LEAD-ACID BATTERY EVALUATION BASED ON OPEN CIRCUIT VOLTAGE FLUCTUATION MEASUREMENT

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Abstract: The state of charge and the state of health are two crucial parameters of batteries. Current state of the art methods of their estimation include some as simple as measuring open circuit voltage, all the way to fuzzy logic estimation and constant online battery overview. Some main problems of such methods are either the length of single parameter evaluation cycle, or their inherent inaccuracy due to limitations in battery manufacture precision. This article proposes novel method of the lead-acid battery state of the health estimation, based on open circuit noise measurement. It reports the nature of changes in low frequency noise spectral density, that occur after catastrophic self-discharge failure or avalanche voltage drop in lead-acid batteries.

Keywords: lead-acid battery, low frequency noise, state of health estimation

1. INTRODUCTION

Electronic batteries became an essential part of all modern technologies, ranging from portable electronics such as telephones and laptops, through larger devices such as electric and hybrid cars, all the way to several MAh battery installments residing at some power plants. In contrast to lithium and nickel based rechargeable systems, the use of lead based batteries in consumer electronics dwindle, disappearing completely from hand-held devices. The prevalent reasons being smaller energy density and specific energy. Despite some of its obvious shortcomings, lead-acid batteries are still in large use in applications, where safety is of concern, for that other rechargeable solutions are prone to violent/combustive malfunctions.

The basic mode of operation of any lead-acid battery resides in simple chemical reaction, summarized by the double-sulfate theory in equation (1). Here lead dioxide and sponge lead are the active materials in the positive and negative plates, respectively. Sulfuric acid is the electrolyte, converted to lead sulfate and water during discharge reaction near both plates. [1]

$$PbO_2 + Pb + H_2SO_4 \Leftrightarrow 2PbSO_4 + 2H_2O \tag{1}$$

where discharging happens from left to right and charging from right to left.

The state of health (SOH) and the state of charge (SOC) evaluation of valve-regulated lead-acid (VRLA) battery is impeded by inherent high internal resistance variance, caused by imperfections of the manufacturing process. Several methods of SOH/SOC estimation were developed e.g., coulomb counting, open-circuit voltage (OCV) measurement, impedance spectroscopy, electromotive force, fuzzy logic, and several variations of Kalman filtering. Continuous monitoring needs to be performed over the battery lifetime, in order to evaluate and predict its parameters precisely, since single time measurements are often skewed due to the aforementioned internal resistance variation of VRLA. The specific gravity rating is often impossible without the commitment of a full charge-discharge cycle. [1-2]

Lead sulfate (PbSO4) and water are products of discharge reaction (1). Lead sulfate is crystalline substance with no magnetic polarity and modest electric resistance. Water blends with sulfuric acid, reducing its concentration and specific gravity. Both lead sulfate and water slowly diffuse into the bulk electrolyte after they are formed.

Noise is a random fluctuation of electric signal. It can be evaluated in a form of power spectral density (PSD), which shows the proportion of energy manifesting itself at different frequency ranges of studied signal in relation to its mean value. Since the noise is reckoned using Fourier transform of square root of the measured signal, it is crucial for the signal to be distributed around common midpoint. This criteria is difficult to achieve for real-life battery OCV measurement, as the voltage changes slowly over time.

2. EXPERIMENTAL

Measurement setup for long-term OCV fluctuation acquisition of up to two parallel VRLA cells was constructed. Several samples were selected and measured. An unexpected phenomenon was observed during the OCV measurement, exhibiting itself through sudden self-discharge of some measured VRLA cells. Novel method of precise open circuit fluctuation evaluation was utilized to express such noise before and after self-discharge phenomenon.

2.1. MEASUREMENT SETUP

In the heart of the measurement setup lies HS3 handyscope device, connected to PC via USB. Custom software was created for its operation. This program is light weight, with almost no memory overhead, so that it can produce high frequency long-term measurements. Acquired data are saved in coma-separated-value format in several kB batches, best suited to eliminate the bottleneck of writing to standard hard-drive. Diagram of this measurement setup follows.

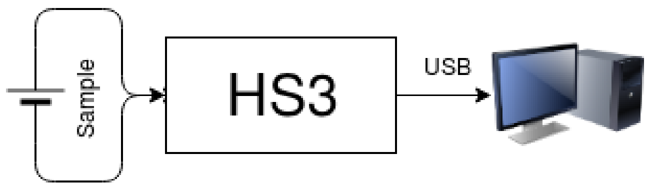

Figure 1: Measurement setup, single sample shown

TiePie engineering HS3 handyscope device is dual channel USB enabled oscilloscope, capable of streamed measurement of up to 10 kHz at 16 bit resolution, using Delta-Sigma analog to digital conversion. In order to evaluate low-frequency noise and to preserve disk space, sampling rate of 20 Hz is utilized. Since all the samples are VRLAs with nominal voltage of 2 V, input DC sensitivity used is ±4 V. This gives the single step resolution of 0.12 mV per channel per acquisition, which is more than sufficient for purpose of OCV measurement. Impedance of single HS3 input channel is 10 MΩ and 20 pF as per datasheet.

2.2. SAMPLES

Six samples are evaluated for the purpose of this paper, designated Pb4A – Pb4F. Each sample is single off the shelf VRLA cell manufactured by Alarmguard (CJ12-1.3) in 2002, with stated nominal capacity of 1.3 Ah and nominal voltage of 2 V. Evaluated cells are salvaged from an old security system, where the usage profile is reckoned to be low current draw several times per month, and remaining on full charge for the remainder of its lifetime. All the cells lied in storage for several months prior to the measurement. The initial capacity of cells was not evaluated precisely, but is assumed to be in the region of over one half of its rated capacity.

2.3. LONG-TERM MEASUREMENT

Each sample cell was cycled (discharged and charged) to its full capacity prior to the measurement, using Bantam BC-6 charger. Aforementioned catastrophic self-discharge failure phenomenon occurred in two of the studied cells during the long-term OCV measurement. Namely Pb4E and Pb4F. Each were able to fully recharge to its rated voltage after the breakage by 645 mAh and 720 mAh, respectively.

For the purpose of this paper, evolution of the Pb4F sample is analyzed. After a full charging cycle, the sample was measured for almost 9 days. Voltage of sample Pb4F settled at 2 V as expected, but began to slowly decline over the period of first 6 days. Figure 2 shows cutout of OCV of sample Pb4F since day 7 until almost the end of the measurement. On the bring of 8th day, the self-discharge occur and the voltage unexpectedly drops to roughly 1.5 V, as if some sort of load is applied. It is to be noted, that through out the measurement, only the effective 10 MΩ of HS3 input channel resistance is attached to sample's terminals, and that room temperature is stable at 25 °C.

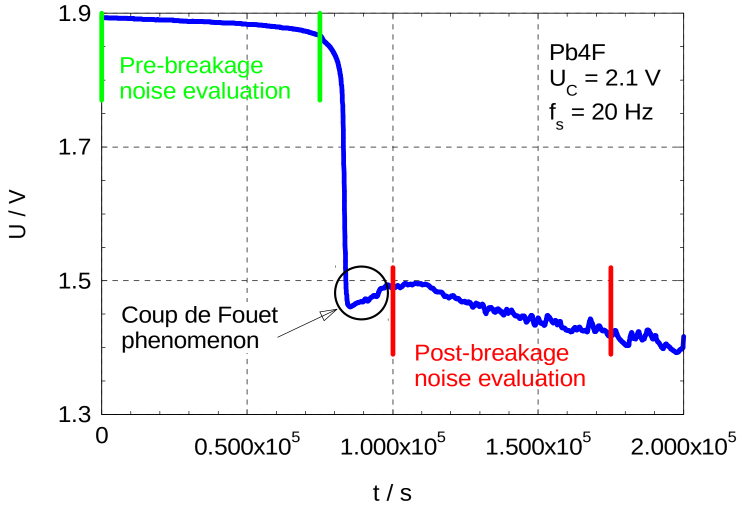

Figure 2: Open circuit voltage of sample Pb4F, during the self-discharge process

After the 9 day measurement, self-discharge breakage, and potential drop to 1.5 V; the voltage on Pb4F's terminals settled at 1.45 V. Sample was re-charged to its nominal voltage, adding 0.5 Ah. After a period of roughly a week, the self-discharge phenomenon occurred once again. The OCV was measured for initial 6 days, after which the breakage reappeared.

2.4. NOISE EVALUATION

In order to reduce the impact of voltage change within measured signal, we propose to introduce 1st order high-pass filter. This will maintain the midpoint reference level of studied signal, the cost being an attenuated PSD at low frequencies. Several approaches to digital filtering are available. Due to the large sample size and high accuracy required, moving average smoothing is opted for. First the data are smoothed, which introduces 1st order low-pass filtering, then the smoothed values are subtracted from the original signal, which inverts the filter around its cut-off frequency.

Using the Nyquist theorem, boundary may be set to the highest frequency represented by Fourier transform. This is to be half of the sampling frequency. The lower bound, i.e. the cut-off frequency, may be determined, using analogous approach, as an inverse of the smoothing span, multiplied by twice the sampling rate. Range of applicable frequencies may be determined using:

$$f = \left(\frac{2 \cdot f_{sample}}{N_{smooth}}, \frac{f_{sample}}{2} \right) [Hz] \quad , \qquad (2)$$

where N_{smooth} is the smoothing span window width.

Once proper filtering is applied, PSDs are calculated. Resulting densities before and after the self-discharge phenomenon are presented in figure 3. Data segments, used for PSD evaluation, are highlighted in figure 2, so that the green curve in figure 3 holds evaluated OCV noise of the corresponding green segment from figure 2. The same holds for the red curve and segment. Voltages associated with given curves are rough estimates of cells potential during the measurement.

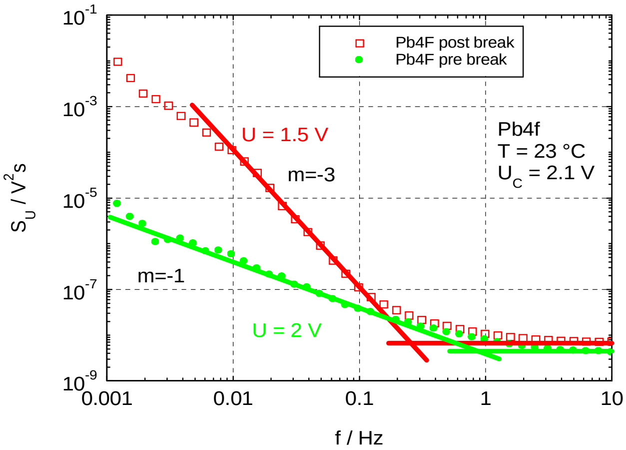

Figure 3: Noise spectral density of sample Pb4F, before and after the breakage

After the first occurrence of self-discharge phenomenon, sample Pb4F was fully charged once again. Following figure holds its OCV noise evaluation in blue. The data segment for blue line noise evaluation was again ~0.75 x 10^5 s shortly after the charging has ended.

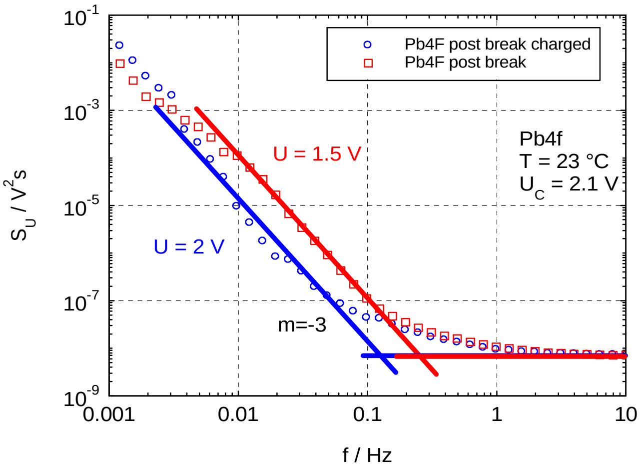

Figure 4: Noise spectral density of sample Pb4F, after the breakage and after consequent recharging

3. DISCUSSION

The voltage of VRLA cell tends to be positively related to the sulfuric acid concentration at its plates. In theory, the battery voltage should slowly decrease, while cationic lead combines with anionic sulfuric oxide and the sulfuric acid disappears during the discharge process. But we hypothesize, that due to the reactants diffusion speed limitation, the voltage drop is faster, because the sulfuric acid is not replenished fast enough near the plates. This hypothesis is supported by the study of the Coup de Fouet phenomenon [3], which occurs immediately after a full discharge of sample Pb4F and Pb4E. Its position is highlighted in figure 2. The rapid avalanche discharge process stops abruptly during this phase, preventing complete battery discharge to 0 V. It is not yet completely understood, why this voltage spike occurs [3].

It is reasonable to assume, that the health of the sample is permanently affected, and that such self-discharge breakage will occur again after charging. Rapid self-discharge failure is accompanied by telltale sign of Generation-Recombination (GR) like noise. It manifests itself with a low-frequency PSD slope of f^{-3}. This is most likely caused by free electrons appearing during sulfuric acid depletion and disappearing through an internal short circuit of the battery. Such a short can be caused by lead sulfate shedding, forming conductive crystals inside the battery during discharge. The resistance of such conductive band decreases, with the increase in amount of lead sulfate in the electrolyte bulk, which in turn increases the speed of discharge. Increasing the speed of discharge promotes the disappearance of free electrons, recombining at positive plate. This reaction forms an avalanche like effect, all the way until it is stopped by forces forming the Coup de Fouet spike.

Increased slope of low-frequency ($f < 0.1$ Hz) noise after the first occurrence of self-discharge (See figure 4) serves as a good indicator of an eminent voltage drop. It follows, that a slope larger than f^{-1} has a contribution of GR processes, which indicate poor SOH and therefore the usage of such battery should be avoided. It is to be noted, that slight uplift at low frequencies might be expected, due to quantization noise error, caused by acquisition step of 0.12 mV. This error however is insignificantly small in comparison to the measurement, and is therefore omited.

4. CONCLUSION

Catastrophic avalanche self-discharge failure phenomenon of VRLA cells, commonly accredited to the battery being dead, must happen inside of the battery due to G-R like processes. We hypothesize, that these processes are associated with rapid dissolution of sulfuric acid into lead sulfate and water. This self-discharge process only seizures after the Coup de Fouet phenomenon occurs.

This paper presents a method for detection of a looming VRLA self-discharge. It is based on observation of increased OCV noise at low-frequencies. Advantage of this method lies in its relative speed in comparison to other methods. Another advantage is that it solely relies on an OCV measurement, not needing full charge-discharge cycle, nor permanent battery monitoring.

ACKNOWLEDGEMENT

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