivity (e.g., 1.7 Ω cm to 1.3 Ω cm, respectively, for an electrolyte temperature of 25 °C), where being outside this range results in a substantial increase in resistivity. Furthermore, he has shown that the resistivity of the electrolyte has an inverse relationship with temperature, with electrolyte temperatures higher than 40 °C offering the lowest resistivity, and temperatures below 0 °C resulting in a reduction in available power and energy for a LAB [19].

Finally, the resistance of the separator is a function of its porosity and tortuosity factor (i.e., the ratio of the mean path length the ion will travel, to the actual thickness of the membrane) [21]. Thus, one is able to reduce the electrical resistance of the separator by increasing its porosity and by decreasing the tortuosity factor.

With these characteristics in mind, measuring the IR of a LAB can be used to obtain information about its power performance and its relative "state-of-health". This can be accomplished using two different methods: alternating current (a.c.) impedance measurements, and direct current (d.c.) impedance measurements. In its most advanced form, the a.c. impedance is measured using electrochemical impedance spectroscopy, which injects an a.c. excitation current into the battery with frequencies ranging from a few millihertz to several kilohertz. Alternatively, a single a.c. current frequency can be injected with the goal of isolating the ohmic resistance from the other impeding components [22]. In either case, Ohm's law is used to calculate the impedance based on the change in a.c. voltage and, in some cases, the corresponding phase shift. Huet et al. [22] measured the high-frequency resistance (HFR) of a LAB during charge and discharge conditions with the goal of evaluating the feasibility of state of charge (SoC) characterization. They developed an electronic device capable of processing the voltage response of a 1200 Ah, 2 V cell to a high-frequency current perturbation (10 A a.c. at 500 Hz) supplied by a galvanostat. Using a discharge current of 10 A d.c., the authors showed minimal change in the HFR of the cell for the first 75% of discharge (i.e., 900 Ah), after which it increased rapidly from 0.2 mΩ to 1.7 mΩ as the cell reached a fully discharged state. The HFR of the cell relaxed towards 1.0 mΩ once the cell stopped discharging and was in open-circuit. The authors attributed the sharp increase at the end of the discharge to either a reduction in available active material, or to an increase in resistivity of the electrolyte in the pores of the active mass. In contrast, the relaxation in HFR after discharging the cell could be attributed to the dissolution of the $PbSO_4$ crystals formed at the end of discharge, or to the increase in concentration of electrolyte ions diffusing towards the pores of the active mass. Using a charging current of 10 A d.c., the authors showed a quick initial decrease in HFR during charging of the LAB from 1.0 mΩ to 0.25 mΩ, explained by the rapid dissolution of unstable $PbSO_4$ crystals. The resistance then increased slightly for the second part of charge due to the progressive formation of