Journal of Power Technologies 101 (2) (2021) 112–126

Coup de fouet effect in estimating battery state of health

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Abstract

The *coup de fouet* phenomenon (crack of the whip) is a dip in the discharge voltage observable during the first minutes of the discharge period of a lead acid battery, followed by a transient recovery. This leads to the formation of an interim plateau transforming later into a typical discharge curve characteristic of a galvanic cell. The phenomenon was considered as a basis for a state-of-health(SoH) assessment, where the depth of the dip was used to measure the battery's SoH. However, the validation process showed the two variables lacked clear correlation, mandating a revision of this approach. Therefore an attempt to correlate certain aging processes to the behavior of the cell of interest associated with the presence of the coup de fouet phenomenon was attempted for a set of diverse lead-acid battery designs. A set of estimators based on the coup de fouet was devised and their relation to the aging processes was explored and described. The research led to the conclusion that there is a direct relation between the coup de fouet and sulfation. This relation is best defined by $\Delta \quad \tau_{plateau}$ – the time taken between the voltage reaching the lowest point of the dip and then reaching the highest observable plateau voltage.

Keywords: Methods of SoC determination of lead acid battery Batteries, Lead-acid, Coup de fouet, Diagnostics, VRLA, Flooded, Maintenance-Free, Aging, Sulfation

1 Introduction

Many systems require uninterruptible power. Diesel generators are used to ensure the power supply in the event of a lengthy grid failure. However, there is a short period to cover before the diesel generators are up. For this purpose, an array of batteries is attached to such systems, providing power during shorter blackouts or during the generator start-up period. Lead-acid batteries form the backbone of most such systems due to features such as: low cost, ease of use, resistance to overcharging and ease of linking the batteries in a string due to their relatively high voltage being in the 2.2-2.3V range [1]. The basic design of many of these systems has remained remarkably unchanged for many years. Despite minor upgrades in terms of monitoring the temperature and voltage of the battery strings, little progress has been made toward introducing full battery management systems. Since both manufacturers and users alike are usually resistant to making changes to well-known and extensively tested design solutions, developments in the realm of battery diagnostics tend to be sidelined.

During their lifetime lead-acid batteries suffer capacity loss due to multiple aging processes and it is desirable to have a better understanding of the factors related to these processes. The state of health (SoH) of the battery is an arbitrary measure of how the battery is worn in comparison to its nominal state. For the best operational performance this parameter should be monitored during the whole period of battery usage, to ensure no malfunction when the system is engaged. It should be noted that the SoH of lead-acid batteries is a non-unified measure of the degree of wear of a battery. This contrasts starkly with the SoH used for Li-Ion batteries, which is clearly defined with IEC norms [2]. Many battery manufacturers and battery testing laboratories develop their own ways of measuring the SoH parameter, integrating multiple variables and measurement techniques. Moreover, at the current state of knowledge, estimation of the SoH in lead-acid batteries is a difficult task without performing offline checks. Laboratories offer a variety of tests and procedures to properly estimate a battery's SoH, but most of these solutions would not be applicable in field applications. Thus the development of new methods that can be used to roughly estimate a battery's SoH based on simple tests is desired. Such methods usually include estimations based on measurements of the battery's OCV and density of the electrolyte, among others. Since such methods are inaccurate in describing possible aging, more complex methods were devised. Some of them include estimation of the battery's internal resistance, derived from the response of the battery to a single-frequency square signal to its terminals. More complex methods are under consideration or in use in industry, including exploration of mechanisms occurring during aging and devising estimators based on them to calculate the SoH.

The coup de fouet effect has been used as a basis for SoH estimation for various proposed systems [3][4]. It was also used as a basis for several successful patents such as [5] [6] [7] which describe how to assess aging. Nevertheless, it is important to reassert the viability of this phenomenon and to try to relate it to specific aging processes.

2 Theory

There are numerous aging processes in the lead-acid battery that can occur during its lifetime, such as capacity loss caused by either sulfation or corrosion of the positive plate, internal mechanical microdamage and loss of electrolyte. All of these processes can impact the SoH. Moreover, various methods of SoH estimation can better expose the severity of certain forms of aging. For most basic purposes SoH can be equated to the relative fraction of nominal capacity, which in most cases does not show the possible extent of cell aging. However, this method is mostly insufficient for the purpose of predicting immediate battery failures. The complex nature of aging processes is not properly reflected by capacity loss – as this method does not differentiate which part of the capacity has been irreversibly and reversibly lost. The diagnostic procedure does not provide any information about the state of the electrolyte and the plates, limiting the prediction ability regarding possible failure of the battery. It should also be noted that registered capacity is affected by the value of the discharge current – the larger the current, the smaller amount of charge can be drawn from the battery. Thus, it is imperative to develop more complex methods to more accurately assess the risk of battery failure under operational conditions.

Another problem encountered during SoH estimation using the capacity method is the need to disconnect the battery string from the emergency system. This increases the risk of system failure during the time the battery string is disconnected. Also with this procedure, the emergency system might not be running at full capacity for up to a few days. Thus there is a need to develop techniques that can be either applied on site or applied in situ on the batteries to prevent such problems.

2.1 Coup de fouet

During the battery's charge/discharge it is possible to observe an effect termed *coup de fouet*, meaning crack of the whip [3][4][8][9] [10] [11]. After applying charge or discharge to the battery, a bump or dip can be observed on the voltage curve (Fig.1) before the voltage stabilizes into a plateau and the battery discharges with its normal discharge characteristics.

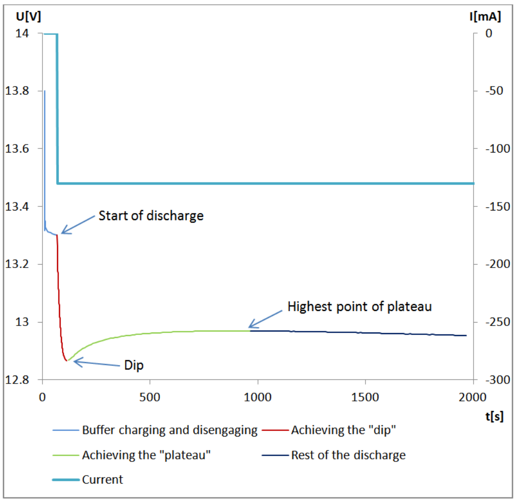

Figure 1: Methods of SoC determination of lead acid battery. Example of coup de fouet registered during discharge.

Coup de fouet has been investigated many times to determine which electrode processes in the lead-acid batteries it corresponds to [12][13][14][15]. The most common theory ties the effect to the limited speed of reaction of the dissolution of lead from the negative electrode into the electrolyte and to its saturation with Pb^{2+} ions prior to the initial nucleation of $PbSO_4$ crystals [12][13][16]. A number of research publications point out that the appearance of the dip in voltage, one of the elements of the coup de fouet phenomenon, is not tied exclusively to the behavior of the negative plate, but also with the processes occurring at the positive plate [13]. In the paper [15] these mechanisms are only assumed, not explained reliably. Some researchers even note that the commonly accepted explanations of the coup de fouet mechanism might not be correct [14]. Finally, it can be concluded that the current state of knowledge does not supply a solid explanation of the nature of the coup de fouet phenomenon and further exploration is still required. However, for a new battery from a freshly manufactured batch, this phenomenon is troublesome, as it reaches a significant and observable magnitude exclusively when the battery ages. A reasonable approach to investigating this effect in isolation would center on preparing specially modified battery designs. That said, due to uncertainty as to the conditions that cause the coup de fouet to appear, it is very hard to condition batteries to isolate it as a part of the aging process.

To properly describe the coup de fouet effect, several parameters characterizing it have to be taken into consideration. The first is the depth of the dip/bump [4] – the difference between the voltage at which discharge/charge starts and the lowest/highest registered voltage before reaching the plateau. The other parameter to consider is the difference between the lowest/highest dip/bump voltage and the plateau voltage – highest/lowest voltage registered when the charge/discharge voltage reached the plateau. The last one is the time interval between registering the lowest point (middle) of the dip and achieving the highest voltage value of the plateau.

2.2 Battery types and construction

Two main types of batteries can be categorized by their construction [8][11]: the flooded design and the suspended electrolyte design. Both designs have derivative variants. Flooded batteries can be separated into classical and maintenance-free batteries. For suspended electrolyte designs, the variants are AGM (absorbant glass mat), gel, hybrid and silicone (in situ hydrolyzed silica gel). Suspended electrolyte batteries are often referred to as VRLA – valve regulated lead acid – due to their specific sealed design. Manufacturers claim that the main difference between them relates mostly to their cost (for the average user), but in reality the battery construction affects its longevity and resistance to aging.

The flooded battery design[8][11] is derived from the original Plante design [17] – based on two electrodes (lead and lead oxide in the form of plates) submerged in a sulfuric acid solution with a separator in between. An evolution of that design uses lead paste suspended on a lead grid as the plates. The electrolyte is in liquid form, meaning this battery design has an operational hazard of spillage and therefore can only be used in applications which mitigate this risk. The typical flooded battery design features a removable cap (or caps) so that the water lost through evaporation and electrochemical decomposition can be replenished. Maintenance-free battery designs compensate for these losses through an excessive supply of liquid electrolyte, but there is no way to replenish the water lost due to evaporation or due to "gassing" (hydrogen evolution). An important factor in MF design is the plate itself – where the composition of the electrode paste as well as the alloy that makes up the grid matters. It is specially tailored to reduce gassing and minimize water loss to prevent increase in the acid's concentration.

AGM and gel battery designs [8][11] are more advanced – electrolyte immobilization prevents the electrolyte from spilling due to tilting of the battery. The sealed design of the batteries seeks to prevent electrolyte loss due to gassing by recombining the released oxygen and, sometimes, hydrogen inside the case. This ensures that excess gas is reverse converted into water, maintaining the immobilized liquid inside the battery at virtually constant levels.

Recombination occurs in two possible ways – chemical/electrochemical and catalytic. The first of these two mechanisms is known as the oxygen cycle [18]. It occurs at the negative plate, toward which the gaseous oxygen liberated at the positive plate migrates through the pores of the electrodes separator that are not fully saturated with the electrolyte. There are disagreements in the literature about whether the process is predominantly chemical or electrochemical in nature. As regards the chemical process, the following reaction scheme (Eq. 1 2 3) occurs:

$$2PbSO_4 + 4H^+ + 4e^- \leftrightarrow 2Pb + 2H_2SO_4 \tag{1}$$

$$2PbSO_4 + O_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \tag{2}$$

which when added together give:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{3}$$

Another possibility is attributed to the direct electrochemical reaction of gaseous oxygen with H^+ ions and electrons leading finally to the same reaction (Eq. 3). It must be noted here that the oxygen cycle inhibits gassing only to some extent, as hydrogen evolution correlated with positive grid corrosion is still possible.

Therefore, in some modern VRLA designs noble metal catalysts[19] were introduced in the headspace to assist the recombination of hydrogen-oxygen back into water. The presence of these catalysts changes the overall dynamics of the oxygen cycle and lessens the impact of battery overcharge during float operation.

If both of the above mechanisms fail, a build-up of pressure due to abnormally rapid electrolyte decomposition can be avoided by releasing excess gas through a system of valves, hence the term: Valve-regulated lead-acid battery.

While the differences in battery design have no impact on the battery's basic chemistry (the electrode reactions remain the same), they have a huge impact on aging processes. It has been observed that flooded batteries with replenished electrolyte most often exhibit differently behavior as regards SoH tracking than maintenance-free and VRLA batteries. This is a direct effect of replenishing the water in the system, lowering the impact of capacity loss due to water loss and in turn affecting acid concentration. So, when discussing the progression of the aging process each battery design has to be analyzed and discussed separately.

2.3 Aging

The aging processes that impact battery capacity[1],[8] can be divided into those that are reversible and those that are irreversible in nature [20]. Capacity loss due to reversible aging processes can be regained through special charging techniques and other dedicated procedures. With irreversible processes only preventive countermeasures can extend the battery's operational life. Therefore the ability to analyze those processes and to differentiate between them is a vital stepping stone in SoH assessment.

One reversible aging process is acid stratification[8] – a non-uniform distribution of acid concentration in the electrolyte due to gravity and the ohmic drop occurring within the plate during high current operation of the battery, which causes lower local current densities in distant (typically lower) parts of the electrode plates. [21]. This effect can affect both flooded and suspended electrolyte batteries. Over time the acid concentration transitions from uniform to gradient distribution, with the most dilute solution on top. This leads to higher acid concentrations at the bottom due to incomplete charges/discharges. All of these effects can eventually lead to uneven currents occurring at the lead grid and promote corrosion where the acid concentration is the highest.

Sulfation is another reversible process that has a large impact on battery life[1][8][9]. This process occurs during normal battery operation during the discharge step, when crystals of $PbSO_4$ are formed:

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \qquad (4)$$

Some of these crystals are rendered inert to the charge reaction, forming deposits of trapped active material. Currently, the state of knowledge lacks a full explanation of the intrinsic mechanics related to this process. However, it has been observed that certain additives to the electrode paste can affect these mechanics and reduce the impact of the process [22]. If the portions of capacity loss attributable to this process were identified, charging strategies could be developed to counteract sulfation. On the other hand keeping a lower charging voltage ensures greater longevity of the battery as sulfation is considered 'reversible', while aging processes related to high cell voltages are not. It should be noted that many laboratories [23] have researched possible 'desulfating regimes' – charging strategies geared toward periodic freeing of the electrode material from inert $PbSO_4$ crystals. These strategies include higher charging voltages, impulses, overlaying specific wave over the charging voltage. Such strategies are risky in applications, as they can cause damaged batteries to lose all capacity and go completely dead.

Irreversible aging processes include, first and foremost, corrosion of the positive plate [8][11]. The lead grid on which the electrode material is suspended can corrode during the battery's lifetime, leading to loss of structural integrity. It can also promote the shedding of electrode material, which can finally result in loss of capacity or battery failure. While the process slowly occurs normally over time due to the presence of an acidic environment, gassing and acid stratification can hasten it. It should be noted that this process can lead to an increase in volume in the PbO_2 plates, due to the differences between the molar volume of the PbO_2 compared to Pb. That process can lead to perforation of the battery vessel, as expansion of the material causes the vessel to break.

There is a group of aging processes in which the water in the electrolyte is broken down due to high charging voltage, commonly referred to as "water loss"[1][8][11]. It occurs in the lead acid battery when the battery's charging voltage crosses threshold the water's electrochemical stability (2.3V per cell in ambient conditions). Then kinetic hindrances preventing water decomposition are not present and the process can proceed. It should be noted that the materials used to construct the grid can affect that value (high antimony lead alloys decrease the water decomposition voltage). Two effects can be observed (i) "hydrogen evolution" in which H_2 from the water splitting is produced on the negative plate and (ii) the lead grid on the positive plate is converted into PbO_2. As with positive grid corrosion, this process can lead to similar effects in terms of damage to the grid and the lead paste, and gassing in which gaseous H_2 is similarly produced on the negative plate while gaseous O_2 is produced on the positive plate. As H_2 accumulation poses an explosion risk, the battery compartments should be kept well ventilated. With flooded type batteries, the water loss aging process be classified as reversible since the water can be replenished.

Numerous SoH estimation techniques have sought to accurately match the aforementioned processes to the behavior of the charge/discharge curves. It is desirable to develop a diagnostic technique that can properly map the extent of each of these processes, but no unified solution currently exists to do so. The search is still ongoing for diagnostic techniques that can properly map at least one of these processes in on-line applications.

This work provides new insight into the feasibility of using the coup de fouet effect to determine the SoH. The experiment explored possible relations between the variables derived from the coup de fouet effect and both capacity or cycle number . Cycle number as one of the variables was chosen in this particular case, because the interval between the cycles was constant.

3 Experiments

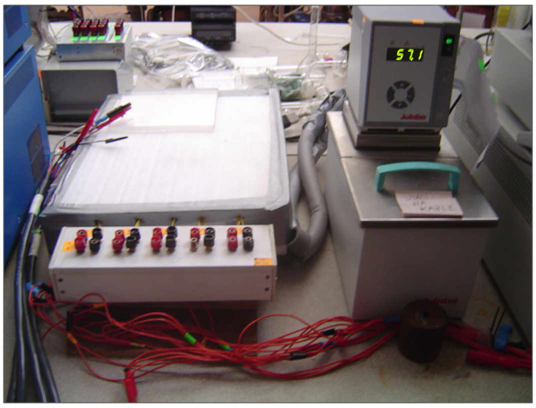

Figure 2: Oil bath setup for the first series of tests

The experiment was performed on several types of batteries maintained in various buffering regimes. All of the batteries studied were tested in a paired configuration to ensure control of the reliability of the results. Measurements were taken at an interval of one week, during which time the batteries were buffered with voltages described below. The batteries used in the tests were connected to the measuring equipment through a custom-built junction box to ensure operational convenience. All of the tests were performed using a Bio-Logic VMP3 potentionstat equipped with a 20A booster.

Table 1: Battery pairs' buffer regimes

Battery pair	Float voltage [V]	Regime
I	13.800	Normal
II	13.350	With temperature compensation
III	13.000	Sulfation regime

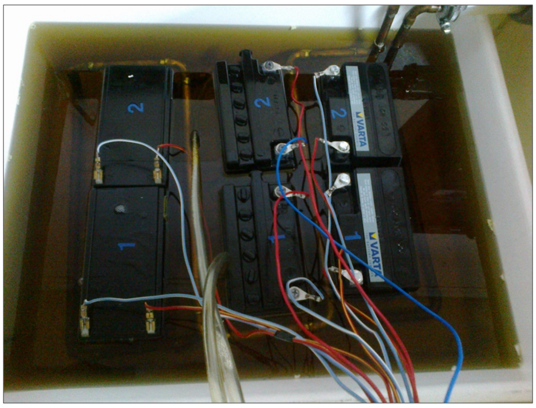

Figure 3: Oil bath setup for the second series of tests

In the second series of tests a set of three types of batteries were used: VARTA YB4L-B type flooded batteries, VARTA YTX5L – BS type flooded maintenance-free batteries and Panasonic LC-R123R4PG VRLA batteries. All of the batteries had a nominal voltage of 12V. Both types of VARTA batteries had a nominal capacity of 4Ah while the Panasonic batteries had a nominal capacity of 3.4Ah . Batteries were tested in pairs and both batteries in a particular pair originated from the same production lot. As in the first experiment, the batteries were placed in a heat-isolated oil bath, equipped with a thermostat (Fig. 3). A temperature of 55°C was applied to all of the batteries in this experiment to speed up the deterioration process in the cells [24]. The batteries were then discharged with C/1 current and charged with C/10 current.

Due to other experiments being performed in parallel, the charging and discharging strategy of the batteries included a very specific trait. For each hour of charge/discharge there was a 15 minute interval before the charging/discharging was resumed. This specific procedure did not affect the analyses reported, as it was not present for the constant voltage stage of the charging (the buffer charge in between cycling)

4 Results and discussion

Discharge curves were registered for all the batteries tested and their capacities were determined in order to correlate the changes with the parameters characterizing the character of the coup de fouet phenomenon occurring in the batteries. Three groups of estimators were set up based on complexity. They were used to analyze the region in which the coup de fouet phenomenon occurs and to find a relation between the phenomenon and the aging of the batteries.

The first group of estimators was based on single variables derived from the characteristics of the coup de fouet curve. The second group was a product of the variables derived from the previously mentioned curve qualities. And the third group was based on using integration to analyze the coup de fouet phenomenon. These estimators were devised to adhere to standard SI units.

The research focused on comparing the estimators in terms of the highest degree of correlation with capacity loss or time passed. The results are presented below.

4.1 Analysis of single variable based estimators

The first set of estimators investigated includes these based on one of the four variables that could be used to describe the coup de fouet effect and in turn relates to battery capacity [3][4].

The following estimators were considered:

$\Delta\tau_{dip}$ - the time between the start of the discharge and reaching the point of the lowest voltage of the dip.

$\Delta\Upsilon_{dip}$ - the voltage difference between the starting voltage and the lowest voltage registered in the dip.

$\Delta\tau_{plateau}$ - the time between the point of the lowest voltage in the dip and the final voltage stabilization at the plateau.

$\Delta\Upsilon_{plateau}$ – the voltage difference between the lowest registered dip voltage and the plateau voltage.

A simple observable relation between any of these estimators and battery capacity would be desirable for the purpose of developing a simple method of SoH estimation, without needing to make additional mathematical calculations. Alternatively, a relation between the estimators and the cycle number or battery use could be considered as a measurement of advancement of aging processes.

The correlation of $\Delta\tau_{dip}$ with the capacity and cycle number has no clear trend for any of the battery types. Thus, the best explanation for such relation is that the value of $\Delta\tau_{dip}$ is related with the charging regime/starting voltage of the measurement, not with aging.

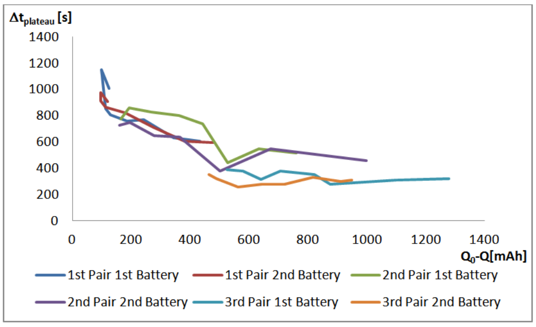

Figure 4: Relation of $\Delta\ t_{plateau}$ vs capacity for VRLA batteries charged in various regimes

For the VRLA batteries tested in various charging regimes a trend was observed between the value of the $\Delta\ \tau_{plateau}$ estimator and observed capacity (Fig. 4). However, the trend is not only clearly nonlinear in nature, but attempts to fit it with a logarithmic correlation have not proved effective, leading to the conclusion that this relation is not useful for the purpose of simple SoH estimation.

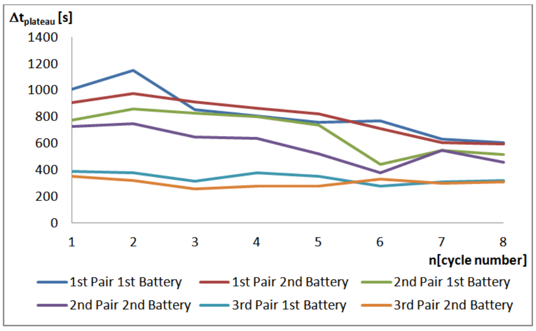

Figure 5: Relation of $\Delta\ t_{plateau}$ vs cycle number for VRLA batteries charged in various regimes

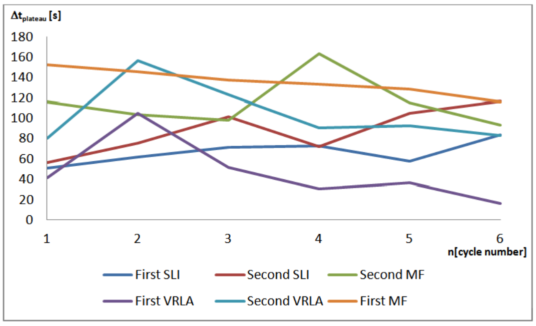

Figure 6: Relation of $\Delta\ t_{plateau}$ vs cycle number for three different types of batteries

A downwards trend of $\Delta\ \tau_{plateau}$ vs. cycle number can be observed for both the MF batteries and VRLA batteries in Fig 5 and 6. Much clearer correlations between $\Delta\ \tau_{plateau}$ and cycle numbers can be seen (compared to those between this estimator and capacity) in both experiments. The VRLA (Fig. 5) and MF (Fig. 6) batteries show a linear trend of decreasing $\Delta\ \tau_{plateau}$ over time, proving that the aging of the battery is directly tied to the value of the estimator. On the other hand, it should be noted that for the VRLA batteries cycled in the sulfation regimes the value of $\Delta\ \tau_{plateau}$ in relation to the cycle number is very close to constant, as evidenced by Fig. 5. It should also be mentioned that the spike in Fig. 6 for VRLA batteries should be attributed to the initial 'formation' of the plates during the first charge, not to the changes in battery performance.

The best possible interpretation of these phenomena, based on the current state of knowledge, is that the decrease of the time between the dip and the plateau is related to a higher number of active centers where nucleation can take place. As sulfation progresses the amount of lead(II) sulfate crystals that can act as nucleation centers for crystal growth increases and, thus, the time needed for system equilibration and therefore for reaching the plateau decreases. Due to the complex nature of the effect it is impossible at this stage of research to confirm this theory in full. It can be stipulated that for various battery types their design-related features can affect the studied phenomenon in a significantly different manner. An innate theory can also be formulated in relation to the above described observation – the high value of $\Delta\ \tau_{plateau}$ can be attributed to the low number of nucleation centers. As sulfation progresses the value of $\Delta\ \tau_{plateau}$ lowers until it reaches a plateau observable in Fig. 5 for the 3^{rd} battery pair. This observation can, therefore, lead to two independent conclusions (and more explanations): there is a limit to the number of nucleation centers occurring at high sulfation and there is a limit to the value of $\Delta\ \tau_{plateau}$. As for the sulfation regime - $\Delta\ \tau_{plateau}$ reaches its lowest possible value, so it is possible to treat it as a reference point in studies of the behavior of identical batteries cycled in different conditions. Any values registered that are higher than the said base are an indicator of nucleation originating hindrances in the battery operation.

As with the case of the relation observed between capacity and $\Delta\ \tau_{dip}$, the value of the $\Delta\ \Upsilon_{dip}$ estimator cannot be reasonably correlated with the decrease in battery capacity.

Moreover, the relation of the capacity to the $\Delta\ \Upsilon_{plateau}$ estimator differs for batteries maintained in various charging regimes (Fig. 7). For the charging regimes with and without temperature compensation, the relation exhibits some degree of linearity. The correlation is best for the regime without temperature compensation. However, for the regime promoting sulfation the value of $\Delta\ \Upsilon_{plateau}$ does not exhibit any correlation to the capacity decrease. Moreover, for the other three battery types, there are no linear trends observable. The relation of the $\Delta\ \Upsilon_{plateau}$ estimator versus cycle number exhibits (Fig. 8) better correlation for the VRLA 1200mAh batteries, particularly visible in regimes with and without temperature compensation. For the MF batteries (Fig. 9) a similar correlation between the estimator and cycle number

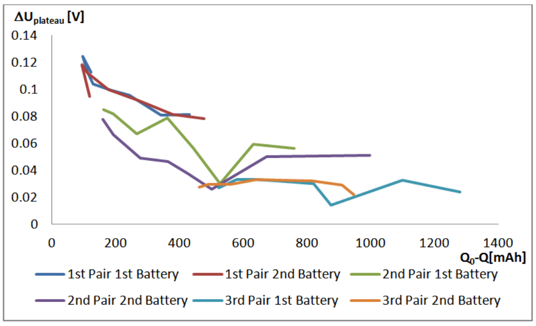

Figure 7: Relation of $\Delta\ U_{plateau}$ vs capacity for VRLA batteries charged in various regimes

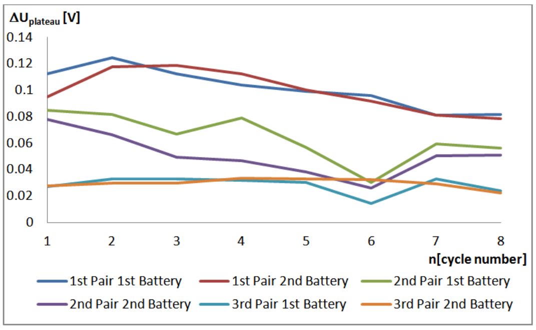

Figure 8: Relation of $\Delta\ U_{plateau}$ vs cycle number for VRLA batteries charged in various regimes

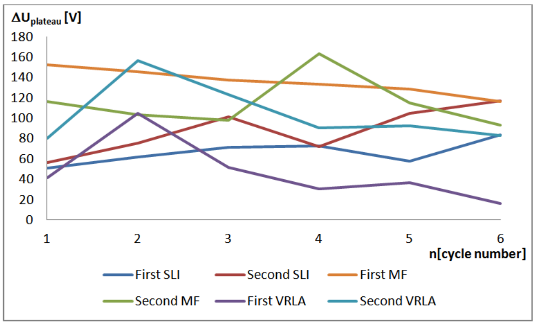

Figure 9: Relation of $\Delta\ U_{plateau}$ vs cycle number for three different types of batteries

can be observed. Based on these trends, similar conclusions to the ones presented for the $\Delta\ \tau_{plateau}$ can be drawn as regards how the coup de fouet is affected by the battery's age.

Thus, in the course of this analysis it was determined that a relation of the one-variable based estimators of the coup de fouet effect - $\Delta\ U_{plateau}$ and $\Delta\ \tau_{plateau}$, produce a reasonably solid trend showing a decrease in their value as the battery ages. In turn, it shows that capacity alone does not reflect the changes present in the batteries due to aging, and usage of these estimators might be a better approach in SoH determination. It was also observed that exploration of the coup de fouet effect for the SLI batteries produced no clear results compared to the other types tested.

4.2 Two-variable based estimators – a failed attempt

There were attempts at creating two-variable estimators, but they have not proven able to describe the coup de fouet phenomenon to a better degree than the one-variable estimators. Furthermore, the devised two-variable estimators do not have any physical sense compared to the one- or three-variable estimators. It was very hard to anchor them with known and observable phenomena like nucleation, and thus they were rejected for the purpose of this discussion.

4.3 Analysis of three-variable based estimators

Previous observations gave rise to the approach that the intensity of the coup de fouet can be understood as the energy needed to create initial nuclei of lead(II) sulfate. To calculate such energy, the first method was devised - the $\Delta\ \tau_{plateau}$ and $\Delta\ \Upsilon_{plateau}$ variables had to be multiplied by each other and then by the discharge current value (I) using a standard equation for determining work of an electrical system:

$$W = I \cdot U \cdot t \tag{5}$$

Thus, after substitution of the variables:

$$E_{nucl1} = \Delta U_{plateau} \cdot \Delta t_{plateau} \cdot I \tag{6}$$

To study if inclusion of the initial part of the coup the fouet in nucleation energy calculations (the one before achieving the lowest point of the dip) has any impact on the correlation between capacity/cycle number and nucleation energy, a second method for E_{nucl} estimation was devised. Calculating the energy using the sum of $\Delta\ \tau_{plateau}$ and $\Delta\ \tau_{dip}$ multiplied by $\Delta\ \Upsilon_{plateau}$ and the discharge current value (I).

$$E_{nucl1} = \Delta U_{plateau} \cdot (\Delta t_{plateau} \cdot \Delta t_{dip}) \cdot I \tag{7}$$

So for both methods of calculating E_{nucl} the following relations can be studied:

$$E_{nucl} = f(Q) \tag{8}$$

$$E_{nucl} = f(n_{cycle}) \tag{9}$$

A comparison between these two methods should answer whether the initial stages of coup de fouet, where a reaction of dissolution of lead and lead oxide into the electrolyte occurs, are important in nucleation energy calculation. The outlined method, with better correlation, should be an indicator of which of these two approaches is correct.

For the VRLA batteries in the sulfation regime the observed correlation between the E_{nucl} estimator and capacity was proven to be similar to that of $\Delta\ \tau_{plateau}$ and $\Delta\ \Upsilon_{plateau}$ with a similar lack of linear correlation between capacity and the value of E_{nucl1} and E_{nucl2} for the sulfated battery pair. It was also determined that there is only a minimal difference between the first and second method in relation to battery capacity and, thus, the first method can be used instead for simplicity. For the experiment comparing the behavior of three different battery types, there are clear observable linear correlations between the value of the estimator and capacity for all three types studied.

For the VRLA batteries conditioned in various regimes, the correlation between E_{nucl} and cycle number shows trends (Fig. 10,11) similar to the correlation between the $\Delta\ \tau_{plateau}$ and the cycle estimator number (Fig. 5). This is to be expected, as $\Delta\ \tau_{plateau}$ is a component of the E_{nucl} estimator, as is evident in Eq.6 and Eq.7. For the experiment involving various types of batteries, only the VRLA and MF batteries show some noticeable correlation between the said

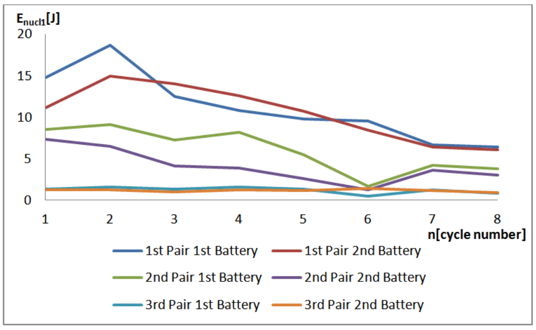

Figure 10: Relation of E_{nucl1} vs cycle number for VRLA batteries charged in various regimes

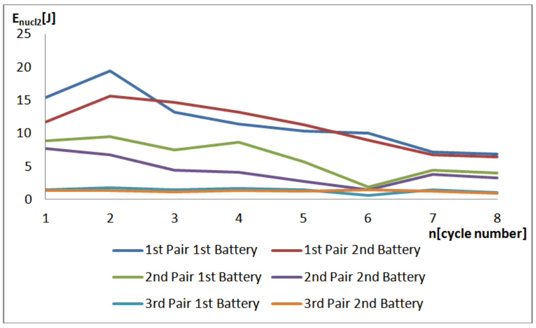

Figure 11: Relation of E_{nucl2} vs cycle number for VRLA batteries charged in various regimes

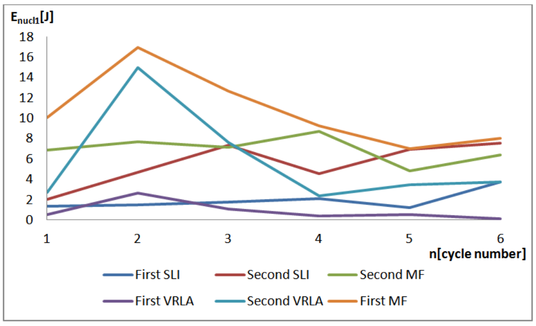

Figure 12: Relation of E_{nucl1} vs cycle number for three different types of batteries

estimator and the cycle number, as is evidenced in Fig. 12 and 13. MF batteries (Fig. 12) also exhibit a trend similar to that of $\Delta\ \tau_{plateau}$ (Fig. 6), in the same way as the aforementioned VRLA batteries in the regimes experiment do.

The estimator E_{nucl} being a derivative of $\Delta\ \tau_{plateau}$ and $\Delta\ \Upsilon_{plateau}$ shows similar trends to these variables. However, it should be noted that using more than one variable to construct the estimator causes an accumulation of possible value uncertainties. Moreover, after comparing both methods of E_{nucl} estimation it was determined that the second one offers much better correlation to the cycle number than the first.

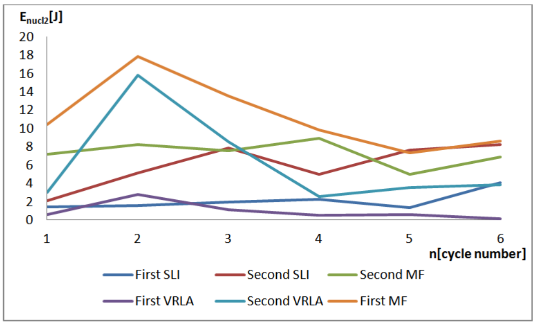

Figure 13: Relation of E_{nuc2} vs. cycle number for three different types of batteries

4.4 Analysis of the applicability of the current integration in calculation of E_{nucl}

It was therefore postulated that an even more refined method could be used to calculate E_{nucl} to ensure a smaller margin of error. Instead of using three variables such as $\Delta\ \tau_{dip}$, $\Delta\ \tau_{plateau}$ and $\Delta\ \Upsilon_{plateau}$ to approximate the value of a E_{nucl} as in the case of the estimators described earlier, a more complex method was devised – based on integration of voltage.

To properly calculate the current-voltage integral, a baseline time dependence must be estimated for the same discharge curve. This estimated dependence is to be free of any occurrence of coup de fouet or other possible effects, reflecting a simple relation between time and observable voltage of the battery. Later, this dependence is used as an upper limit of the area considered for integration.

Taking the simplest approach possible, it can be assumed that in certain parts of the discharge curve, the relation between the value of voltage and time is linear:

$$U_{theory} = U_0 - \alpha t \tag{10}$$

where α is a certain rate of discharge specific to the battery type, the discharge current and the battery's SoH.

However, in the registered discharge curves, one can recognize effects observable within their initial part related to such phenomena as: reaction startups, initial nucleation, polarization, among others. This causes the relations between voltage and time, and voltage and charge to be non-linear in that area of the discharge curve. To measure the said phenomena and relate them to the values of the estimators studied, one should apply integration.

$$E_{nucl3} = I \cdot \int_{t_{plateau}}^{t_0} (U_{theory}(t) - U_{real}(t))dt \quad (11)$$

The result of integration can be interpreted as the value related to the energy of nucleation and therefore can be correlated with the intensity of the coup de fouet occurring in the battery under investigation.

The discussed method of estimation of E_{nucl3} shows that this value can be correlated to both capacity and cycle number in a manner similar to that which was previously defined for the three-variable based E_{nucl} estimator. However, this method produces generally worse correlations than the three-variable based estimator method. The deteriorated quality of the integral base estimator appears to originate from a invalid assessment of the above mentioned baseline reference voltage-time dependence. Therefore the origin of error for the integral method may well come from a invalid estimation of the value of U_{theory} . E_{nucl3} estimators calculated, for the VRLA batteries cycled under the sulfation regime, the lowest values compared to the ones calculated for the other types of batteries. This is similar to the previous conclusion as regards the other estimators discussed.

In the experiment involving three different types of batteries, it was devised that the integration method of calculating E_{nucl3} is only applicable to the VRLA type as the other ones show poor correlation between E_{nucl3} and the cycle number. Moreover, there is little to no correlation between the estimated E_{nucl3} and capacity. The VRLA battery types exhibit a trend similar to that observed in previous estimator studies performed on those battery types. The trends observed for the first MF battery shows similarity in behavior to the VRLA batteries, but due to the lack of an observable trend of the second MF battery, it is hard to determine if the behavior is identical.

4.5 Method comparison

In the above described methods, it was crucial to find a simple linear relation to either time passed (cycle numbers) or capacity to ensure their applicability in SoH estimations. To find those correlations, the values of coefficient of determination (R^2) were compiled in the form of a table:

The criteria for suspected linear correlation were based on the value of R^2 above 0.65. When analyzed graphically, most of the estimators with such value of R^2 exhibited a correlation that can be perceived as linear. Such a low number was assumed to be the boundary at which it can be assumed that the relation is linear. Correlating the values of R^2 which the observations are based upon, the graphic representations of the relations show that in most cases the conclusions were similar. However, for the sulfation regime (where it was assumed that the values of estimators reached the lowest plateau value) the value of R^2 was very low, which could be very deceptive in terms of recognizing the actual behavior of the correlation if one relied only on the mathematical method.

After analyzing the behavior of all the estimators studied in correlation with capacity and cycle number, it was determined that the best rate of correlation was found between the $\Delta\tau_{plateau}$ estimator and cycle number. The trend for the estimator showed that during the battery's aging processes, the time needed to reach the plateau voltage value after the initial voltage dip steadily decreased over the course of the experiments. This means that there is a certain intrinsic aging process to which this element of coup de fouet effect is tied. It was also assessed that the E_{nucl1} and E_{nucl2} estimators – the ones that are a product of three variables (Eq. 6 and 7) and the one that is calculated using integration (Eq. 11) are also reliable in the estimation of battery deterioration due to aging. It was also determined that the estimators that are a product of three variables are slightly better correlated to the cycle number than the ones calculated by integration.

The observed relations between the estimators and capacity showed that there is no observable trend for the SLI and MF batteries. But for the VRLA batteries charged in various regimes there were trends that could be observed that are non-linear (closer to logarithmic) and linear. It was also noticed that as in the case of the sulfation regime, a plateau of the estimator values was observed.

This behavior of correlation between the estimators and cycle number could perhaps be explained with the hypothesis that there is a finite number of $PbSO_4$ nucleation sites that can be achieved in the battery. As the battery ages, the progressing sulfation causes the conditions in the battery to promote the creation of more and more nucleation sites, and this continues until it reaches values close to the plateau where the battery has the maximum number of sites. Batteries maintained under the sulfation buffer regime exhibit trends in which the value of the estimator is close to constant. This is perhaps due to the fact that in these regimes the maximum number of nucleation sites was achieved fairly early on. And thus, further capacity loss is owing to the progressing sulfation due to optimal conditions for non-dissolvable $PbSO_4$ growth.

4.6 Exhibition of the coup de fouet effect and its relation to time

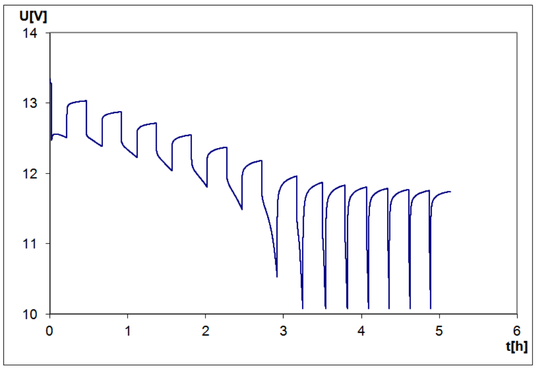

Figure 14: Discharge curve with intervals

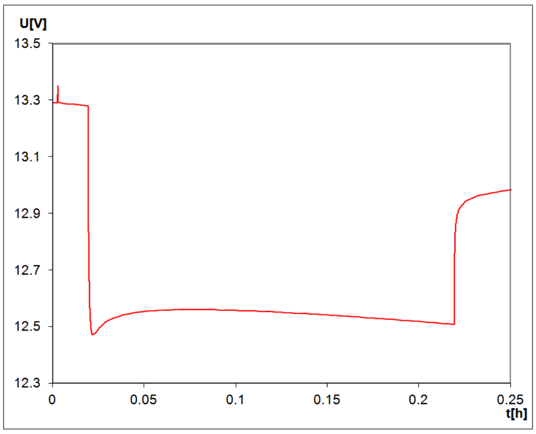

Figure 15: Initial stages of discharge

To examine whether the coup de fouet effect can be observed every time a charge or discharge current is applied to the battery, the current was applied for 1 hour and followed with a 15 minute OCV interval. This was repeated until the battery reached the voltage equal to that of the buffer voltage for charging current, or equal to 10.08V for discharging current. During the course of the analysis it was determined that the coup de fouet can be observed only during the initial stages of the discharge, as seen in Fig. 14 and Fig. 15. The effect can only be observed after the battery has been connected to buffer voltage for a long time and then discharged. Any other discharges that follow the initial discharge do not include the coup de fouet. This leads one to the conclusion that certain conditions need to be met. The leading factor in making the coup de fouet effect appear seems to be the time batteries spend in buffer regimes or disconnected. The short intervals that were applied during the course of the discharge/charge experiment were too short for the effect to re-exhibit. But the time between the measurement cycles (1 week) was sufficient for the battery to reach the state in which this phenomenon can be observed.

Thus, the hypothesis can be made that long term buffering or open circuit state of the battery causes an equilibrium to form. In this state of equilibrium the battery suffers aging processes dependent on the buffer voltage or lack thereof. It is most likely that this equilibrium is also related to how the nucleation process of $PbSO_4$ progresses in such state, since sulfation is a natural aging process of the lead-acid battery. When the discharge current is engaged, that equilibrium is disrupted and what we see as the coup de fouet effect is the battery's shift from that equilibrium state to one associated with the discharge phase. When the discharge/charge phase is over, time needs to pass until an equilibrium comparable to that prior to the charge/discharge phase is reached once again, so that the coup de fouet effect can be observed again.

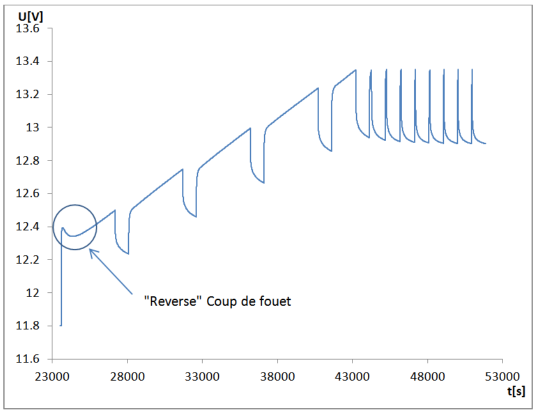

Figure 16: Reverse coup de fouet during charging

It is worth noting that as the battery ages, sulfation of the batteries sets in, and the coup de fouet effect can be observed during the battery's charging phase, as is evidenced in Fig 16. To date, it has proved impossible to put forward a conclusive theory on the nature of the coup de fouet effect or to establish a way to observe the effect in a repeatable manner.

Table 2: Correlation constants (R2) for various estimators in relation to capacity for the batteries studied

	1st Pair Battery 1	1st Pair Battery 2	2nd Pair Battery 1	2nd Pair Battery 2	3rd Pair Battery 1	3rd Pair Battery 2	1st SLI	2nd SLI	1st MF	2nd MF	1st VRLA	2nd VRLA
$\Delta\tau_{\delta\iota\pi}$	0.2086	0.2148	0.0443	0.0000	0.2135	0.7556	0.0167	0.6011	0.0364	0.0545	0.5023	0.3868
$\Delta\tau_{\pi\lambda\alpha\tau\epsilon\alpha\upsilon}$	0.6685	0.9331	0.7080	0.5378	0.3738	0.0083	0.0016	0.6462	0.8268	0.0016	0.2992	0.4479
$\Delta\Upsilon_{\delta\iota\pi}$	0.2484	0.5391	0.0532	0.3686	0.3924	0.2734	0.6067	0.1399	0.0329	0.1663	0.8707	0.0793
$\Delta\Upsilon_{\pi\lambda\alpha\tau\epsilon\alpha\upsilon}$	0.8510	0.8025	0.4583	0.1536	0.0837	0.0778	0.3130	0.1160	0.3175	0.0477	0.4455	0.1709
E_{nucl1}	0.6905	0.3532	0.4207	0.3627	0.3411	0.2743	0.2010	0.4413	0.5097	0.0568	0.2266	0.2605
E_{nucl2}	0.6930	0.8837	0.6884	0.3583	0.2499	0.0973	0.2058	0.4504	0.4780	0.0658	0.2380	0.2795
E_{nucl3}	0.0968	0.8854	0.6843	0.5790	0.4489	0.1404	0.1315	0.5647	0.5633	0.4851	0.185	0.2959

Table 3: Correlation constants (R2) for various estimators in relation to cycle number for the batteries studied

	1st Pair Battery 1	1st Pair Battery 2	2nd Pair Battery 1	2nd Pair Battery 2	3rd Pair Battery 1	3rd Pair Battery 2	1st SLI	2nd SLI	1st MF	2nd MF	1st VRLA	2nd VRLA
$\Delta\tau_{\delta\iota\pi}$	0.2343	0.3013	0.0189	0.0644	0.1496	0.3315	0.7891	0.6961	0.0292	0.0380	0.8101	0.4443
$\Delta\tau_{\pi\lambda\alpha\tau\epsilon\alpha\upsilon}$	0.8295	0.8834	0.6863	0.7322	0.4972	0.0277	0.4727	0.6899	0.9763	0.0012	0.3758	0.1459
$\Delta\Upsilon_{\delta\iota\pi}$	0.5480	0.8969	0.0467	0.1875	0.2332	0.3409	0.3228	0.2985	0.0474	0.0802	0.6069	0.0181
$\Delta\Upsilon_{\pi\lambda\alpha\tau\epsilon\alpha\upsilon}$	0.8720	0.5312	0.5221	0.4011	0.1274	0.0703	0.2665	0.4004	0.2133	0.0792	0.3356	0.1049
E_{nucl1}	0.8270	0.7224	0.7184	0.6322	0.4058	0.1729	0.4123	0.6209	0.4090	0.1436	0.2845	0.1454
E_{nucl2}	0.8270	0.7232	0.7132	0.6276	0.3310	0.1261	0.4404	0.6314	0.3809	0.1545	0.2990	0.1587
E_{nucl3}	0.0854	0.2903	0.4229	0.7665	0.6140	0.3315	0.4724	0.6031	0.3872	0.5844	0.2791	0.2791

5 Conclusions

Reproduction of the coup de fouet effect in completely controlled conditions has proved impossible. Hence, it was impossible to fully separate the occurrence of the said effect from the impact of other aging factors and study it in isolation. However, by careful examination of possible factors that cause the effect to occur, it was possible to relate coup de fouet to the process of sulfation.

Reported research has proven that although in short-term applications coup de fouet cannot be reliably used for SoH estimation, it can be fully exploited in long-term applications such as quarterly check-ups of batteries as a preliminary method to weed out sulfated batteries.

Another factor to be considered is the degree of sulfation. As mentioned in the discussions above – the more sulfated the battery is, the smaller the values are of the estimators tied with the coup de fouet effect. The initial findings described in [25] are confirmed by the research presented in this paper.

The variables that can be used to describe the coup de fouet were explored and their correlation to battery wear was tested. Analysis of the values of all of the presented estimators lead to several observations as regards the changes in coup de fouet intensity over time. The variable $\Delta\tau_{plateau}$ exhibits variability with battery wear, decreasing in time until it reaches a plateau. While the specific mechanism for this behavior is unknown, several theories for this phenomenon have been considered. It was deducted that the most probable explanation for the behavior of $\Delta\tau_{plateau}$ during the battery's lifetime is related to the reactions occurring in the battery during the early stages of the discharge phase, namely to the initial nucleation of $PbSO_{4,}$ as well as to the saturation of the electrolyte with Pb^{2+} ions. The mechanisms of the initial dissolution of the lead and lead (IV) oxide into the electrolyte, formation of the first lead (II) sulfate nuclei and initial crystal growth result in the voltage dip in the early stages of battery discharge. As the battery ages, the values of $\Delta\tau_{plateau}$ decrease, which suggests that due to the rise in the degree of sulfation, little to no additional nucleation is needed for additional crystals to occur. This leads to the conclusion that possibly the estimator $\Delta\tau_{plateau}$ that could be associated with determining the SoH is not tied to overall battery wear but to a very specific quality – the progression of sulfation. This observation is further supported by the determined value of $\Delta\tau_{plateau}$ reaching its lowest observable value during the sulfation promoting regime based experiment. Analysis of the $\Delta\Upsilon_{plateau}$ estimator showed that its change over time is less pronounced than the one characterized for the $\Delta\tau_{plateau}$; thus, it might not be as useful as $\Delta\tau_{plateau}$ in determining the rate of aging of the battery. It should be noted, as well, that the values of $\Delta\tau_{dip}$ and $\Delta\Upsilon_{dip}$ estimators did not exhibit any noticeable change during the experiment, and it was determined that the depth of the coup de fouet effect prior to the lowest point of the dip is not related to aging of the battery. This runs contrary to the findings presented in [3][4] which discuss how the value of $\Delta\Upsilon_{dip}$ should be used as a prime estimator in determining the battery's remaining capacity and, by proxy, its SoH. It could be that the estimator value presented here was measured right after disengaging the buffer voltage, causing a difference in how the data was collected and leading to such discrepancies.

The E_{nucl} estimator, as the product of $\Delta\tau_{plateau}$, $\Delta\Upsilon_{plateau}$ and the discharge current, was also reliable in terms of describing the aging process. However, calculation of the value of E_{nucl} using the integration method did not deliver any improvement over the estimator based on the product of the three said variables. This can be attributed to estimation of the U_{theory} over time trend, with a degree of error due to inaccuracy of the algorithm and to the not-fully-linear nature of the discharge curve after the coup de fouet. A reliable algorithm to properly estimate the said trend has to be developed for the integration method to prove accurate in long term application. It should also be noted here that multiplication of estimators compound all the possible errors that might have been encountered when the values creating them were registered. Thus the more complex the estimator is and the more variables it embraces, the larger the degree of error.

Despite the fact all of the discussed estimators had a very poor linear relation to the battery's capacity changes, showing no visible trend whatsoever. It is worth noticing, though, that for the VRLA batteries, a trend that is close to logarithmic could be observed for the estimators in their relation to capacity. But, upon closer observation, it proved not to be logarithmic in nature. Moreover, the estimators related to cycle number (which as previously mentioned, can be assumed to be 'time passed') showed a good amount of linearity. Thus, it is most like that the aging process of sulfation is independent of the capacity changes, and in turn can be related to the coup de fouet phenomenon. In the discussion of the estimators, the issue of active centers of nucleation was raised – perhaps the coup de fouet effect is tied to a very specific aspect of sulfation such as the amount of inert crystals. And said are measured not by weight or volume, but understood in terms of grain size distribution and the size of the crystals' facets surface (which in turn relates to the fraction of the initial battery capacity 'trapped' in them). As it is currently difficult to assess whether the large or small inert crystals have a bigger impact on the coup de fouet effect, further work in this area is needed to determine the exact relation between the inert crystal size and its effect on coup de fouet. A series of tests with various sulfation and desulfating regimes should be considered to observe if the coup de fouet phenomenon depends on decrease in the amount of inert $PbSO_4$ crystals. For example, a regime that applies a buffer voltage of 2.16V/cell can be used to deliberately sulfate the battery for a period of one month (during which time data from the battery were gathered) and can be later followed by application of the desulfating procedure e.g. as described in [23]. The latter would be applied in an attempt to restore the capacity lost as a consequence of the former. A buffering regime of 2.3V/cell (a normal charging voltage without temperature compensation) will then be applied to the battery and coup de fouet data will be gathered for the purpose of comparison with the period under sulfation. As was previously mentioned, if the coup de fouet relates to the level of sulfation of the battery, there should be a decrease in the values of observed estimators, proving the validity of the hypothesis of the connection between both phenomena.

It should be stressed that the methodology of measurement of the observables used to determine the value of the estimators was found to be sensitive to electrochemical noise, as even small voltage changes are meaningful. The methodology of measurement of time and voltage requires equipment with a good sampling rate (at least 10 samples per minute) and importantly with high enough voltage resolution. And while the former is easily achievable on modern systems, the latter might prove a bigger obstacle, as most integrated circuits that measure voltage used in equipment tend to have up to 14 bits analog to digital conversion chipsets, while it was found that 20 bits are needed to provide reliable data for estimator calculations. It should be stressed that, apart from the ever-present noise, other errors in measurements could also be a factor in producing poor quality readings. Consideration should be given to integrating a good algorithm in the measuring tool to filter out these erroneous readings and minimize the impact of these errors.

Identifying the middle of the plateau is not necessarily straightforward, as it might not correspond to the highest registered value of voltage after the dip. This is a major obstacle to applicability of analysis using the coup de fouet. As can be seen in Fig. 17, the possible registered interference can lead to a false positive recognition. If applicable (as a mean of removal of such) an array of simple mathematical methods, such as finding the maximum value, can be applied to the dataset. A more sophisticated algorithm has to be used or filtering applied to eliminate any possible noise registered in the measurement. A variety of methods to remove registered noise should be considered, for example the moving mean average.

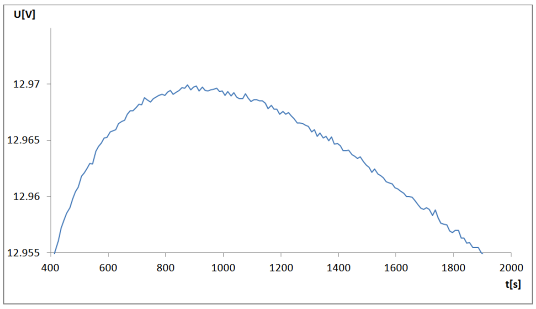

Figure 17: Noise affecting estimation of the plateau point

It should be noted that none of the estimators proved reliable for the SLI batteries, for any manner of application. This might be related to water evaporation and replenishment during the course of the experiment, causing the electrolyte concentration to change in a non-monotonic fashion. Replenishing the water level changes the concentration of the Pb^{2+} and SO_4^{2-} ions and most importantly the acid concentration, and upsets the balance in the battery. As evidenced in [23], the solubility of $PbSO_4$ in H_2SO_4 is better, the lower the acid concentration is. Moreover, lower concentration can be achieved through water replenishment and aging processes. Thus, this process causes irregularities that disrupt the linear trend of the estimators, as a new balance is established after water replenishment. This affects any flooded batteries where there is replenishment to offset "water loss", ruling out coup de fouet methods as a means of reliably monitoring SoH.

To conclude - the coup de fouet related estimators cannot be used as a sole contributor to SoH estimations. However, they could be used in conjunction with other methods to deliver a better analysis of the extent of aging processes in the battery. As was proven earlier, the method described earlier is good at detecting sulfation, it should be used to estimate how much of the capacity was lost due to it, isolating its impact from the aging processes present. Other methods should be used to estimate what other aging processes impacted the battery's capacity. Moreover, to complement the techniques presented in this paper, sophisticated algorithms should be developed and sufficient signal filtering applied to limit the possibility of error in sulfation assessments.

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