Evolution of internal resistance during formation of flooded lead-acid batteries

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HIGHLIGHTS

- Apply current pulses during laboratory formations of flooded lead-acid batteries.
- Compare ohmic and interfacial components of measured internal resistance.
- Observe both ohmic and interfacial resistances decay to a steady-state value.
- Validate findings using electrochemical theory.
- Conclude current pulses can be used to detect formation completion.

ARTICLE INFO

ABSTRACT

This study employs experimental techniques to measure the changing internal resistance of flooded, flat-plate lead-acid batteries during container formation, revealing a novel indicator of formation completeness. In order to measure internal resistance during formation, d.c. current pulses are super-imposed over the constant formation current at set intervals, while change in voltage is measured. The resulting "pulsed" internal resistance is divided into ohmic and interfacial components by measuring the ohmic resistance with short d.c. pulses as well as with a.c. injection. Various constant-current container formations are carried out using different current levels, plate thicknesses, and pulsing techniques, yielding an array of resistance trends which are explained using Butler-Volmer kinetic theory. Ohmic and interfacial resistance trends are shown both theoretically and experimentally to eventually decay to a predictable steady-state value as the formation proceeds, suggesting that this internal resistance method can be used to detect the completion of the formation. The same principles are shown to apply to recharge cycles as well, but with potentially limited practical implications in comparison to formation.

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1. Introduction

The manufacturing process for a lead-acid battery (LAB) involves an energy-intensive step known as 'formation', in which inactive electrode materials are converted into electrochemically active ones. As the battery undergoes formation, its electrical conductivity improves, and the electrochemical reaction kinetics evolve with the changing electrode/electrolyte composition. The electrical conductivity and reaction kinetics determine the total internal resistance of the battery, so it follows that the trending battery resistance may display unique characteristics during formation. These resistance trends can be measured at any point during a formation by superimposing electrical current transients over the base formation current and measuring the corresponding voltage response, as per Ohm's law.

Most of the existing research on LAB formation has focussed on charging algorithms and electrode additives. Few, if any, published studies however, examine the evolving battery resistance during LAB formation.

1.1. Modelling of internal resistance

Many existing studies have employed equivalent circuits to model the working voltage (U) of a LAB. While equivalent circuit models can vary drastically in design and complexity, the most widely known is the Randles model [1], shown in Fig. 1a. This circuit models the electromotive force of the battery as an ideal
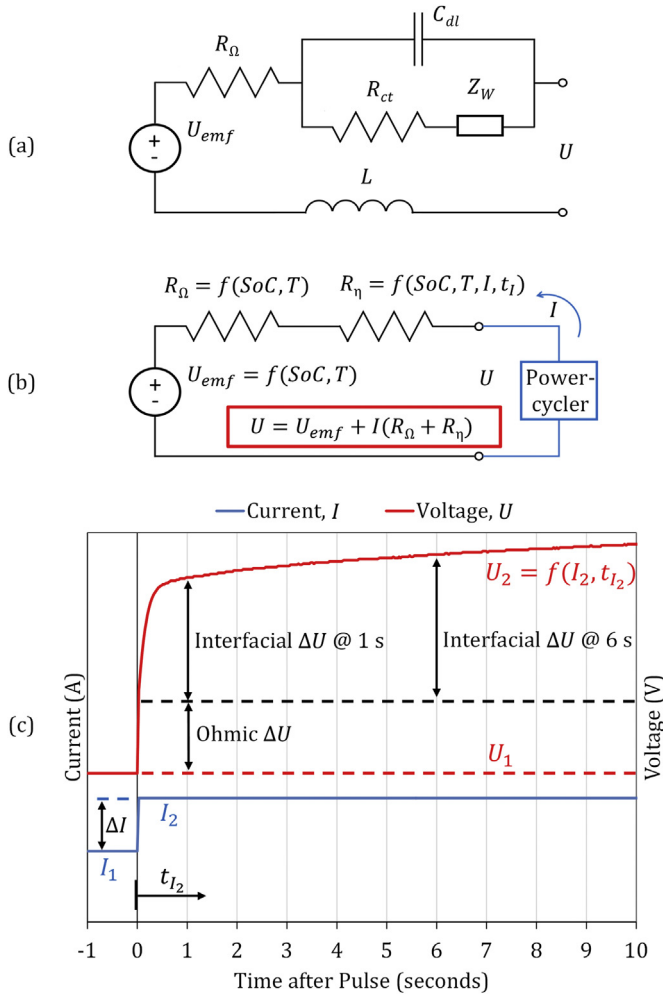
Fig. 1. Graphical explanation of resistance components: (a) Randles model; (b) simplified equivalent circuit; (c) sample of a pulsed-up response.

voltage source (U_{emf}), which represents the unloaded voltage of the battery in equilibrium. The Warburg impedance (Z_W) is a constant phase element used for simplistic modelling of mass transport limitations while the high-frequency inductance of the metallic components is modelled by the series inductor (L). The ohmic resistance (R_Ω) is modelled as the series resistor and is composed of the electronic resistances of the electrodes and metallic current collectors as well as the ionic resistances of the electrolyte and separators. The parallel capacitor is used to model the capacitance (C_{dl}) of the electrochemical double-layer (EDL), while the parallel resistor is used to model the charge-transfer resistance (R_{ct}) for activation polarization.

The activation overpotential (η) is the deviation above or below the equilibrium potential that is required to drive the electrochemical reactions and generate an electric current. The charge-transfer current (I_{ct}) obtained from a given η is described by the Butler-Volmer equation. This is given in Eq. (1), where i_0 is the exchange current density, A is the area of the reaction surface, α is the charge-transfer coefficient, n is the number of electrons transferred, F is the Faraday constant, $\mathscr{R}$ is the gas constant, and T is the temperature.

$$I_{ct} = i_0 A \left[e^{\alpha \frac{nF}{\mathscr{R}T} \eta} - e^{-(1-\alpha)\frac{nF}{\mathscr{R}T}\eta} \right] \tag{1}$$

The Butler-Volmer equation illustrates how electrochemical

reactions are always proceeding in both directions, and how a positive or negative overpotential will favour one reaction direction and produce a net current flow. Eq. (1) also shows how a larger overpotential is required to obtain the same current when the reacting surface area of the electrode is smaller.

The Randles model serves reasonably well for qualitatively describing equilibrium and non-equilibrium conditions of a battery. However, the Randles model is highly simplified, and a wide variety of more advanced models have been developed for more precise modelling of battery behaviour. Of particular relevance to the present work is the LAB charge-acceptance modelling conducted by Thele et al. [2]. For their equivalent circuit model, the authors included additional current pathways in the charge-transfer sub-circuit in order to account for electrolysis side-reactions during charging at high SoC. This allows for the total current to be shared between the side-reactions and the main conversion reactions depending on their relative R_{ct} values.

1.2. Measurement of internal resistance

In their review article, Pilatowicz et al. [3] provide an overview of methods used for measuring internal resistance, including electrical injection, electrical induction, and thermal methods. The most common experimental techniques in literature stem from electrical injection, which can be subdivided into a.c. and d.c. variants. One such method is electrochemical impedance spectroscopy (EIS), which has been widely used in studies of various battery technologies. This method involves injecting low-amplitude a.c. current into the battery at a wide range of frequencies (e.g. mHz to kHz) and measuring the resulting a.c. voltage and phase angle at each frequency. Most studies employing EIS attempt to establish criteria for evaluating SoC during battery operation [4] or develop accurate models of battery behaviour [5]. Pilatowicz et al. [3] also state that the minimum real component of the measured complex impedance is the most precise way to isolate R_Ω from the other impedances of the battery. By comparing EIS data taken at different temperatures, SoCs, and superimposed d.c. discharge currents, the authors found that the injection frequency at which this minimum occurs is reliably near 1000 Hz under all conditions for LABs, as is used in typical a.c. battery internal resistance meters.

Electrical injection can also be achieved with d.c. pulsing, which involves a sudden application, interruption, or adjustment of d.c. battery current. Through Ohm's law, a resistance value can be calculated from the voltage change that results from the current change. Compared to EIS, d.c. pulsing techniques are rare in recent LAB studies. Such studies typically involve short ($\leq$ 50 ms) discharge pulses from equilibrium in order to measure R_Ω as an indicator of the maximum discharge current capability of a battery [6] or the state-of-health of a battery over its life [7]. The LAB standards set by IEC [8] also include a d.c. internal resistance measurement, which involves performing two subsequent long ($\geq$ 5 s) discharge pulses from equilibrium.

While there is an abundance of published studies on resistance of LABs during operation, resistance during formation does not appear in literature. One exception can be found in an abandoned U.S. patent application by McKinley et al. [9], which proposes a system and method for pulsed-current formation/charging of LABs. One of the claims of this patent application states that by measuring the voltage at the end of the current pulse (pulse width ranging from 1 μs to 7 m), the resistance (R_Ω) of the battery can be measured. They also claim that internal resistance change over a period of time can be used to determine when the battery is fully formed/charged, but no theoretical background for this claim is provided and no supporting experimental data is reported.