A NEW METHOD OF ESTABLISHING THE STATE OF CHARGE OF LEAD–ACID BATTERIES WITH ELECTROLYTE CIRCULATION

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Summary

The proposed method of monitoring battery state-of-charge is based on electrolyte density measurements. It is reliable, applicable in all cases to batteries with a circulating electrolyte, and is very useful for high discharge rates.

An empirical law, based on results obtained from different experiments has been developed. This law allows isolation of the accumulator state-of-charge as a function of the maximum state-of-charge density at the test point and a proportionality constant, n.

Testing methods

There are many different methods of establishing the state-of-charge of static electric accumulators. All fall into two main groups: Classical and Evolved.

The Classical group of tests includes:
(a) open circuit voltage
(b) internal resistance
(c) electrolyte density
(d) total discharge
(e) voltage during charge or discharge processes
(f) ampere-hour accounting
(g) consumed energy
In the Evolved group tests we can include:
(h) controlled discharge
(i) electrolyte density in a system with circulating electrolyte
(j) open circuit voltage in a circulating electrolyte system
(k) charge/discharge voltage in a circulating electrolyte system

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Testing method analysis

Even though all of the proposed methods can be considered useful for determining the state-of-charge of batteries, most of them have serious drawbacks or are unreliable. A brief review reveals the most advantageous.

(a) Open circuit voltage test [1]. This test has the disadvantage of needing a long time before steady state after charge or discharge is reached, usually hours. The test is therefore impractical, especially when the battery is on standby and, hence, likely to be used within a shorter time than that taken to reach the final steady state potential.

(b) Internal resistance test [2]. The disadvantages of this test are the need to use discontinuous current bridges (expensive and sophisticated), and low precision. The internal resistance varies during charge or discharge, depending on parameters not linked to the state-of-charge, and is therefore an unreliable test. On the other hand, due to the very low resistance of the battery, any error will have a large and negative influence.

(c) Electrolyte density test. This gives one of the most accurate values of the state-of-charge. Unfortunately, in static batteries (without agitation), a stratification process is developed during charge or discharge. This results in a density gradient and density checking is not representative of the whole solution. Overcoming the problem by sampling at diverse points is not possible because non-linearities in the gradient make it impossible to obtain a sufficiently accurate average value.

(d) Total discharge test. This is totally impractical in a working accumulator.

(e) Voltage test during charge or discharge. The advantage of this test lies in the fact that the voltage can be monitored under dynamic and continuous conditions. It is, however, affected by acid stratification which causes errors, generally of the maximum state-of-charge at the time of the test. The phenomenon is more evident during charging.

(f) Ampere hour test. Monitoring the ampere hours during charge and discharge is difficult due to the variable efficiency during charge [2] which leads to cumulative errors.

(g) Consumed energy test. This test is based on checking the delivered ampere hours and the voltage [3]. The need of a computer to study possible errors and to process the data is the most important drawback of this test.

(h) Controlled discharge test. This test is the best of the methods already discussed. Its main advantages are a high sensibility, good reliability, and independence of the electrolyte density. It does, however, have one

important disadvantage. Previous studies [4] have shown that discharge conditions depend on the cell characteristics, so parameters involved in estimating the state-of-charge must be changed when using different types of battery.

((j)(k)) Open circuit voltage tests and charge–discharge cycle voltage tests. Both have similar problems; the most important is their dependence on the kind of process and charge–discharge conditions.

Establishment of an empiric law for the state-of-charge

Electrolyte concentration and density increase and decrease during charge and discharge in a lead–acid battery. The electrolyte density changes linearly during charge or discharge in a circulating system [5]. A linear relationship can therefore be established between the state-of-charge and the density.

The density at the sample point can be established during discharge as a function of the initial state according to:

$$\rho(i) = \rho(o) + qK_n \tag{1}$$

where $\rho(i)$ is the test density, $\rho(o)$ the density at the maximum state-of-charge, q the discharge curve slope and K_n the percentage charge received [5].

Considering a general case ($K_n \neq 0$ and $K_n \neq 100$) and taking into account the linearity of the discharge curve, the proposed law might be written as:

$$D = [\rho(o) - \rho(i)]/n \tag{2}$$

for discharge processes, where n is the discharge coefficient, and

$$Q = 100 - D = [\rho(i) - \rho(f)]/n' = [\rho(i) - \rho(f)]/n\eta \tag{3}$$

for charging processes, where $\rho(f)$ is the density at the minimum state-of-charge, n' is the charge coefficient, and η the charge–discharge cycle efficiency.

Density test

Density tests should be carried out in batteries with a circulating electrolyte system because this homogenises the electrolyte and eliminates the type of problem associated with unagitated batteries [5].

(i) Experimental procedure

Samples to check the density can be taken at any point, but the most accessible points are the outer connectors and the electrolyte surface layer.

In sealed batteries one is limited to the former for taking samples, but in flooded electrolyte batteries the latter system is easier.

Unfortunately, manual systems are labour intensive while automatic systems need sophisticated and expensive equipment. In very large installations, however, this would be of lesser importance.

The first method to evaluate density involves removing and weighing samples from the battery. This method is simple, inexpensive, reliable and, as with all methods based on gravity measurements, precise (10^{-3} g cm^{-3}). On the other hand, maintenance is costly, the test is slower than electronic methods, and large samples (> 30 cm^3) are needed.

Two important electronic methods of density determination are based on:

(a) *Light diffraction*. A light beam is passed through the battery electrolyte and the diffraction is monitored. Samples are not needed: a continuous signal which can be recorded is obtained but the system requires sophisticated and expensive equipment [2].

(b) *Ultrasonic monitoring*. A peristaltic pump transfers electrolyte to an ultrasonic monitor before returning it to the battery. This system has several advantages:
   — quick and could be automated
   — highly reliable
   — high resolution ($< 0.1\%$)
   — continuous recording
Its disadvantages are:
   — expensive
   — reading is slow
   — a linking system is necessary to record data
   — an auxiliary pump must be used or a system linked to the outer channel.

(ii) Results

Our density tests were made by weighing and checked later using ultrasonic sensors. Results from both methods were in good agreement.

(iiA) Discharge

(a) *Discharge curve linearity*. Results from the experiments carried out in both laboratories (Grupo de Energia Solar and FEMSA) have been plotted in Figs. 1 and 2. Note the highly linear relationships for the discharge curves obtained from the data (Table 1) and that the discharge slope decreases rapidly from an initial value.

(b) *Supplied charge*. We calculated the total charge supplied to the cell using the following expression:
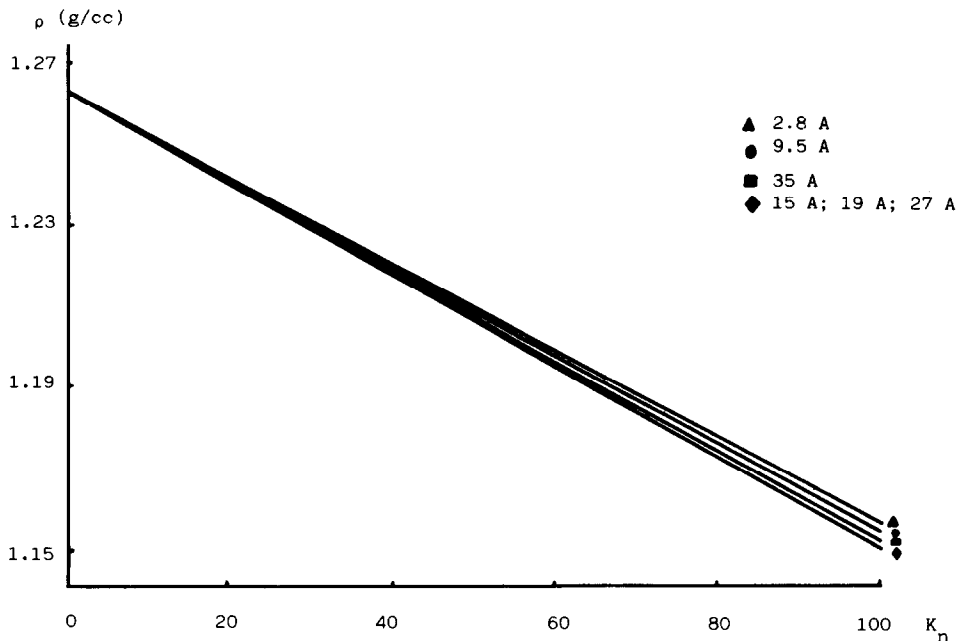
Fig. 1. Electrolyte density as a function of the state-of-charge at various discharge currents in static lead–acid batteries with electrolyte circulation.
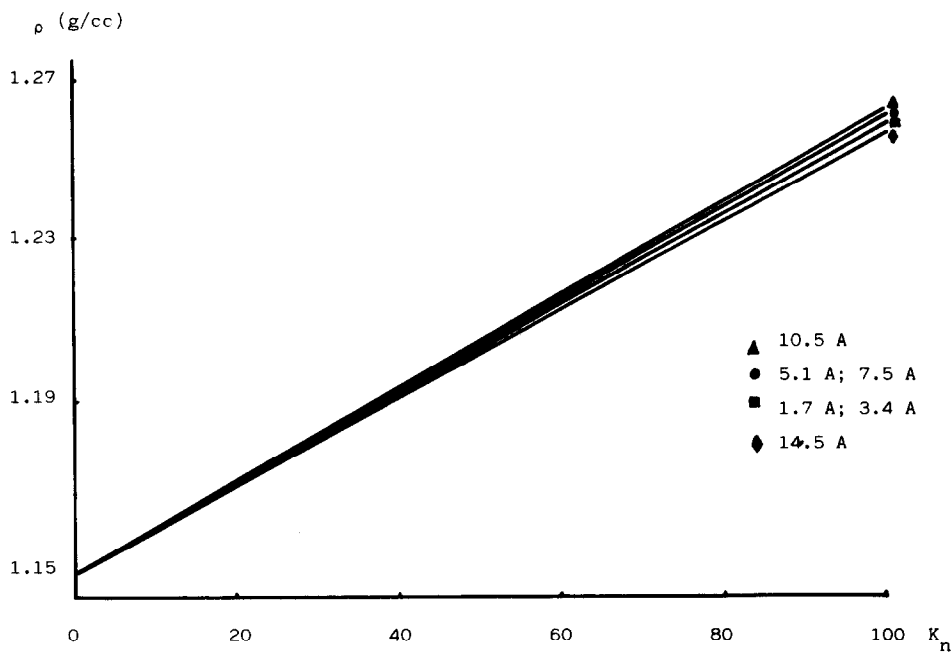

Fig. 2. Electrolyte density as a function of the state-of-charge at various charging currents in static lead–acid batteries with electrolyte circulation.

TABLE 1

Discharge process — circulating system

I (A)	2.8	9.5	15	19	27	35
Q (A h)	212.2	209.0	208.5	210.9	135.0	105.0
$\Delta\rho$ (g cm^{-3})	0.103	0.103	0.101	0.103	0.035	0.030
m_a (mg cm^{-3} vs. h)	1.4	5.0	7.9	9.9	10.3	11.3
m_r	1.03	1.03	1.01	1.03	0.35	0.30
m/I (mg cm^{-3} vs. A h)	0.50	0.54	0.53	0.52	0.37	0.32
n ($\times 10^{-3}$)	1.06	1.08	1.10	1.10	1.10	1.09
r	0.999	0.997	0.999	0.999	0.992	0.968

I, discharge current; Q, total charge delivered; $\Delta\rho$, absolute density variation; m_a, absolute slope of the discharge curve; m_r, relative slope of the discharge curve; m/I, speed reaction coefficient; n, state-of-charge coefficient; r, linear regression coefficient.

$$Q = \int_{t_0}^{t_i} I \, dt \tag{4}$$

where $I = V/R$, V being the output voltage and R the outer discharge resistance.

Assuming R to be constant, expression (4) can be transformed as follows:

$$Q = (1/R) \int_{t_0}^{t_i} V \, dt \tag{4'}$$

The results from the experiments are shown in Table 1: from it we can see that the charge from the battery is similar under all conditions other than for very high currents, and does not depend on the discharge current rate — contrasting with unagitated batteries. This is one of the most important consequences of the use of electrolyte circulation in lead–acid batteries.

(c) Coefficient m/I. This new parameter reflects the order of the reaction speed.

It is known that the reaction speed depends on the discharge conditions and increases as the discharge current increases [6, 7]. As a consequence, sulfuric acid depletion occurs and the concentration weakens.

From Table 1 it can be seen that the new coefficient is almost constant for all discharge conditions, independent of the current, except at high values.

The state-of-charge is continuously varying with time according to the discharge rate but the ratio between the state-of-charge and the discharge rate is linear for the duration of the process.

We also observed that if discharge current was varied (and consequently the discharge time) the total energy delivered by the cell remained the same. This is due to the slope of the discharge curve varying with the current.

Despite the good results obtained from experiments, the new parameter is affected by both internal and external agents such as temperature, plate components, additives, battery geometry, plate type, accumulator characteristics, etc. As a consequence the results can only be applied under restricted conditions and it is necessary to check them when conditions are changed. The main restrictions are the electrolyte reserve (usually at the top), whose volume might change significantly, the proportionality constant n, and the type of plates. In our case, tubular and flat plates were used for the positive and negative electrodes, respectively, and the reserve of electrolyte was assumed to be approximately 10% of the cell volume.

The experiments we carried out have provided a good and very useful method to predict the battery behaviour during discharge at high, and low, currents.

(iiB) Charge

(a) Charge curve linearity. Charge and discharge processes are linear in a lead–acid battery with electrolyte circulation (see Figs. 3 and 4).
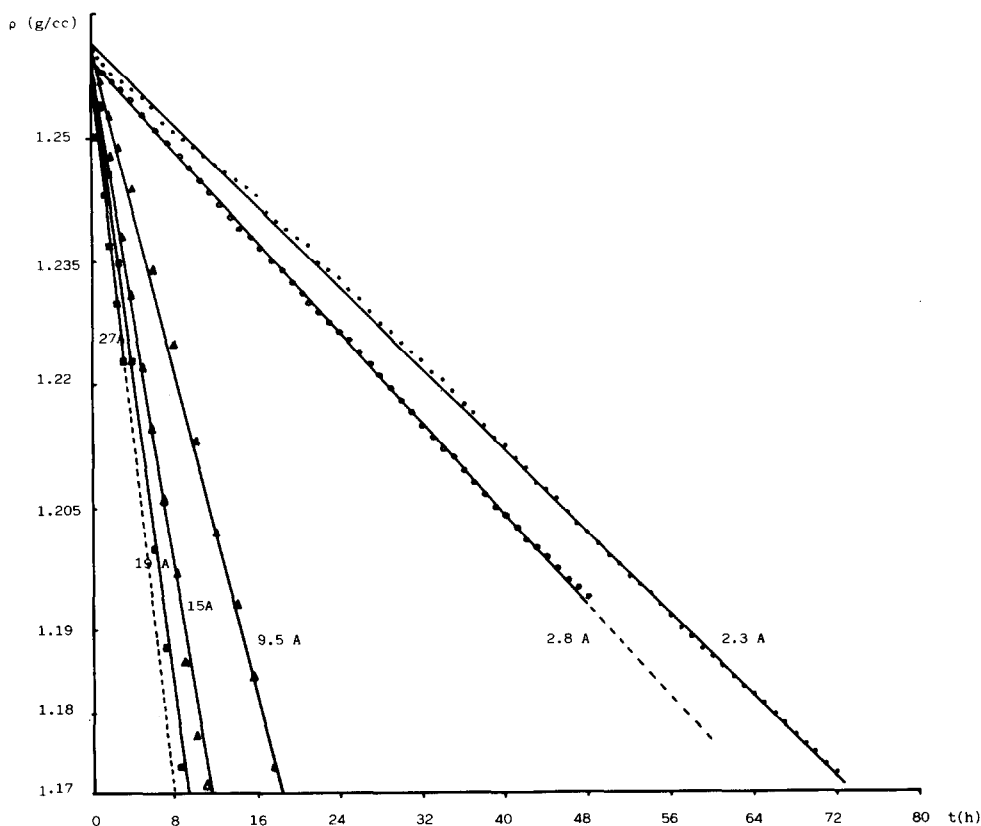

Fig. 3. Electrolyte density as a function of time at various discharge currents in static lead–acid batteries with electrolyte circulation.
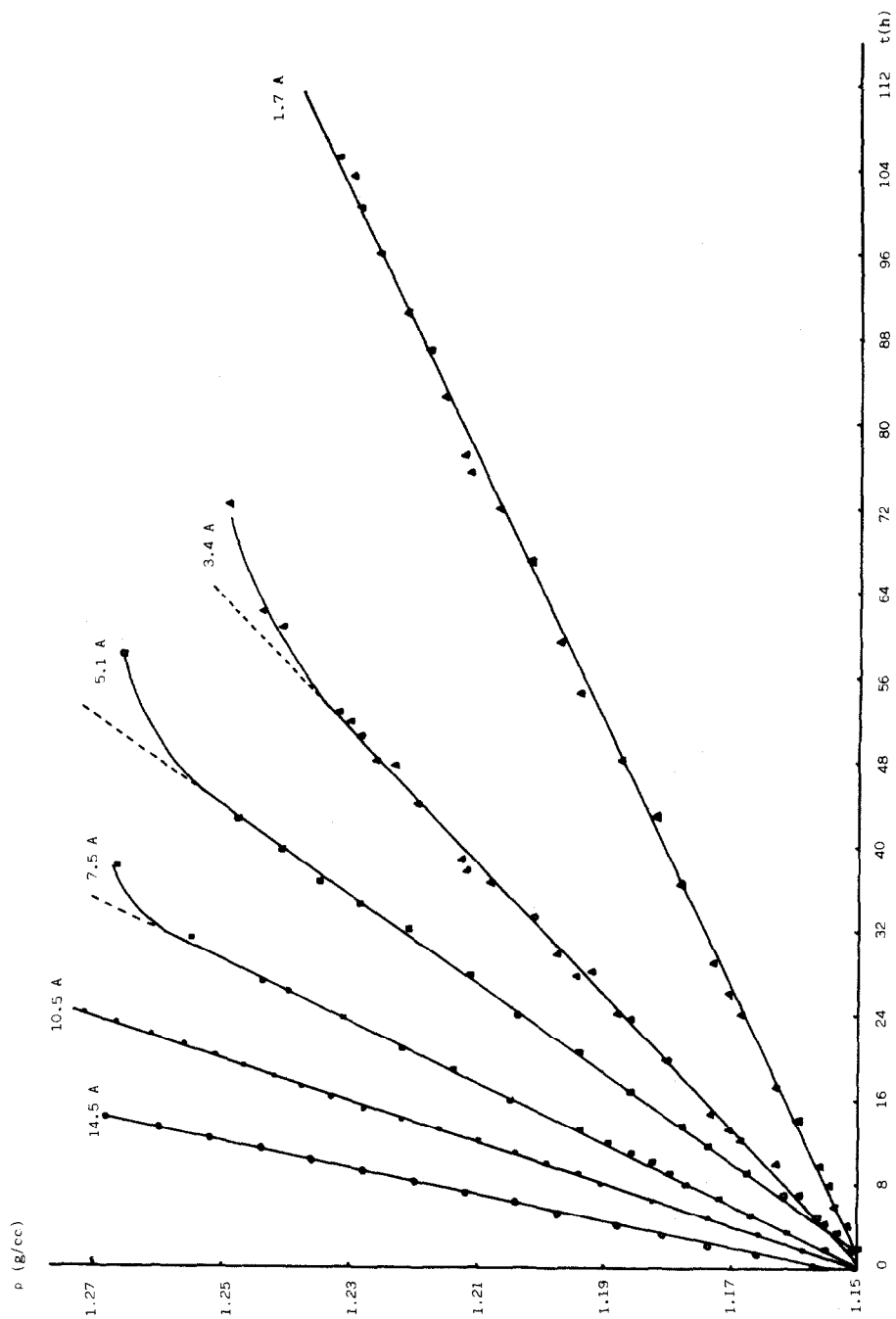
Fig. 4. Electrolyte density as a function of time at various charging currents in static lead–acid batteries with electrolyte circulation.

(b) Charge supplied to the battery from the source. The battery was charged using a constant current source and was considered to be fully charged when the density remained constant for 3 h.

During the charge process it was observed that the energy necessary to achieve full capacity was similar in every case, at all conditions, and independent of the charge rate.

The results from these experiments are presented in Table 2. From them we can see the excellent characteristics shown by this circulating lead–acid cell for all the processes. Also, a high charge–discharge process efficiency is revealed. These results are in good agreement with those obtained in previous experiments [8].

TABLE 2

Charging process — circulating system

I (A)	1.7	3.4	5.1	7.5	10.5	14.5
Q (A h)	234.3	235.8	234.7	232.5	233.1	232.0
$\Delta\rho$ (g cm^{-3})	0.103	0.109	0.104	0.105	0.112	0.108
m_a (mg cm^{-3} vs. h)	0.8	1.58	2.44	3.6	5.11	6.75
m_r	1.03	1.09	1.04	1.05	1.12	1.08
m/I (mg cm^{-3} vs. A h)	0.48	0.47	0.48	0.48	0.49	0.47
n ($\times 10^{-3}$)	1.10	1.10	1.12	1.12	1.13	1.09
r	0.996	1.000	0.999	0.992	0.998	0.999

I, charge current; Q, total charge supplied; $\Delta\rho$, absolute density variation; m_a, absolute slope of the charge curve; m_r, relative slope of the charge curve; m/I, speed reaction coefficient; n, state-of-charge coefficient; r, linear regression coefficient.

(c) Coefficient m/I. The parameter m/I also maintains a high constant value in the charge processes, though it is smaller due to the reduced cycle efficiency [8].

State-of-charge tests

Charge and discharge processes in lead–acid cells with electrolyte circulation are highly reproducible due to the homogenization of the bulk solution which eliminates density and chemical gradients. As a result, density values obtained at any point can be used to determine the state-of-charge and to predict cell behaviour.

(i) Experimental

The density was checked using samples taken either manually or automatically. Values obtained by weighing and by the ultrasonic probe procedure were in good agreement.

(ii) Results

Experiments were undertaken to check the empiric law which permits us to estimate the battery state-of-charge at any time as a function of three parameters: *i.e.*, the density at maximum state-of-charge, a state-of-charge coefficient, n, and the electrolyte density at the test point.

The state-of-charge coefficient, n, was obtained by discharging the battery from an initial maximum state-of-charge to the cut-off point at different discharge currents. It was found to be independent of the current as Table 1 shows.

(iii) Coefficient n

Figure 2 shows the density as a function of K_n for different charge currents. It can be seen that they all fall within a very narrow band with a slope called the state-of-charge coefficient, n.

As stated previously, the cell does not show perfect linear behaviour so n and q are not equal. Very close agreement was achieved by means of a computer numerical analysis when the value of n was found to be: $n = 1.085 \times 10^{-3}$. Replacing this value in eqn. (2) we get:

$$D = 922[\rho(\text{o}) - \rho(\text{i})] \tag{5}$$

(iv) Coefficient n′

Taking into account the same considerations for the charge processes as for the discharge processes we can now write for the charge process:

$$Q = [\rho(\text{i}) - \rho(\text{f})]/n' = 100 - D = 100 - [\rho(\text{o}) - \rho(\text{i})]/n \tag{6}$$

Due to a reduction in the theoretical charge–discharge cycle efficiency, however, $n \neq n'$. We are thus forced either to measure n' by charging the cell at diverse rates or to use the value n from the discharge studies and correct it for the residual error.

In practice we obtained the coefficient n' by charging the cell at different currents, keeping it constant for each test. Greater dispersion between the results was found than during the discharge tests, probably due to small secondary effects of unknown origin.

Combining all the curves and plotting the density as a function of K_n, the coefficient n', the representative slope, was found to be

$$n' = 1.144 \times 10^{-3}$$

The discharge expression will then be:

$$Q = 874[\rho(\text{i}) - \rho(\text{f})] \tag{7}$$

The use of different formulae (one for each process) gives accurate results but, to reduce the amount of calculation, a single expression for both charge and discharge processes has been developed. Combining all the discharge and charge curves into a composite curve we obtained a representative slope: $n = 1.100 \times 10^{-3}$.

Then,

$$D = 100 - Q = (1/n)[\rho(o) - \rho(i)] = 910\Delta\rho \tag{8}$$

$\Delta\rho$ being positive.

The use of a single expression for the whole cycle results in an error (ϵ) which must be estimated. From eqns. (2) and (3), using $n' = n\eta$ and considering $\rho(i) - \rho(o) = \Delta\rho = 100n$,

$$\epsilon = [\rho(f) - \rho(i)]/[\rho(i) - \rho(o)] = |Q(1 - \eta) - 1|/100 \tag{9}$$

Cycle efficiency must be known to estimate the error at any point during charge or discharge. Except for very deep discharges, however, the cycle efficiency is almost constant [9] and the estimated error will never exceed 6.5%, being, in general, the accuracy of the state-of-charge prediction to better than 93.5%.

The maximum value of ϵ is given by the maximum of expression (9), which leads to the value $\epsilon = 0.065 = 6.5\%$.

(v) Discharge process irregularities

Irregularities in the discharge half-cycle at high currents were observed (Table 1).

Relative changes in density were lower than expected. This might be due to an increasing deficiency of sulfuric acid in the pores of the active material, reduced diffusion, and the formation of passivating $PbSO_4$ layers [10]. This led us to reconsider the possibility of modifying the circulating system for high discharge currents.

(vi) Corrections to the proportionality constant n

Recent experiments have shown that when dealing with high capacity accumulators one may observe a slight deviation from the proposed law, especially with deep discharges at very low rates. In such cases the proportionality constant n is affected by the extra energy delivered by the cell, being modified by a factor, f:

f = increased capacity/nominal capacity

This case has no significant effect on the range of application of the law, so that low discharges are only used in photovoltaic arrays and the elements are never totally discharged.

Conclusions

Electrolyte circulation provides an homogeneous bulk solution which is an aid to linear cell behaviour in charge and discharge processes.

We have investigated the possibility of establishing a law to determine accurately the state-of-charge in lead–acid batteries with circulating electrolyte. This law also allows the state-of-charge and disposable energy to be determined using different coefficients for the charge and the discharge

halves of the cycle. The use of a single parameter for charge and discharge processes, however, does not introduce a significant error ($<6.5\%$) and simplifies calculations.

Using this law cell behaviour can be predicted due to the linearity of the charge–discharge cycles and the excellent symmetry between the two processes. A correction factor should be used, however, when dealing with very high capacity accumulators, deeply discharged at very low rates.

One important conclusion from the tests was the need to improve the circulating system in batteries used at high discharge rates.

List of symbols

D	Depth of discharge (%)
I	Current (A)
K_n	Charge delivered by the cell over the total (%)
Q	Charge level (%)
R	Load resistance (Ω)
V	Output voltage (V)
n	State-of-charge coefficient (for discharge and general processes)
n'	State-of-charge coefficient (for charging processes)
q	Discharge curve slope (g cm^{-3} $vs.$ h)
t	Time (h)
ϵ	Estimated error in the state-of-charge (%)
η	Charge–discharge cycle efficiency (%)
$\rho(\text{o})$	Maximum state-of-charge density (g cm^{-3})
$\rho(\text{f})$	Minimum state-of-charge density (g cm^{-3})
$\rho(\text{i})$	Density at time of the test (g cm^{-3})

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