

## DETERMINATION OF THE STATE-OF-CHARGE IN LEAD-ACID BATTERIES BY MEANS OF A REFERENCE CELL

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### Summary

A knowledge of the state-of-charge of any battery is an essential requirement for system energy management and for battery life extension. In photovoltaic power plants and stand-alone photovoltaic installations, a knowledge of the state-of-charge helps one to predict remaining energy, to determine time remaining before battery turndown, and to avoid failures during operation. A reliable method of predicting the state-of-charge will allow reduced installation costs because less reserve capacity is needed to guarantee a reliable energy supply. We propose an on-line method based on simple electrical measurements combined with a new electrolyte agitation technique which avoids systematic control of the battery state-of-charge. The method is very accurate and reduces the standard error in the state-of-charge prediction.

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### Introduction

Lead-acid batteries play a major role in storing electric energy. Since they first appeared in the last century their design and structure has not changed much, but the number of applications is continuously increasing. Today, despite improvements in other types of electrical accumulators such as nickel-cadmium, REDOX, lithium, etc., lead-acid batteries continue to be the most common type in general use, especially in large installations, uninterruptible power supplies, hospitals, submarines, telephone and nuclear control, etc. They are also used in small applications such as in supplying energy to remote areas, marine lamps, and cars (the most important and widespread use of the lead-acid battery). Nevertheless, fears of a potential shortage of natural energy sources (fuel, gas, coal, etc.) has led to serious consideration of alternative energy sources such as the sun, wind, and waves, among others. The output of these sources is irregular and there is a storage requirement. For such large applications the lead-acid battery has no competitors because of the high cost per unit of stored energy of its

rivals. The new uses of the lead-acid battery, however, have brought some problems which must be overcome in order to make them totally reliable and safe.

One well known alternative source of energy is the photovoltaic array. The cost of a photovoltaic system is greatly influenced, in most cases, by the capacity of its battery [1]. Much money can be saved if a smaller battery can be used without degrading the safety factor. This requires an accurate knowledge of the state-of-charge, so that both overcharging, which wastes energy and leads to electrode corrosion, and very deep discharges, which cause unexpected system failures and reduce cell life, can be avoided.

### Previous research

Several methods have been used to determine the state-of-charge of electrical accumulators [2 - 4]. Weiss and Appelbaum [5] improved the existing procedures by avoiding traditional problems and typical errors. This method extends the well known open-circuit-voltage-to-charge relation to a battery on-load-voltage-to-charge relation and combines it with ampere hour accounting for finite periods. It uses electrical measurements with periodic sample tests of both cell voltage and current. The system operates while the battery is in service during both charge and discharge processes, controlling the aforementioned parameters at regular intervals. Based on an electrical model, Weiss and Appelbaum [5] estimated the state-of-charge of a lead-acid cell by successive sample tests giving good accuracy ( $\pm 12\%$ ). This used the combined processes of open-circuit voltage measurement and ampere hour accounting to improve the prediction and reduce the systematic and inherent errors associated with older methods. The method, however, has its limitations. First, the route by which the state-of-charge is determined is complicated by the need to overcome inherent errors associated with open-circuit-voltage measurements and systematic errors in the ampere hour accounting. Second, the time required to determine the state-of-charge is lengthy (one day on average). This time is acceptable for systems which operate over long periods of time such as photovoltaic or stand-alone installations, but it is not suitable for UPS and power supplies which have to deliver the stored energy rapidly.

The method currently proposed is based on density measurements but avoiding the inherent errors of this process. The use of sample electrolyte density tests would, inevitably, result in unavoidable errors in the state-of-charge because of electrolyte stratification during cycling. This problem has been overcome with the new electrolyte circulation technique [6].

The new method appears to be better than any other previously proposed. Its usefulness extends between 15% and 100% discharge compared with the range from 30% to 70% in the case of the method of Weiss and Appelbaum. The current range has also been increased to cover discharge rates between  $C/50$  and  $C/5$ .

The procedure has the advantage therefore of being applicable to systems with both long and short time scales. It can also be applied to both conventional lead-acid batteries\* (lead-antimony) and the low self-discharge elements (lead-calcium).

The effects of temperature on cell performance are well known [7] and can be compensated. On the other hand, the ageing effects are being studied to determine their influence on batteries which are deeply cycled at frequent intervals.

## Experimental

The test system consisted of two batteries, each of six lead-acid cells, one of 625 A h, the other of 150 A h and both rated at a 10 h discharge time.

Each battery was submitted to the same charge-discharge rates to compare the results of different experiments and to check the influence of capacity on the state-of-charge determination.

The cells of the two batteries were divided into three groups of two: the first pair was unmodified, while the new circulating system was attached to the other two pairs of cells, one pair of which incorporated an electrolyte reservoir in a lateral tank to increase the electrolyte-active mass ratio (see Fig. 1). The system was placed in an air-conditioned room maintained to within  $\pm 2$  °C to reduce any influence occasioned by temperature changes.

Internal heating generated at low current rates (usually lower than 50 W for the high capacity cells and less than 6 W for those of low capacity) had a negligible effect on battery performance. In the case of large current rates, with input or output powers up to 30 W in the low capacity cells, the influence of self-heating is partially compensated by the removal of heat by the circulating electrolyte\*\*.

The discharge rates covered a wider range than is normal for lead-acid battery applications: from very low discharge rates ( $C/70$ ) up to accelerated discharges ( $C/5$ ).

The batteries were continuously checked during cycling, the data being stored for later correlation with the discharge values obtained from ampere hour accounting<sup>†</sup> at the end of the test.

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\*Lead-antimony batteries with a 4% monthly mean self-discharge require charge equalization if the system does not operate for long periods. However, the frequent addition of water is not required because of the overcharging control of the system.

\*\*The balance between internal heat production and electrolyte circulation heat removal is being evaluated at the present time.

<sup>†</sup>This method does not introduce significant errors because of the short operation time.

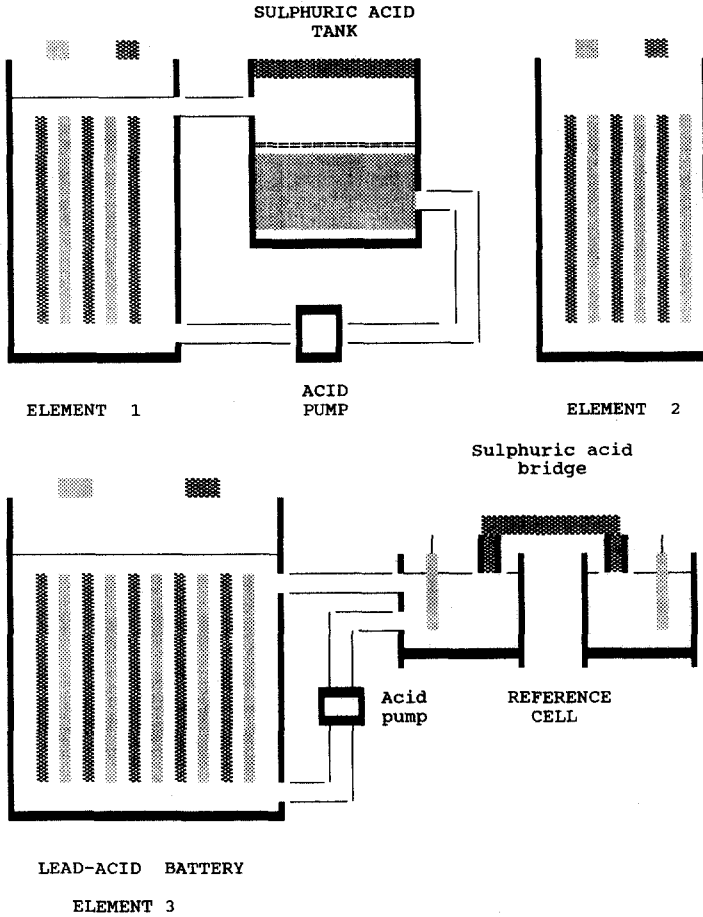


Fig. 1. Experimental device.

### Reference cell engineering design

This cell consists of a small double tank ( $100 \text{ cm}^3$ )\* containing a reference solution of constant density in one tank and the circulating electrolyte from the battery in the other (see Fig. 1). The electrolyte from the battery was constantly circulated between the reference cell and the battery with a peristaltic pump. This system also helps to avoid stratification in the main cell. The double tank was electrolytically linked by a sulphuric acid bridge for ion transport. The electrodes (reference and testing) were made from lead dioxide with a rapid response to acid concentration variations and very low self-discharge, and were connected to a data logger and a digital voltmeter so that the reference voltage could be automatically checked at regular intervals.

\*The sizes of the high and low capacity cells are 20 and 5 l, respectively.

## Reference voltage–density relation

The almost perfect linearity of the density variation throughout the charge–discharge cycles of a lead–acid battery with electrolyte circulation is one of the most significant characteristics of these systems. In previous experiments density variation was found to be linear to better than 99% [8], which led to an equation defining the state-of-charge in lead–acid batteries with electrolyte circulation [9]. The use of a sample density test method, however, needs to be automated to prevent it from being too labour intensive. The additional cost of this automation adds only a small percentage to the total investment in large installations, but it would significantly increase the cost to small applications, and would not be economically viable. Attention was therefore focussed on voltage measurements, which are easy to obtain and less expensive to install. The object was therefore to determine the relation between the reference cell voltage and the battery state-of-charge.

The relation between the open-circuit voltage and the state-of-charge of a lead–acid cell is well known [10]. To measure a cell's steady open-circuit voltage, however, requires that it be disconnected from the operating system, thus interrupting normal operation and interfering with charge–discharge cycling. It would also take hours to make this process effective. The working voltage during normal operation, however, provides useful information from which one can establish the state-of-charge. This is the basis of the method of Weiss and Appelbaum [5]. Unfortunately, it has a serious drawback: inherent errors occurring in the state-of-charge determination by cell voltage measurements due to electrolyte stratification. Stratification modifies the instantaneous reading of the local electrochemical potential, increasing the voltage in zones of high density and reducing its value in diluted zones. The problem can be overcome by electrolyte agitation, and several methods have been proposed [6, 11–14]. Once stratification has been eliminated the working voltage is directly related to the state-of-charge. Unfortunately, direct readings of the battery voltage cannot be used to obtain a reliable value of the state-of-charge because it changes continuously during operation, thus introducing systematic errors. It was to avoid this problem that we introduced the reference cell.

During operation the electrolyte density changes and produces electrochemical potential variations in the reference electrode according to the Butler–Volmer equation [15]. 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 state-of-charge and the reference voltage can be deduced.

As an electric current flows through the external circuit of the reference cell during normal operation, the study must be focussed on the non-equilibrium state. In such conditions the reference potential cell difference is given by  $\Delta\Phi = \Delta\Phi_e + n$  where  $\Delta\Phi$  is the instantaneous voltage,  $\Delta\Phi_e$  the potential difference at equilibrium (given by the Nernst equation) and  $n$  is

the overpotential. The overall overpotential,  $n$ , is the result of smaller contributions  $n_a$  and  $n_c$ , the activation and concentration overpotentials, respectively. Consequently the reference voltage is given by the expression,

$$\Delta\Phi = \Delta\Phi^\circ + (RT/nF) \ln c_r + n_a + n_c \quad (1)$$

where  $\Delta\Phi^\circ$  is the electrode potential and  $c_r$  the concentration ratio.

The overpotential,  $n$ , is caused by charge exchange at the surface of the electrode and lasts as long as the electrolyte concentration difference at the electrode surface exists and electric current is being drawn. To simplify the proposed model we assume that the electrochemical reaction proceeds rapidly, with the overpotential becoming zero in a short time. Then, expression (1) is transformed into

$$\Delta\Phi = \Delta\Phi^\circ + (RT/nF) \ln c_r \quad (2)$$

which is valid since equilibrium is reached, and depends only on the concentration gradient and the temperature. As mentioned above, the system is in an air-conditioned room and temperature effects are eliminated. It follows, therefore, that the reference voltage depends on the concentration gradient alone.

Eliminating the electrode potential with both electrodes of the same material,

$$\Delta\Phi = (RT/nF) \ln c_r \quad (3)$$

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

$$\Delta\Phi = k_1 + kc_r \quad (4)$$

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

### Determination of the state-of-charge

Once a relation between the reference cell voltage and the electrolyte density has been established, the state-of-charge of the battery can be easily determined using the expression proposed earlier [9], which links electrolyte density gradient and state-of-charge through the linear dependence

$$Q = 100 - D = 100 - k_2 \nabla \rho \quad (5)$$

If we now substitute concentration ratio in eqn. (4) by density gradient we obtain:

$$\Delta\Phi = k_1 + k \nabla \rho \quad (6)$$

or

$$\nabla\rho = k' + k_1'\Delta\Phi \quad (7)$$

Combining eqns. (5) and (7),

$$Q = 100 - D = 100 - [k_2(k' + k_1'\Delta\Phi)] = 100 - (K + K'\Delta\Phi) \quad (8)$$

which gives us a linear expression to determine the state-of-charge,  $Q$ , from the reference cell voltage,  $\Delta\Phi$ .

## Experimental development and results

Experiments were run independently in both batteries. Electrolyte density and the reference voltage were recorded at regular intervals during cycling. Battery voltage, current rate, and temperature were also recorded to determine the real discharge and the state-of-charge.

The capacity effects in both batteries at discharge rates other than 10 h were compensated for by means of an empiric law tested in previous experiments. The real state-of-charge at the end of the discharge process was calculated by ampere hour accounting.

Electrolyte homogenization was checked from time to time with test samples removed from the bottom and the top of every battery. These samples were also used to check electrolyte density.

Charge and discharge processes were run at a constant current rate. Charging was considered to be complete when maximum electrolyte density was reached and the voltage remained constant for more than 1 h. Discharge depths ranged from very low (15%) to full discharge (100%) to validate the model for conventional as well as for PV applications.

During experiments the reference electrode response was found to be slower than expected. This was attributed to the thick layer formed during the lead dioxide electrode growth. Sudden changes in electrolyte density delayed the electrode response depending on the concentration change. To determine the average time of the electrode response a closed circuit consisting of a reference cell and a tank containing sulphuric acid was tested. The solution in the tank was renewed at regular intervals. The voltage difference created by the sudden concentration change was recorded every 5 min until a stabilized value was reached. Density changes varied from  $0.080 \text{ g cm}^{-3}$  to  $0.200 \text{ g cm}^{-3}$ , a larger variation than occurred in lead-acid battery operation\*. In Fig. 2 the stabilization time *versus* initial reference cell density variation is shown. From this Figure we can see that the stabilization time over the extended range from 3.4 to 4.7 h is linear in the normal operation range of lead-acid batteries. If we transform stabilization time and density variation into mass production rate detection, it is shown that the working reference electrode can detect a minimum of  $26.5 \text{ mg cm}^{-3} \text{ h}^{-1}$

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\*Maximum density variations for the 5 and 50 h discharge experiments were  $0.160 \text{ g cm}^{-3}$  and  $0.090 \text{ g cm}^{-3}$ , respectively.

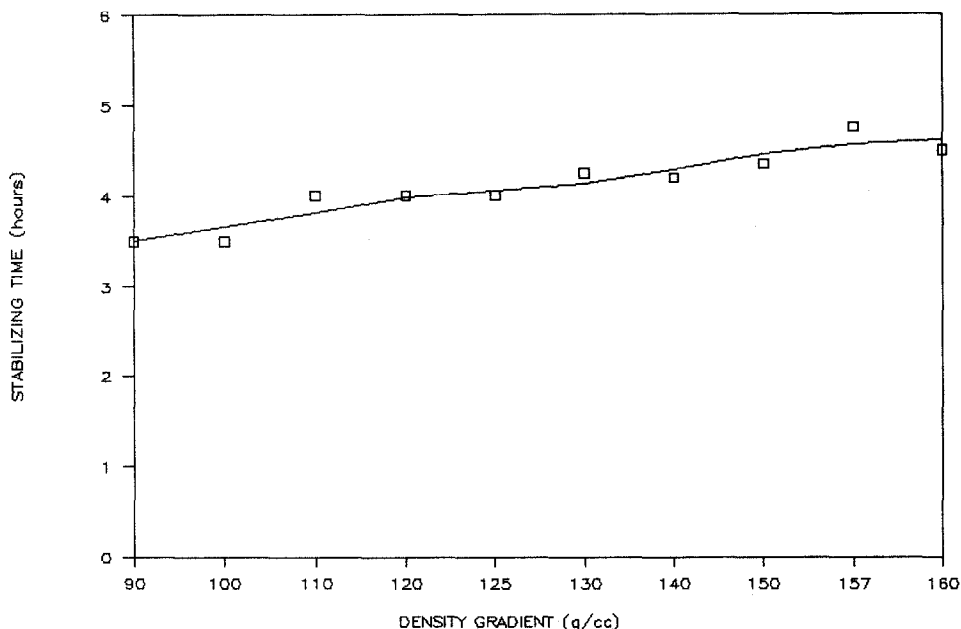


Fig. 2. Reference cell stabilizing time vs. density variation.

TABLE 1

Detection rate of mass production of acid (Reference electrode)

Density variation ( $\text{g cm}^{-3}$ )	90	100	110	120	130	140	150	160
Stabilizing time (h)	3.4	3.6	3.8	3.95	4.15	4.3	4.5	4.7
Rate of detection ( $\text{mg cm}^{-3} \text{h}^{-1}$ )	26.5	27.8	28.9	30.4	31.3	32.6	33.3	34.0

and a maximum of  $34.0 \text{ mg cm}^{-3} \text{ h}^{-1}$  (see Table 1). Comparing these results with sulphuric acid production at high current rates (5 h of discharge) and high capacity elements (625 A h) (which are the most severe lead-acid battery operating conditions) we find that the mass production rate is  $13 \text{ mg cm}^{-3} \text{ h}^{-1}$ \*. This value is considerably lower ( $\approx 50\%$ ) than the minimum detection range of the reference electrode which assures the reliability of the voltage readings, even under battery operation.

From the stabilized voltages of the reference cell the linear regression coefficient of density against voltage was found to be sufficiently high (0.996) to validate the proposed model. The experimental values of the density gradient *versus* the reference voltage are shown in Fig. 3.

Table 2 summarizes the coefficients of eqn. (7), the correlation parameters and the standard deviation.

\*A similar value has been found for the low capacity elements under the same operating conditions.



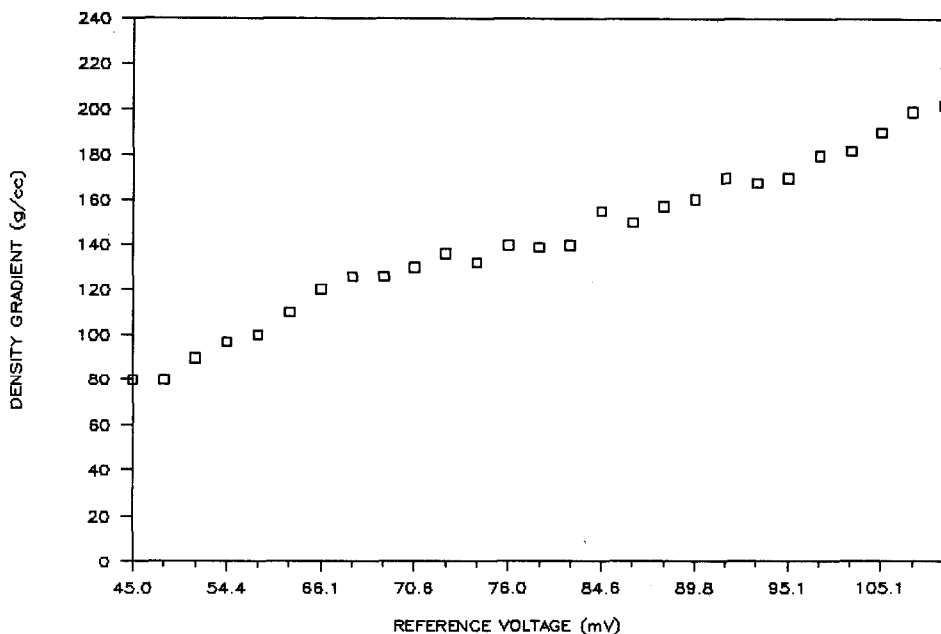


Fig. 3. Correlation of experimental values of density variation vs. reference voltage.

TABLE 2

Correlation parameters

Correlation equation	$k + k'\Delta\phi$	$k = -2.595; k' = 1.834$
Regression coefficient	0.996	
Average error	1.88	
Standard deviation	1.11	
Standard error	0.22	

Once the coefficients of eqn. (7) are known we substitute them in eqn. (8) obtaining the final expression for the state-of-charge. The calculated values can now be correlated with the measured discharge depths, as shown in Fig. 4, where the dotted line is the accepted error (see below).

#### Error determination

As in all monitoring systems, this is subject to random and systematic errors. There are random errors in the voltage measurements from small temperature fluctuations and from computational rounding. The most significant random error usually comes from the battery voltage measurement, since it is not very sensitive to changes in the state-of-charge. This problem has been partially avoided in the present method by the use of the reference cell whose response is much faster, as explained above. Systematic errors can arise from the assumption that the battery behaviour is linear,

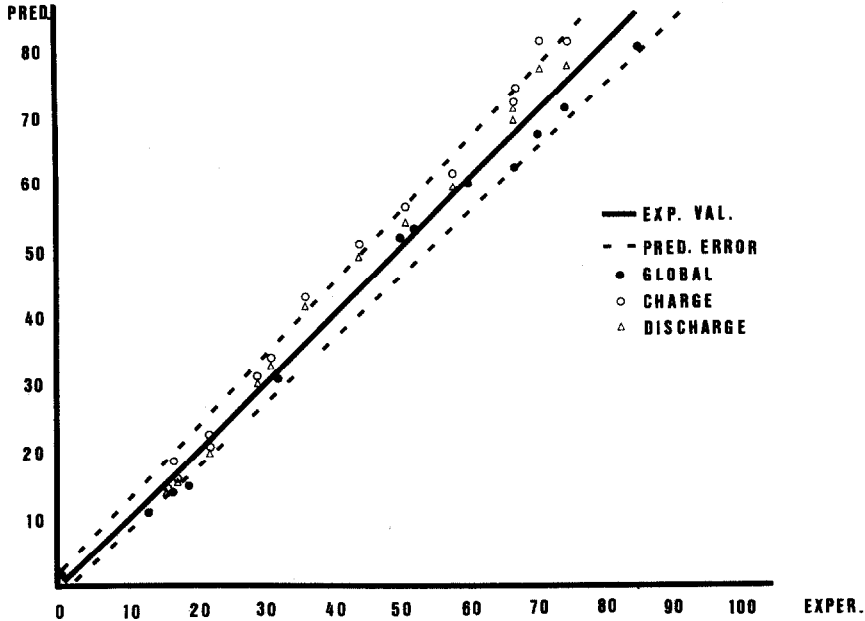


Fig. 4. State-of-charge vs. reference voltage.

errors in computing the battery model parameters, and the estimation of charge, discharge, and global coefficients in eqn. (8)\*.

As we have used a double relation to determine the state-of-charge from the reference voltage, we have to add the inherent errors from each one. Using a probabilistic formula [16] to find the effect of errors on the reference voltage-density gradient relation we have,

$$\epsilon = s_{\delta} / \nabla \rho \quad (9)$$

being

$$s_{\delta} = \sqrt{\{[\Sigma(\nabla \rho_i)^2 - a_0 \Sigma(\nabla \rho_i) - a_1 \Sigma V_i(\nabla \rho_i)] \quad (n - 2)\}} \quad (10)$$

the standard error in density variation estimation,  $\epsilon$  is the error of the reference voltage-density variation relation,  $\nabla \rho$  the density variation,  $a_0$  and  $a_1$  are constants.

From the linear electrolyte density behaviour in a circulating lead-acid cell [9] we get,

$$\rho_i = \rho_0 - n(1 - Q) \quad (11)$$

and

$$\rho_f = \rho_i - n\eta Q \quad (12)$$

where  $\rho_0$  and  $\rho_f$  are the electrolyte densities in the fully charged and fully discharged states, respectively,  $\rho_i$  is the current density at the reference

\*Global term refers to a charge-discharge cycle.

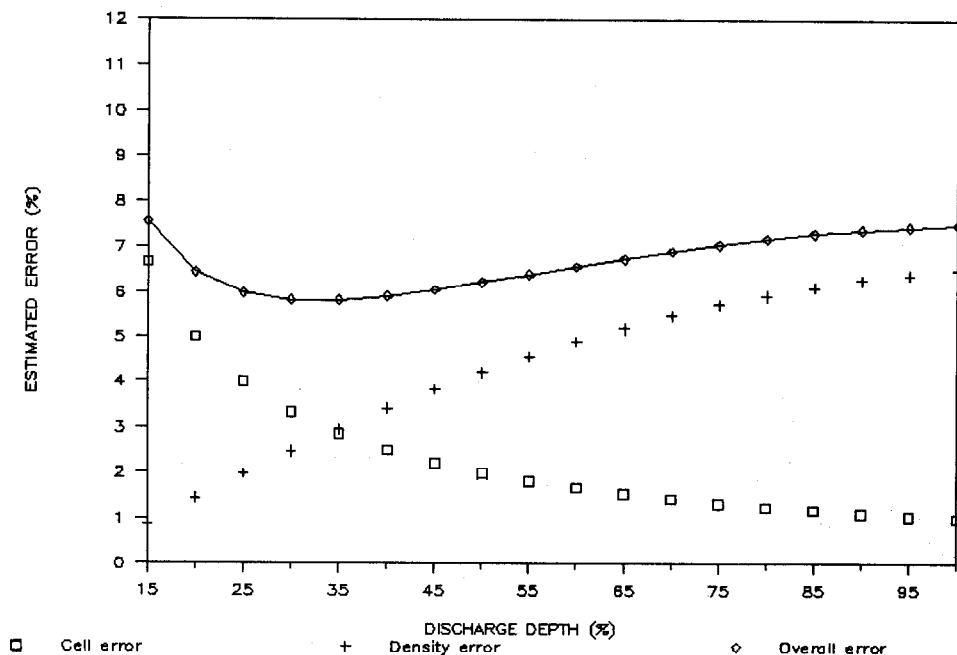


Fig. 5. Estimated error in the state-of-charge determination.

point,  $n$  the cycling coefficient,  $\eta$  the cycling efficiency\*, and  $Q$  the state-of-charge. Using eqns. (11) and (12) we get,

$$\epsilon' = (\rho_t - \rho_0)/(\rho_i - \rho_0) = [Q(1 - \eta) - 1]/100 \quad (13)$$

The overall error is then,

$$\Gamma = \epsilon + \epsilon' = \{(s_b/\nabla\rho) + [(1 - Q)(1 - \eta)] - 1\} \quad (14)$$

Figure 5 shows the estimated error for the overall range.

### Analysis of the results

From Fig. 5 we can see that high discharge depths lead to the highest errors in the state-of-charge determination. Although the estimated theoretical error is almost constant throughout the range (see Fig. 5), in practice, the contribution from errors in the state-of-charge-to-density-variation relation increase the error in the state-of-charge values estimated for deep discharges.

A better determination of the state-of-charge is obtained if the overall coefficient is used in expression (8) [9] instead of discharge or charge co-

\*Values of cycling efficiencies of lead-acid batteries with electrolyte circulation can be found in a previous study made by the author [17].

efficients, but the discharge coefficient provides a sufficiently accurate estimation and can be considered to be reliable.

A tendency to overestimate the discharge depth (or to underestimate the state-of-charge) with the use of the discharge or charge coefficient has been observed. The use of the overall coefficient, however, leads to underestimated values for very deep discharges, but is more accurate over the rest of the range.

## Conclusions

The proposed method allows the user to determine the real state-of-charge of a lead-acid battery, with electrolyte circulation errors less than  $\pm 7\%$  on average.

The use of the overall coefficient to establish the state-of-charge in the state-of-charge-density gradient relation gives very accurate results, but overestimates the state-of-charge at very deep discharges. In such cases the overall coefficient can be substituted by the discharge coefficient which tends to underestimate the state-of-charge.

The method has been validated for a wide range of discharge rates ( $C/5 - C/50$ ), and for all discharge depths between 15% and 100%.

The reference electrode response is fast enough to compensate for concentration changes in battery sulphuric acid.

The durability of the reference electrode has been tested for 6 months and required only minor maintenance.

## Practical consequences

Despite the good time response of the reference electrode, it will need to be reduced for certain applications. Thinner layers of lead dioxide will improve the electrode time response but reduce its durability. The compromise between rapid response and durability is arrived at by providing a very thin reference electrode for those applications requiring a very fast response, and adding a "feeding" thick electrode which will "feed-back" to the working reference electrode through an independent electric circuit when the battery is not operating. This somewhat complex solution reduces the maintenance cost and personal dependence without significantly increasing the initial investment.

## Acknowledgements

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## List of symbols

$c_r$	Concentration ratio
$D$	Discharge depth
$Q$	State-of-charge
$s_\delta$	Standard error
$V$	Reference voltage
$\Gamma$	Estimated error in the state-of-charge determination
$\epsilon$	Estimated error in the voltage-density relation
$\epsilon'$	Estimated error in the density-state-of-charge relation
$\Phi^\circ$	Electrode potential
$\Phi$	Potential difference
$\Phi_e$	Potential difference at equilibrium
$\eta$	Efficiency
$\rho$	Density
$\rho_0$	Fully charged battery density
$\rho_f$	Fully discharged battery density
$\rho_i$	Current density

## References

- 1 G. J. Jones and D. G. Schueler, in *13th IEEE Photovoltaic Specialists Conf.*, 1978.
- 2 S. Sathyanarayana, *J. Appl. Electrochem.*, 9 (1979) 125.
- 3 C. Beder, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 155.
- 4 W. J. Bifano, in *13th IEEE Photovoltaic Specialists Conf.*, 1978, p. 1262.
- 5 R. Weiss and J. Appelbaum, *J. Electrochem. Soc.*, 129 (9) (1982) 1928.
- 6 J. Doria, M. C. de Andrés, C. Armenta, J. Fullea and F. Graña, *J. Power Sources*, 22 (1988) 115.
- 7 H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1975, p. 95.
- 8 J. Doria, M. C. de Andrés, C. Armenta, J. Urrutia, J. Fullea and F. Graña, in J. Doria, M. C. de Andrés and C. Armenta (eds.), *Proc. 3rd Spanish Congr. Solar Energy, Madrid, 1987*, p. 271.
- 9 C. Armenta, J. Doria, M. C. de Andrés, J. Urrutia, J. Fullea and F. Graña, *J. Power Sources*, 27 (1989) 189.
- 10 G. Smith, *Storage Batteries*, Wiley, New York, 1964, p. 42.
- 11 J. Doria, M. C. de Andrés, C. Armenta, J. Urrutia, J. Fullea and F. Graña, in J. Doria, M. C. de Andrés and C. Armenta (eds.), *Proc. 3rd Spanish Congr. Solar Energy, Madrid, 1987*, p. 263.
- 12 K. Tomantschger, *J. Power Sources*, 13 (1984) 137.
- 13 J. Bohman, U. Hullmeine, E. Voss and A. Winsel, *Varta Batterie AG, ILZRO Project LE-277*, Final Report, Int. Lead Zinc Research Organization Inc., New York, 1982, p. 6.
- 14 M. S. Inkmann, *U.S. Pat. No. 4,221,847* (1980).
- 15 J. O' M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Reverté, Barcelona, 1979, p. 927.
- 16 A. Meyer, *Introductory Probability and Statistical Applications*, Addison-Wesley, New York, 1970, p. 270.
- 17 C. Armenta, *Solar Wind Technol.*, accepted for publication.

**Bibliography**

- B. Manivannan and S. Palanichamy, *Bull. Electrochem.*, 3 (2) (1987) 195.  
E. E. Finger and J. M. Wheatcroft, *Technical Rapport*, Curtis Instr. Inc. (1985 - 1986).  
J. E. Cooling, *Surf. Technol.*, 24 (1985) 15.  
M. Tsubota, *New Mater. New Processes*, 3 (1985) 248.  
C. Swoboda, *IEEE Trans. on Sonics and Ultrasonics*, 30 (2) (1983) 69.  
W. Visscher, *14th Int. Power Sources Symp.*, 1984.