

Statistical analysis of the error function in the determination of the state-of-charge in lead/acid batteries

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Abstract

The state-of-charge (SOC) has proved to be itself, one of the main control parameters in the lead/acid battery operation. Battery-disposable charge depends on the SOC, so the system operation time will also depend on it. The accurate calculation of the SOC is then of extreme importance, though big errors would make the system to fail prior to the expected ending time, according to theoretical calculations. The method to determine the SOC in lead/acid cells proposed by one of the authors has been treated and analysed. A mathematical treatment of the associated error to this calculation has been carried out, and theoretical predictions compared with experimental results. Based on this procedure, a statistical analysis of the error function has been developed, deducing a mathematical expression which gives the probability of the error related to the SOC value. The results have been then applied to the methodology of the aforementioned determination of the SOC to obtain the average error value of the calculated SOC.

Introduction

The determination of the state-of-charge (SOC) in lead/acid batteries has been, and still being, one of the main focus in lead/acid batteries research. Some promising advances have been made during the last decade, and specially in the past few years. Many new methods have been developed in the eighties [1–9], but really few [1, 10] give numerical values or analytical expressions of the error associated to the SOC calculation. The more accurate the SOC is computed, the less probability of failing in the system, the lower initial investment, and the less maintenance cost. From this point of view, a method which predicts the SOC in lead/acid batteries with higher accuracy, improves the system design, the battery performance, and saves money and time.

It is true that, for certain kind of devices, the SOC has not to be calculated within a high precision, avoiding complicated technology, long operation time, and sophisticated equipment. On the contrary, other type of systems like photovoltaic arrays, work under strict operation conditions depending heavily on the SOC. In these cases, even a small error in the SOC calculation may cause a considerable alteration in the normal battery operation, with feasible battery failing, and the resulting breakdown of the system.

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The try of developing a method with the minimum possible error in the determination of the SOC in lead/acid batteries, even using some short of sophisticated equipment and more or less complicated development, is not out of focus. Efforts devoted to this purpose will produce the logical benefits, a better design of the whole system, with less cost and smaller size.

Batteries which operate in a reduced depth cycling, usually 20% or lower, are specially indicated to be the focus of this kind of study, so the relative errors in the computation of the SOC strongly influence the battery and system behaviour.

Determination of the state-of-charge

The method used in the determination of the SOC has been based on the linear relation between electrolyte density and output voltage of a reference cell linked to the main cell [11].

Changes in the SOC can be determined through the changes in the electrolyte density, considering their relation to be linear, which for a circulating lead/acid battery is true.

During operation the electrolyte density changes and produces electrochemical potential variations in the reference electrode of a reference cell linked to the main cell, according to the Butler-Volmer equation. These potential variations create a potential difference between the reference cell electrodes, which changes with the electrolyte density variations in the battery. From this, a function relating the SOC and the reference voltage can be deduced.

In conditions of the non-equilibrium state, the reference potential cell difference is given by $\Delta\Phi = \Delta\Phi_e + n$ where $\Delta\Phi$ is instantaneous voltage, $\Delta\Phi_e$ the potential difference at equilibrium (given by the Nernst equation) and n is the overpotential. Consequently the reference voltage is given by the equation:

$$\Delta\Phi = (RT/nF) \ln c_r \quad (1)$$

where R is the general constant of gases, T the absolute temperature, c_r the solute concentration and K, K' are defined as correlation constants, which is valid since equilibrium is reached, and where electrode potential influence has been discarded.

As we are dealing with small concentration changes a linear dependence on the concentration can be inferred, and the general reference voltage expression is

$$\Delta\Phi = k_1 + kc_r \quad (2)$$

where a new constant, k_1 , has been introduced to cover small potential differences due to slight differences in electrode composition and the sulfuric acid bridge resistance of the reference cell.

Using a former relation which links the SOC (Q) and the density variation ($\Delta\rho$) in a lead/acid cell when being charged or discharged, and taking into account there is a linear relation between density and concentration for sulfuric acid cells, we can conclude the SOC expression being:

$$Q = 100 - (K + K'\Delta\Phi) \quad (3)$$

Some details should be mentioned prior to the development of the statistical analysis: the calculation of the SOC has been made according to the referred technology, but corrected for non-standard discharges as one of the authors [12] has explained in a previous paper.

The experiments have been carried out in lead/acid batteries of 150, 240 and 625 A h of nominal capacity of 10 h discharge.

Discharges were extended from 10% to full discharge (100%), at rates between C_{10} and C_{100} , for all type of batteries, except for the group of 240 A h where maximum discharge achieved the 85% of the global capacity at the working discharge current rate.

Operation conditions remained unchanged with regard to those used in ref. 11.

The results from experiments have been drawn in Fig. 1(a)–1(c). The values are being compared with the real ones calculated from the A h discharge method.

Analysis of the error

Theoretical values of the SOC, calculated through the proposed method, have been determined within an error which should be considered in the battery operation. The errors have been computed from analytical formula, whose expressions can be found in refs. 11 and 13.

The overall error considered for calculation of the SOC is given by:

$$\Gamma = \epsilon + \epsilon' = \left\{ (s_s / \Delta\rho) + [(1-Q)(1-\eta)] - 1 \right\} \quad (4)$$

where s_s is the standard error in density variation estimation, ϵ is the error of the reference voltage density variation relation, $\Delta\rho$ is the density variation, η is the cycling efficiency, and Q is the SOC.

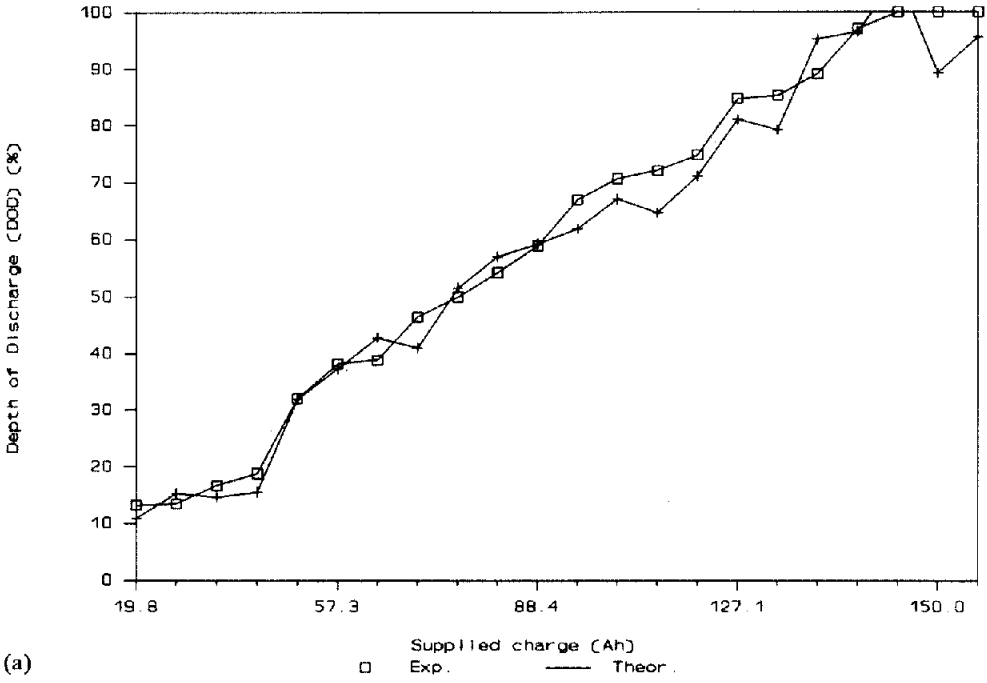
This error will be affected by additional factors as ageing, capacity and operation mode. Further studies will provide us the correction factors for each of these agents, so the general error expression can be accordingly modified.

It has been shown that the combined effects of the reference voltage, from the reference cell, and the determination of the electrolyte density gradient introduce a global error which is limited by a maximum value of 8%. This limit can be considered acceptable in general circumstances, but some special cases deserve a more detailed analysis.

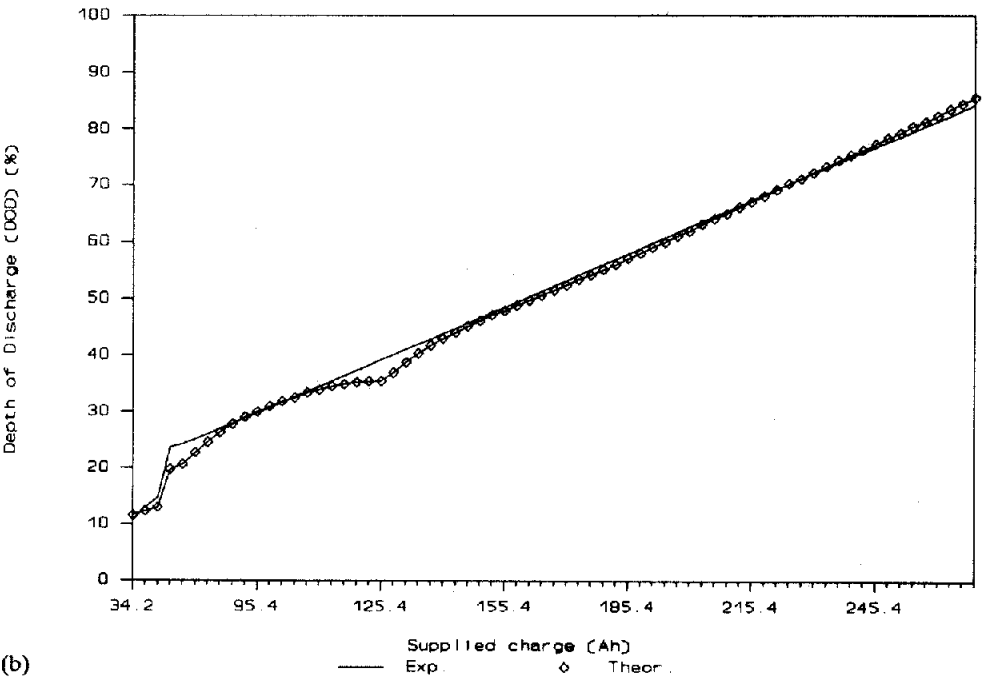
The special cases that should be treated apart are:

(i) *Batteries operating in stand-by mode.* These batteries usually operate at maximum charge, close to 100%, receiving energy from a d.c. source, and supplying charge to the connected device. It is evident that the system cannot fail though an excess of charge remaining in the battery, no matter how long the system receives energy from the accumulator, unless the d.c. source is interrupted. A problem with a low accurate prediction of the real SOC then occurs: as battery is supposed to be fully charged at any time, even a small error such as the predicted 8%, would require the continuous supply of energy when battery is at its maximum SOC, wasting energy, corroding the plates, and provoking water electrolysis which makes the electrolyte level to lower down to a point where plates are oxidized and ruined. This is similar to the problem arising in the overcharge process at the end of the battery charge, when extra energy is forcibly required to equalize electrolyte density, but producing some damages to the cell. An accelerated ageing is the unavoidable consequence of this process, and so it would be in batteries operating in stand-by mode if the SOC is not properly calculated.

(ii) *Photovoltaic systems operating at low discharge rates.* Typical operation of low discharge rate photovoltaic batteries is of 15% to 20% of maximum depth-of-discharge (DOD). The calculated error in the SOC determination moves from 5 to 5.4%,



(a)



(b)

Fig. 1.

(continued)

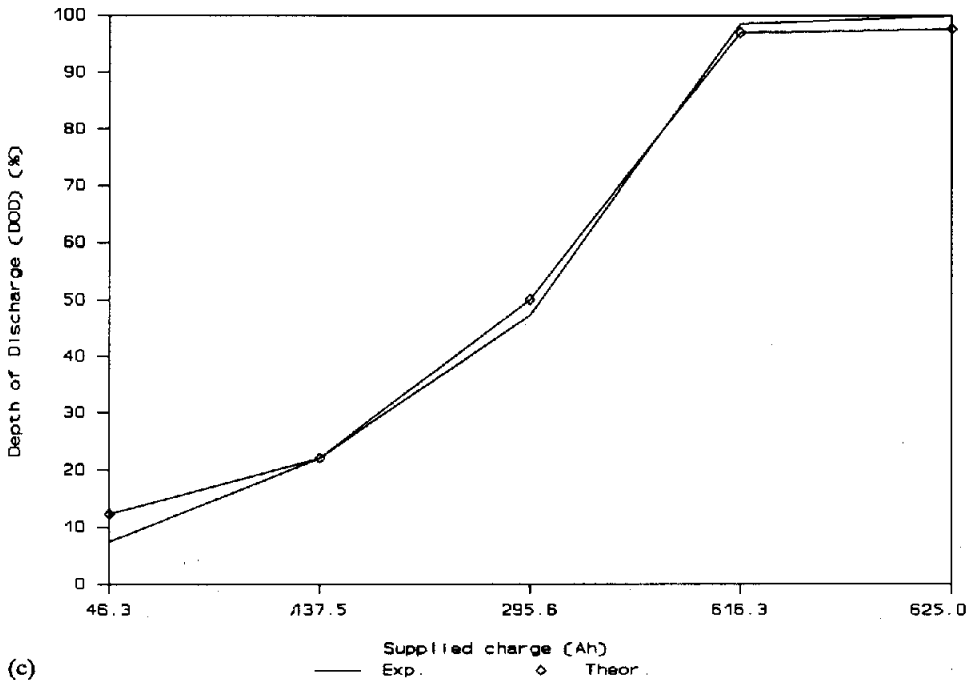


Fig. 1. Experimental and predicted values of the state-of-charge, including corrections for capacitive effects: (a) 150 A h; (b) 240 A h; (c) 625 A h.

depending on DOD. In such a case, a correction factor of 6% would be enough to compensate the deviations in the calculated SOC related to the real value. The error is of minor importance during operation, but specially affects the building and design of the battery system, which should be oversized to counter-balance the error. The bigger the storage system is, the more influence the effect has, increasing initial investment and battery maintenance during the accumulator lifetime.

(iii) *Photovoltaic systems operating at high-discharge rates and Uninterruptible Power System (UPS)*. Typical DOD in these systems are in the range from 65 to 80% which means, according to [11], an average error of 6% in the SOC determination. This value seems to be adequate, but some particular considerations should be taken into account: as we approach the discharge limit in a lead/acid battery, 50% for lead/calcium positive plates, and 80% for lead-antimony, errors become more and more important. The cut-off point of any lead/acid battery discharge is calculated as the turning point from which the battery does not supply energy anymore, or at least it does not supply energy of good quality. What does it mean is that charge beyond the cut-off point corresponds to voltage and current much lower than to the operational values, so it cannot be used by the attached system. If the SOC of the battery is wrongly calculated due to the associated error, and we overpass the discharge limit, a fail in the system may occur, not because of the battery breakdown but for the low standards of the supplied charge (insufficient voltage and current).

An additional problem joins the exposed before when working very close to the discharge limit. Average battery lifetime is calculated according to the type of discharge it is being submitted to; if the maximum DOD is overpassed, the battery ages quicker

than expected due to corrosion effects in the plates, and to the formation of insoluble lead sulfate crystals which are not longer recoverable. As authors have demonstrated [14], battery ageing influences the determination of the SOC by a factor which depends on the ageing itself. The greater the battery ageing is, the bigger the error in the SOC determination will result [15]. The global effect of cumulative errors is the general failure of the system.

Error results

Theoretical values of the error in the SOC determination in lead/acid cells have been calculated from the corresponding formula, and the resulting values compared with the experimental obtained from the experiments. The comparison has been drawn in Figs. 2 and 3, where an already published graph (Fig. 2) [11] has also been included to clarify the explanation and the comparison.

Figure 2 shows the global error produced in the calculation of the SOC through the method of the reference voltage [11]. The partial contributions of the reference cell and of the density gradient measurement have also been included in the graph. We can see from Fig. 2 that the maximum error is limited to a value slightly lower than 8%, according to what was mentioned in a previous paragraph.

Further studies, whose results are at present under review [12], showed that the capacity influences the analytical expression from which the SOC is being calculated, thus affecting the error value. From this new situation, errors values were drastically

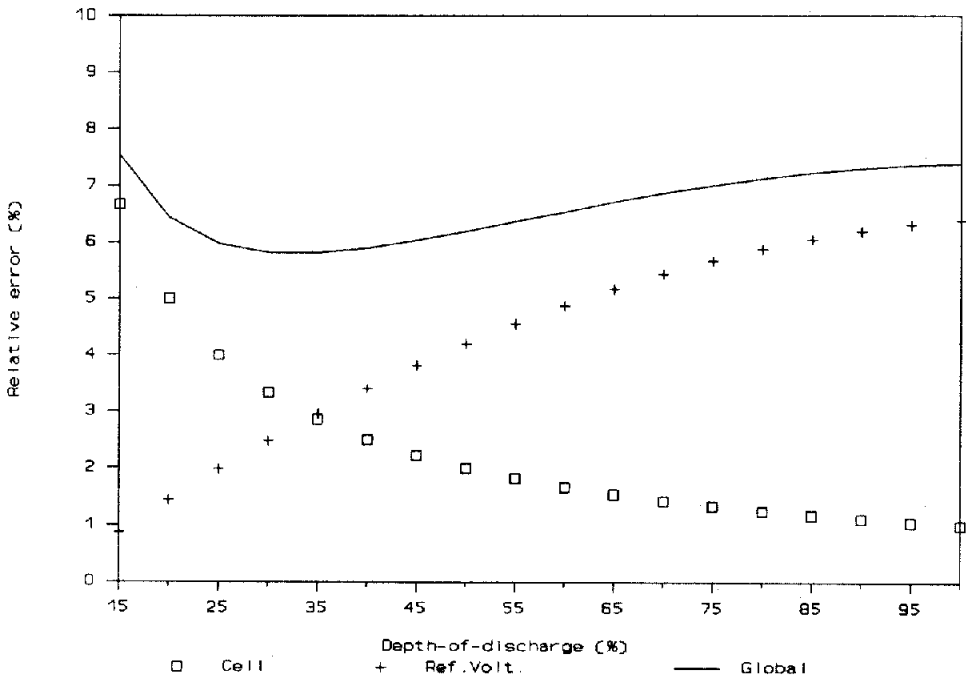
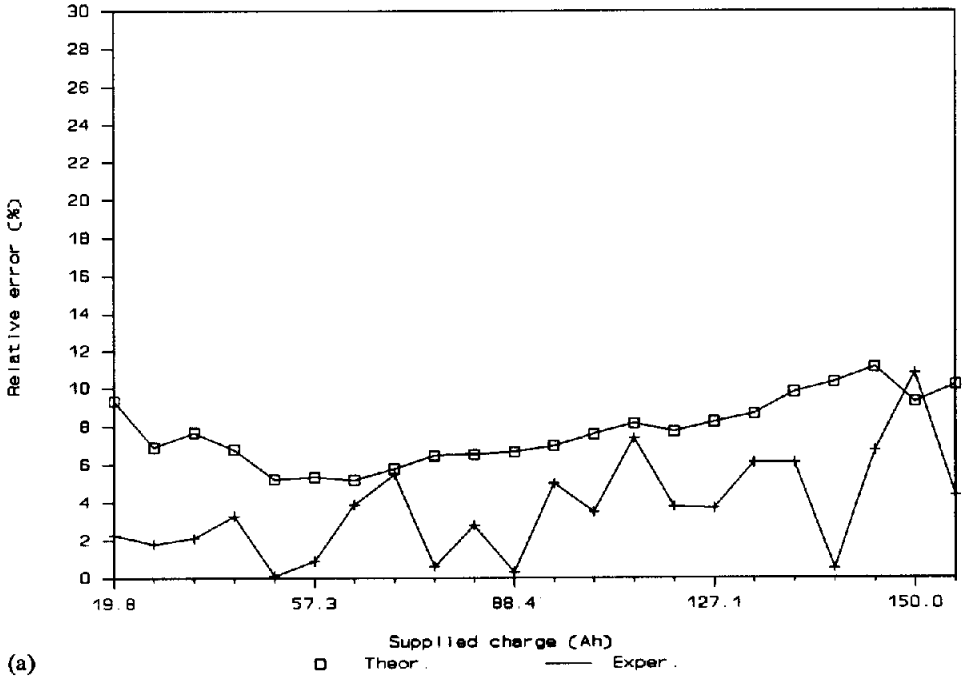
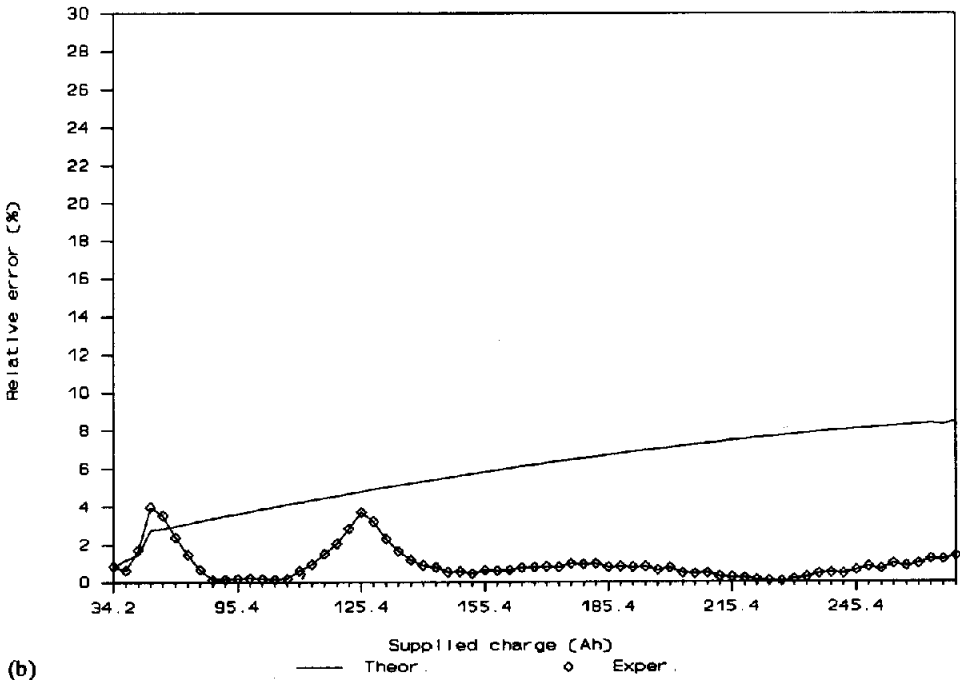


Fig. 2. Estimated error in the determination of the state-of-charge in lead/acid cells.



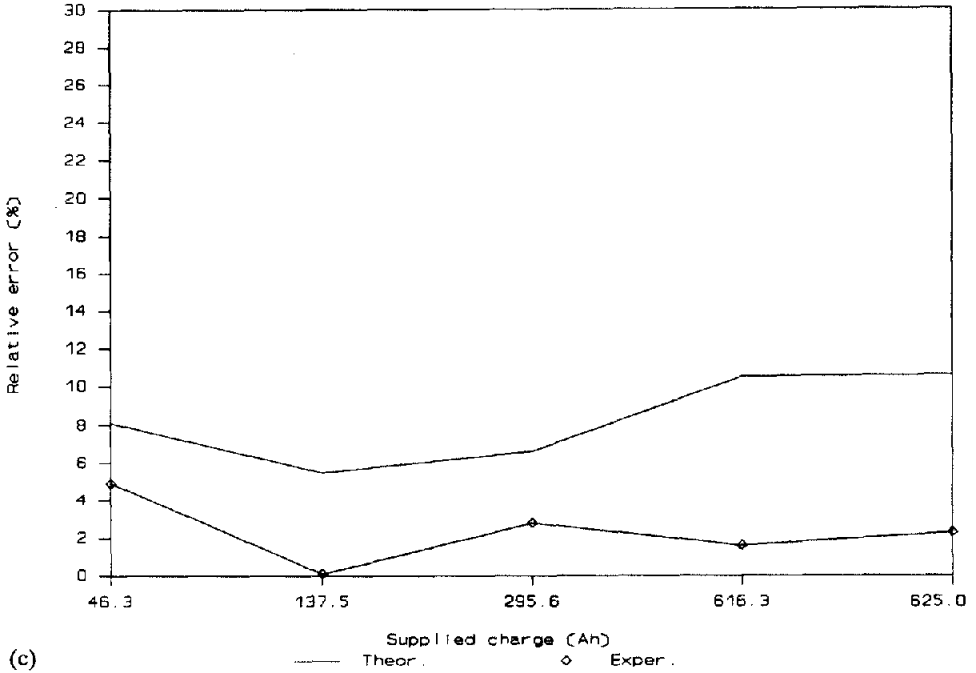
(a)



(b)

Fig. 3.

(continued)



(c) Fig. 3. Theoretical and experimental error in the state-of-charge determination for a lead/acid cell: (a) 150 A h; (b) 240 A h; (c) 625 A h.

reduced to the minimum level attainable with the technology used in the proposed method. These new results are those presented in Figs. 3(a)–3(c).

A simple view of the graphs representing calculated errors for the three groups of batteries, indicates us that error is depending on the extracted charge, and consequently on the SOC itself. Therefore, any time at which the SOC is being calculated, the correcting factor including the error in the SOC determination, that should be applied, changes according to the SOC level. This implies the need to know all error values from fully-charged to fully-discharged states, with at least a minimum precision, or to deduce an analytical expression performing the error path, which can be introduced in a computational programme. The former method supposes to handle a massive amount of data, though every cell has its own error variation with SOC, therefore requiring an excessive man-hours. The latter, is easier to work with, it only requires a simple computational programme and not quite sophisticated computer, provided that the analytical expressions are not very complicated as it is intended.

Why a statistical analysis of the error?

The deduction of analytical expressions for the error in the SOC determination in lead/acid cells reveals itself to be one of the most convenient methods to avoid long and cumbersome treatment of massive data to correct the SOC value, thus avoiding erroneous design of the storage elements, and a probable further failing which would affect the entire system.

Many efforts have been devoted to this purpose, but unfortunately the solution of the problem is not as easy as it was previously thought. The first problem we confronted was the irregular and capricious pathway in which the error run for every case (see Figs. 3(a)–3(c)). This indicated us there was probably not be a simple function representing the error along the SOC variation, even for a single cell. We first attributed this irregularity to the insufficient amount of data we were working with, cases of cells of 150 and 625 A h of capacity, but analysis of the 240 A h capacity cell, where a suitable number of data were being treated, showed similar behaviour in the error pathway. As the solution to find analytical expressions for the error function seemed to be impossible, or at least very complicated, we decided to move to a statistical study of the problem.

Statistical function of the error

To analyse the error from the statistical point of view, we counted all calculated errors matching every error value, and the resulting number was graphically represented versus the error value. The shape of the graph reminded of a classical normal distribution, so this was the first tested function.

As relative errors have the same effect on the SOC calculation, no matter they are positive or negative, we slightly modified the classical normal distribution assuming the parameter x to be always positive, so the function results:

$$f(|\epsilon|) = (2\pi)^{-1/2} \exp(-|\epsilon|^2/2) \quad (5)$$

being ϵ the value of the calculated relative error.

If we now assume the function f represents the probability of making a certain error ϵ in the calculation of the SOC, the eqn. (5) is transformed into:

$$P(|\epsilon|) = (2\pi)^{-1/2} \exp(-|\epsilon|^2/2) \quad (6)$$

where $P(\epsilon)$ is the probability of calculating the SOC within a relative error of ϵ .

First tries demonstrated the function fitted very well for values close to the maximum ($\epsilon \rightarrow 0$), but disagreed if the relative error increased.

Lack of adjustment was tried to be solved modifying the exponent of the error, and letting invariable the other coefficients; the so-transformed function resulted to be of the way:

$$P(|\epsilon|) = (2\pi)^{-1/2} \exp(-|\epsilon|^n/2) \quad (7)$$

where n is a parameter varying from 0 to ∞ .

The successive attempts showed that for $n=1$ the adjustment was rather good, better than for any other value of the parameter n . The resulting function was then represented, observing that there was a displacement to the right in the position of the maximum of the probability function. Fortunately, the displacement was linear, so to center the pseudo-normal distribution at the zero value of the error, we modified the coefficient of the exponential resulting:

$$\exp(-|\epsilon|^n/2) \longrightarrow \exp(-|\epsilon - 1.1|/2) \quad (8)$$

where 1.1 is the linear displacement observed between both centered and displaced distributions.

Despite the shape of the new function was of that of a centered pseudo-normal distribution, calculated values from that function resulted to be ten times higher than

distribution of the experimental. The solution was, once again, to modify the coefficient of the exponential by a factor of ten, then the final function being:

$$P(|\epsilon|) = (2\pi)^{-1/2} \exp(-5|\epsilon - 1.1|) \quad (9)$$

which almost perfectly matches the experimental distribution, as it can be seen in Fig. 4.

The analysis of results included in Fig. 4 indicates us that probability of finding a significant relative error beyond a range of 1% around the center ($\epsilon=1.1\%$) is neglectable. Therefore, we can construct our study to an error band from 0 to 2.2%, centered at 1.1%. All relative values of the error in the SOC determination out of this range have no or so small probability of being, that are out of focus.

The extremely sharpened shape of the probability function also evidences the merit of the determination of the SOC. Maximum probability is of 40% at $\epsilon=1.1\%$, which evidently is quite a low value for the SOC calculation.

The statistical function $P(|\epsilon|)$ is mathematically coherent though the probability of finding an error lower than zero is lower than 10^{-3} , which from any point of view can be considered null as experimental requires.

A final test [16] to check the correlation between the modified pseudo-normal distribution and the experimental results for the relative errors was run, giving the following results: $\text{rms}=0.9991$ and $\sigma=0.0062$ being rms the correlation factor between theoretical and experimental results, and σ the standard error.

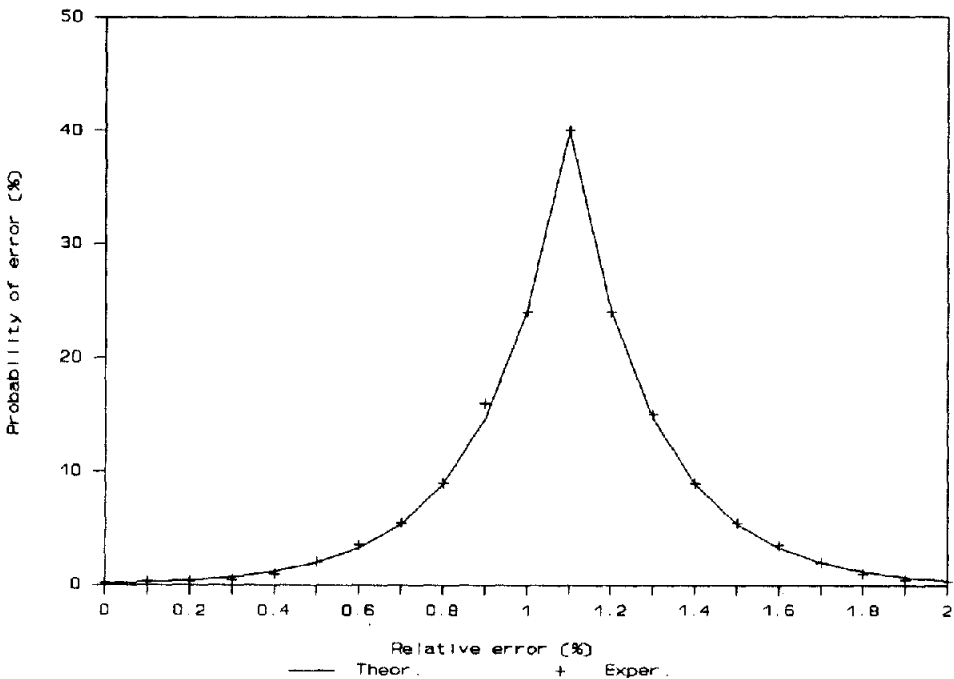


Fig. 4. Probability of error in the determination of the state-of-charge in lead/acid batteries.

Conclusions

The mathematical treatment of the error in the determination of the SOC in lead/acid cells leads to a complicated development with not an easy solution.

The statistical analysis of the error distribution reveals itself to be a perfect method to match experimental results, with minimal deviations, usually lower than 0.6%.

The probability beyond a relative error of 2.2% is neglectable. Therefore, a maximum correction factor for the SOC determination of 1.02 can be used, with a failing hazard factor of 0.1%.

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