Float Behavior of the Lead-Acid Battery System

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We discuss in this article the requirements for satisfactory float operation of lead-acid batteries and analyze behavior during float in terms of the kinetic parameters which characterize the electrochemical processes occurring in the overcharge region. We show how knowledge of these parameters may be used to estimate whether adequate battery maintenance can be expected under specified float conditions. The results emphasize the need for cell uniformity, and the treatment provides a basis for determining what variability is permissible.

I. INTRODUCTION

The design of any battery involves many factors, some to be dealt with empirically and some by analysis in light of more fundamental understanding. These factors combine to determine end behavior and, consequently, utility; detailed considerations of them with regard to the Bell System lead-acid battery appear elsewhere in this series of papers. Here, we consider the more general topic of float operation of lead-acid batteries with as much concern for fundamentals as seems appropriate, using the behavior of typical rectangular lead-calcium grid cells to illustrate the treatment.

Although stationary lead-acid batteries, used for load-averaging and reserve power in the Bell System, are commonly maintained by connection to a constant voltage bus, a procedure known as floating, there is surprisingly little published information about the details of this process and the effects of cell and electrode characteristics on its operation. The standard text on storage batteries[1] makes only brief mention of float operation and, in fact, provides very little information even about the overcharge behavior of cells.

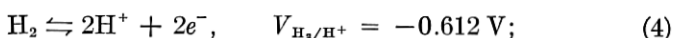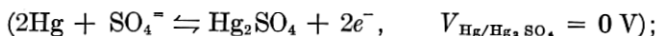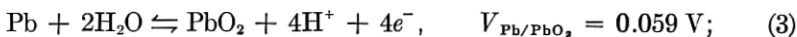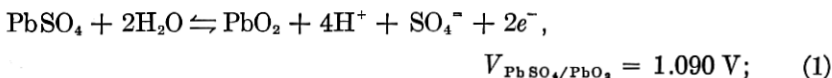The purpose of float is, of course, to maintain a battery in a full state

of charge and to return it to that state after it has undergone discharge. This is accomplished by selecting a bus voltage slightly greater than the open-circuit voltage of the fully-charged battery. To minimize operating voltage variations, it is desirable that the bus voltage be as low as possible. This has the further advantage of avoiding excessive over-charging which increases maintenance and reduces life. On the other hand, if the bus voltage is too low, the rate of recharging may not be adequate, the positive or negative plates may not be kept charged, and the positive grids may start to corrode at a catastrophic rate.

Float operation is, therefore, a matter of a fairly delicate balance as well as a mode of operation dependent on the overall electrical charac-teristics of a battery rather than on some separate indication of its condition. As a result, for satisfactory float operation, the individual cells of a battery must be not only capable of being properly maintained by such a regime but also compatible with one another. The first of these requires a matching or balancing of positive and negative plate behavior in the cells; the second, a matching of cells in the battery. Design, uniformity in manufacture, and conditions of use determine for the most part how well these requirements will be met. Since the basic electrochemical phenomena involved are known (if not completely understood), it is possible to examine in a useful fashion the effects of some of the variables.

The following sections cover, in turn, plate behavior, cell behavior, and battery behavior as they relate to steady-state float operation under conditions relevant to Bell System usage.

II. PLATE BEHAVIOR

The electrochemical reactions of importance in the lead-acid battery are the following, each listed with its calculated, thermodynamically reversible potential in the standard 1.210 sp. gr. H_2SO_4 at 25°C against a mercury/mercurous sulfate reference electrode in the same solution.

$$PbSO_4 + 2H_2O \leftrightharpoons PbO_2 + 4H^+ + SO_4^- + 2e^-,$$

$$V_{PbSO_4/PbO_2} = 1.090 \text{ V}; \quad (1)$$

$$2H_2O \leftrightharpoons O_2 + 4H^+ + 4e^-, \quad V_{H_2O/O_2} = 0.620 \text{ V}; \quad (2)$$

$$Pb + 2H_2O \leftrightharpoons PbO_2 + 4H^+ + 4e^-, \quad V_{Pb/PbO_2} = 0.059 \text{ V}; \quad (3)$$

$$(2Hg + SO_4^- \leftrightharpoons Hg_2SO_4 + 2e^-, \quad V_{Hg/Hg_2SO_4} = 0 \text{ V});$$

$$H_2 \leftrightharpoons 2H^+ + 2e^-, \quad V_{H_2/H^+} = -0.612 \text{ V}; \quad (4)$$

$$Pb + SO_4^- \leftrightharpoons PbSO_4 + 2e^-, \quad V_{Pb/PbSO_4} = -0.971 \text{ V}. \quad (5)$$

The first and last are the charge-discharge reactions of the positive and negative active materials which provide the capacity of the cell and give it a fully-charged open-circuit potential of $1.090 - (-0.971) = 2.061$ V. The temperature coefficient of the open-circuit potential is about 0.25 mV/°C.[1] At the positive plate, oxygen is evolved at a kinetically controlled rate and the lead of the grid material is oxidized. At the negative plate, hydrogen is evolved at a kinetically controlled rate, and, if oxygen is present, it will be reduced at a diffusion-controlled rate. The corresponding oxidation of hydrogen does not, for kinetic reasons, occur at an appreciable rate at the positive. The reactions of other electroactive species, which may be present in practical systems, are not considered here.

Electrochemical processes under kinetic control generally follow a current density-overpotential relation of the form

$$i = i_0[\exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT)], \qquad (6)$$

where i_0, the exchange current density, depends on the concentrations of reacting species and the temperature; α_a and α_c, the anodic and cathodic transfer coefficients, are usually relatively independent of such factors as well as of the potential; and η, the overpotential, represents the departure of the electrode potential from its thermodynamically reversible value, which depends, of course, on concentrations and temperature. F, R, and T are the Faraday, the gas constant and the absolute temperature.

At open circuit and on overcharge in the lead-acid system, the overpotentials for oxygen and hydrogen evolution are large [$\eta_{O_2} \geqq 1.090 - 0.620 = 0.470$ V and $\eta_{H_2} \leqq -0.971 - (-0.612) = -0.359$ V] and only one of the exponential terms is important. This gives rise to Tafel behavior or linear potential-log current relationships for these reactions, and it is convenient for the following discussion to write these in terms of the plate polarizations, that is, the departures of the plate potentials (V_+ and V_-) from those corresponding to the reversible potentials of the charge-discharge reactions, rather than in terms of the overpotentials of the oxygen and hydrogen evolution reactions themselves. Thus, instead of

$$\eta_{O_2} = V_+ - V_{H_2O/O_2} = \frac{RT}{\alpha_{a,O_2}F} \ln \frac{i_{O_2}}{i_{0,O_2}},$$

$$\eta_+ = V_+ - V_{PbSO_4/PbO_2} = \frac{RT}{\alpha_{a,O_2}F} \ln \frac{i_{O_2}}{i_{0+}}, \qquad (7)$$

and instead of

$$\eta_{H_2} = V_- - V_{H_2/H^+} = -\frac{RT}{\alpha_{c,H_2}F} \ln \frac{-i_{H_2}}{i_{0,H_2}},$$

$$\eta_- = V_- - V_{Pb/PbSO_4} = -\frac{RT}{\alpha_{c,H_2}F} \ln \frac{i_{H_2}}{i_{0-}}.$$

(8)

i_{0+} and i_{0-} are thus the extrapolated oxygen and hydrogen evolution current densities at the positive and negative plate open-circuit potentials, and $(RT/\alpha_{a,O_2}F)$ ln (10) and $-(RT/\alpha_{c,H_2}F)$ ln (10) are the corresponding Tafel slopes, b_+ and b_- .

For a given plate design with a particular thickness and method of manufacture, the ratio of effective surface area to ampere-hour capacity at a specified hourly rate is essentially constant, and it is therefore possible, in the Tafel relationships, to use currents per ampere-hour of capacity in place of current densities. Similarly, for a given cell design, the ratio of positive plate ampere-hour capacity to negative plate ampere-hour capacity is essentially constant, and both Tafel relationships can therefore be written, for a given family of cells, in terms of currents per ampere-hour of positive plate capacity, which normally determines cell capacity. Expressed in this fashion, the extrapolated oxygen and hydrogen evolution currents at the positive and negative plate open-circuit potentials at 25°C are, for typical rectangular lead-calcium grid cells, $I_{0+} = 5$–10 $\mu A/Ah$ and $I_{0-} = -(5$–$10)\mu A/Ah$, respectively.[2] The corresponding Tafel slopes at 25°C are $b_+ = 70$ mV/decade and $b_- = -110$ mV/decade[2].

This behavior is reasonably well understood on the negative, for, under slightly different conditions of measurement, a battery electrode of 0.55 cm thickness[3] and a planar lead surface[4] have been found to have essentially the same hydrogen evolution characteristics per true (BET) unit area, with $i_{0-} \cong -10^{-4}\mu A/cm^2$ and $b_- \cong -120$ mV/decade for both. The situation with the positive is more complex because of the existence of two modifications of lead dioxide, α and β, and of an as yet unresolved controversy over whether the characteristics of oxygen evolution on the two are the same.[5,6] According to Giner and others,[6] the two forms differ only because of porosity under the conditions where Rüetschi and his coworkers[5] found Tafel slopes of 60 and 110 mV/decade for the α and β forms, respectively, and nearly the same values of i_{0+} , $\sim 10^{-2}\mu A/cm^2$, for both, the true areas being estimated from capacitance measurements. The original work on capacitance,[3] however, included results which indicate $i_{0+} \cong 5 \times 10^{-4}\mu A/BET cm^2$ for a 0.60 cm

thick positive, suggesting that the total surface area of the porous plate is not used in oxygen evolution.

The temperature coefficients of η_+ and η_- for the previously mentioned typical lead-calcium cells are -2.88 mV/°C and $+2.57_4$ mV/°C, respectively.[2] Taking i_{0+} and i_{0-} (and likewise I_{0+} and I_{0-}) to follow the general relation

$$i_{0\pm} = i_{0\pm}^* \exp\left[-E_\pm/RT\right], \tag{9}$$

equations (7) and (8) give

$$\frac{\partial \eta_\pm}{\partial T} = \frac{\eta_\pm}{T} - b_\pm \frac{E_\pm}{\ln(10)RT^2}. \tag{10}$$

Assuming, as typical values at 25°C, $\eta_+ = 55$ mV with $b_+ = 70$ mV/decade and $\eta_- = -55$ mV with $b_- = -110$ mV/decade, equation (10) gives $E_+ = 17.8$ kcal/mole and $E_- = 10.2$ kcal/mole. (Neglect of the term $\eta_\pm/T$ gives 16.7 kcal/mole and 9.5 kcal/mole.) Although these lie in the normal range of activation energies for kinetically-controlled processes, they should not be considered as such since η_+ and η_- are related to the open-circuit plate potentials corresponding to reactions (1) and (5) and are therefore not true overpotentials.

At the positive plate, in addition to oxygen evolution, grid corrosion, reaction (3), occurs, with the slow oxidation of lead through a passivating film of PbO_2. This is, currently, the process which determines the life of properly designed and manufactured lead-calcium cells. As a result, this process has received a good deal of attention but, unfortunately, not much fundamental understanding. With regard to its effect on float operation and the effect of float conditions on it, the following appears to be a reasonable estimate of the pertinent features.

The rate of grid corrosion is, in the short run, relatively independent of potential.[7] It does, however, increase with temperature and, ultimately, with time in processes associated with the end of cell life. As might be expected, increased temperatures reduce the time to the final, irreversible increase, but, equally important, corrosion studies indicate that extended periods (months to years) of positive plate polarizations which are significantly less than about 25 mV have a similar effect. This, then, is an important factor in float operation, and it is generally considered that adequate maintenance under float conditions requires $\eta_+ > 25$ mV. At 25°C, normal rates of lead-calcium grid corrosion correspond to current densities of the order of $0.2\ \mu A/cm^2$ of grid surface or penetration rates of about 3×10^{-4} cm/yr (1.2×10^{-4} in/yr).[7] Typical rectangular positive plates for stationary batteries have about

20 cm^2 of grid surface per ampere-hour of positive capacity. The contribution of corrosion current to float can therefore be expressed in the same units as I_{0+} and I_{0-}, giving $I_c \cong 4$ $\mu A/Ah$ at 25°C^2. While the potential dependence of I_c can, as a first approximation, be neglected, the temperature dependence is important. Assuming, as for I_{0+} and I_{0-}, that I_c follows a relation of the form

$$I_c = I_c^* \exp [-E_c/RT], \qquad (11)$$

the available data[7] indicate a value for E_c for lead-calcium grids of the order of 10.5 kcal/mole. This is a purely empirical quantity and cannot be given any physically meaningful interpretation.

At the negative plate, in addition to hydrogen evolution, the reduction of any oxygen present in solution takes place at a rate controlled by diffusion and thus independent of potential. In 1.210 sp. gr. H_2SO_4 at 25°C, the solubility of oxygen is about 7×10^{-4} moles/liter,[8] and if its diffusion coefficient is taken to be about 10^{-5} cm^2/sec, the diffusion-limited current due to oxygen reduction from a saturated solution can be calculated from Fick's first law to be about $-3(A/\delta)\mu A/cm$, where A is the effective cross-sectional area through which diffusion to the plate surface can occur and δ is the effective thickness of the diffusion layer. In practice, A may be expected to be largely determined by the area and characteristics (porosity, and so on) of the separator and δ by its thickness, since it is the separator that really defines the paths by which oxygen generated at the positive has access to the negative. For a given cell design (plate thickness), the separator area is proportional to the positive capacity, and thus, like I_{0+}, I_{0-}, and I_c, the oxygen reduction current can be expressed on an ampere-hour basis. For the previously mentioned typical cell at 25°C, this is $I_d = -(20–35) \mu A/Ah$,[2] giving, with the Fick's law estimate, $a/\delta \cong 7–12$ cm/Ah, where a is the effective cross-sectional area per ampere-hour. These same factors control the electrolyte resistance, typically 0.14 ohm Ah.[9] With the electrolyte resistivity equal to about 1.2 ohm-cm, this gives $a/\delta \cong 9$ cm/Ah, in good agreement with the previous estimate. The temperature dependence of I_d is given by the relation

$$I_d = I_d^* \exp [-E_d/RT] \qquad (12)$$

with $E_d = 13.5$ kcal/mole.[2] In cells, as discussed later, there is one further important restriction on the magnitude of $-I_d$: it cannot, in the long run, exceed the oxygen evolution current at the positives.

For a float current $I_f = I_{O_2} + I_c = -I_{H_2} - I_d$, expressed like the others on an ampere-hour basis, the foregoing results can be combined

to give

$$\eta_+ = b_+ \log \frac{I_f - I_e}{I_{0+}} \tag{13}$$

for the positive and

$$\eta_- = b_- \log \frac{I_f + I_d}{-I_{0-}} \tag{14}$$

for the negative. To include the temperature dependences of the various parameters more explicitly, it is useful to re-write equations (13) and (14) in terms of their values at 25°C, which are here denoted with a superscript zero. Then,

$$\eta_+ = \frac{(T/^\circ K)}{298.15} b_+^0 \left[\log \frac{I_f - r_e I_e^0}{I_{0+}^0} - \log \frac{I_{0+}}{I_{0+}^0} \right] \tag{15}$$

and

$$\eta_- = \frac{(T/^\circ K)}{298.15} b_-^0 \left[\log \frac{I_f + r_d I_d^0}{-I_{0-}^0} - \log \frac{I_{0-}}{I_{0-}^0} \right] \tag{16}$$

where $r_e = I_e/I_e^0$ and $r_d = I_d/I_d^0$. For the typical cell discussed above,

$$b_+^0 = 70 \text{ mV/decade},$$

$$b_-^0 = -110 \text{ mV/decade},$$

$$I_{0+}^0 = 5\text{--}10 \ \mu A/Ah,$$

$$I_{0-}^0 = -(5\text{--}10)\mu A/Ah,$$

$$I_e^0 \cong 4 \ \mu A/Ah,$$

$$I_d^0 = -(20\text{--}35)\mu A/Ah,$$

$$\log \frac{I_{0+}}{I_{0+}^0} = 3.89\left(\frac{10^3}{298.15} - \frac{10^3}{(T/^\circ K)}\right), \quad \text{(for } E_+ = 17.8 \text{ kcal/mole)};$$

$$\log \frac{I_{0-}}{I_{0-}^0} = 2.23\left(\frac{10^3}{298.15} - \frac{10^3}{(T/^\circ K)}\right), \quad \text{(for } E_- = 10.2 \text{ kcal/mole)};$$

$$\log r_e = \log \frac{I_e}{I_e^0} \cong 2.29\left(\frac{10^3}{298.15} - \frac{10^3}{(T/^\circ K)}\right), \text{ (for } E_e \cong 10.5 \text{ kcal/mole)};$$

$$\log r_d = \log \frac{I_d}{I_d^0} = 2.94\left(\frac{10^3}{298.15} - \frac{10^3}{(T/^\circ K)}\right), \text{ (for } E_d = 13.5 \text{ kcal/mole)}.$$

These data are used in the following sections as a basis for the con-

sideration of float operation. They refer, of course, only to a "typical" lead-calcium cell design, the characteristics of which are representative of one type of cell suitable for this kind of service.

III. CELL BEHAVIOR, PARAMETERS FOR TYPICAL LEAD-CALCIUM CELLS

When a constant float voltage, V_f, is maintained across a cell, it is the cell polarization which is controlled. This is given by $\eta_{cell} = V_f - V_{cell}^{o.c.} = \eta_+ - \eta_-$ and is related to the float current I_f which flows through both positives and negatives by equations (15) and (16). Thus, specification of V_f and the plate parameters determines the condition of the cell during float operation. While the discussion here deals only with the steady-state, it is clear that a cell inadequately maintained in these circumstances will be no better maintained in actual use. From the previous section, adequate maintenance of positive plates is considered to require $\eta_+ > 25$ mV so that grid corrosion is not accelerated. Adequate maintenance of the negatives requires only that $\eta_- < 0$, but in both cases, some margin is obviously desirable.

The quantities of principal interest, then, are I_f, η_+, and η_-. In the light of the previous discussion, these are taken to be determined by the parameters I_{0+}^0, I_{0-}^0, I_d^0, T, and V_f. In all of the calculations, b_+^0, b_-^0, and I_c are assumed invariant and, together with the temperature dependent factors, are assigned the values given earlier. I_{0+}^0, I_{0-}^0, and I_d^0 depend on design and method of manufacture and can vary considerably. Cells with values lying within the limits given for the "typical" cell of the previous section are described in the following as "normal range" cells. As a point of reference, a cell with mid-range values of these parameters is hereafter described as a "median" cell. Temperature and float voltage depend, of course, on conditions of use and can also vary. Standard conditions, as in the Bell System, are taken here to be 25°C and 2.170 V/cell.

For a given set of parameters, I_f and then η_+ and η_- can be calculated from equations (15) and (16), taking into account two restrictions:

(i) η_+ must be positive or zero and η_- must be negative or zero. Solutions giving negative η_+ or positive η_- are physically inadmissible, for in reality the charge-discharge reactions poise the plate potentials at zero polarization and the plates then discharge. At $\eta_+ = 0$, the net discharge rate of the positive is $I_f - I_{0+} - I_c$; at $\eta_- = 0$, that of the negative is $I_f + I_{0-} + I_d$.

(ii) The rate of oxygen reduction at the negative cannot exceed the rate of oxygen evolution at the positive; that is, $-I_d$ can be no greater

than $I_f - I_e$ or, when $\eta_+ = 0$, I_{0+}. Solutions for which this is not so are also physically inadmissible; instead, I_d can be assumed to become approximately equal to $I_e - I_f$ or I_{0+}. In the case of the former, from equation (14), the negative polarization becomes independent of I_f.

The following results are by no means all-inclusive but indicate, instead, some of the effects to be expected.

3.1 Median Cell, Standard Float Conditions

$I_{0+}^0 = 7.5$ μA/Ah, $I_{0-}^0 = -7.5$ μA/Ah, $I_d^0 = -27.5$ μA/Ah, $V_f = 2.170$ V/cell at 25°C. In this case,

$$\eta_{cell}/mV = 2170 - 2061 = 109,$$
$$= 70 \log \left[(I_f - 4)/7.5\right] + 110 \log \left[(I_f - 27.5)/7.5\right],$$

and $I_f = 50.5$ μA/Ah, $\eta_+ = 55$ mV, $\eta_- = -54$ mV. This represents, more or less, the average behavior of a "typical" or, perhaps more accurately, a desirable cell. Both plate polarizations are good and float operation should be most satisfactory under these conditions.

3.2 Normal Range Cells, Standard Float Conditions

$I_{0+}^0 = 5–10$ μA/Ah, $I_{0-}^0 = -(5–10)\mu$A/Ah, $I_d^0 = -(20–35)\mu$A/Ah, $V_f = 2.170$ V/cell at 25°C. The ranges in the following tables correspond to the range in I_{0+}, 5–10 μA/Ah.

$I_f/(\mu\text{A/Ah})$	$I_d^0 = -20$ μA/Ah	$I_d^0 = -35$ μA/Ah
$I_{0-}^0 = -5$ μA/Ah	35.3–41.2	47.4–52.8
$I_{0-}^0 = -10$ μA/Ah	45.5–54.8	56.8–65.7

η_+/mV	$I_d^0 = -20$ μA/Ah	$I_d^0 = -35$ μA/Ah
$I_{0-}^0 = -5$ μA/Ah	56–40	66–48
$I_{0-}^0 = -10$ μA/Ah	64–49	72–55

η_-/mV	$I_d^0 = -20$ μA/Ah	$I_d^0 = -35$ μA/Ah
$I_{0-}^0 = -5$ μA/Ah	$-(53–69)$	$-(43–61)$
$I_{0-}^0 = -10$ μA/Ah	$-(45–60)$	$-(37–54)$

In all cases the plate polarizations are adequate and float operation should be satisfactory under the standard conditions.

3.3 Median Cell, Standard Float Voltage, Varied Temperature

$I_{0+}^0 = 7.5$ μA/Ah, $I_{0-}^0 = -7.5$ μA/Ah, $I_d^0 = -27.5$ μA/Ah, $V_f = 2.170$ V/cell at 5, 15, 25, 35, and 45°C.

	5°C	15°C	25°C	35°C	45°C
$I_f/(\mu A/Ah)$	11.3	24.4	50.5	100.0	190.3
η_+/mV	70	63	55	48	41
η_-/mV	−44	−49	−54	−58	−63

Although there is some reduction in cell polarization with increased temperature because of the rise in the open-circuit cell potential, the median cell still has what would be considered an adequate positive polarization even at the extreme of 45°C (113°F) and should be capable of float at this temperature. However, this would hardly be recommended, for the higher temperature would bring about an increase in the positive grid corrosion current and a consequent decrease in life.

3.4 *Median Cell and Cells at Extremes of Normal Range Behavior, Low (2.150 V/cell) Float Voltage at 25°C*

The lowest positive polarization in the normal range cells occurs for $I_{0+}^0 = 10 \mu A/Ah$, $I_{0-}^0 = -5 \mu A/Ah$, $I_d^0 = -20 \mu A/Ah$, while the highest occurs for $I_{0+}^0 = 5 \mu A/Ah$, $I_{0-}^0 = -10 \mu A/Ah$, $I_d^0 = -35 \mu A/Ah$. The median cell has $I_{0+}^0 = 7.5 \mu A/Ah$, $I_{0-}^0 = -7.5 \mu A/Ah$, and $I_d^0 = -27.5 \mu A/Ah$.

	Lowest η_+	Median Cell	Highest η_+
$I_f/(\mu A/Ah)$	35.5	44.1	50.6
η_+/mV	35	51	68
η_-/mV	−54	−38	−21

In each case, the plate polarizations are adequate and float operation at this slightly lowered voltage should be satisfactory.

3.5 *Varied I_{0+}^0 in Otherwise Median Cell, Standard Float Conditions*

With $I_{0-}^0 = -7.5 \mu A/Ah$, $I_d^0 = -27.5 \mu A/Ah$, and $V_f = 2.170 V/cell$ at 25°C, an increase in I_{0+}^0 from 7.5 $\mu A/Ah$ results in a lowering of η_+ and a corresponding increase in the negative polarization. η_+ drops to 25 mV as I_{0+}^0 increases to 29.4 $\mu A/Ah$, and here the float current is 71.0 $\mu A/Ah$ and $\eta_- = -84$ mV. (η_+ goes to zero when $I_{0+}^0 = 96.9$ $\mu A/Ah$, at which point $I_f = 100.9 \mu A/Ah$ and $\eta_- = -109$ mV.) A decrease in I_{0+}^0 increases η_+ and decreases η_-, and η_- goes to zero when I_{0+}^0 reaches 0.859 $\mu A/Ah$. Here $I_f = 35.0 \mu A/Ah$ and $\eta_+ = 109$ mV. In an otherwise median cell, then, the maximum range of I_{0+}^0 for adequate plate polarizations at 2.170 V/cell and 25°C is only 0.859 to 29.4 $\mu A/Ah$, and this could be considerably reduced at lower float voltages and other temperatures.

3.6 *Varied I_{0-}^0 in Otherwise Median Cell, Standard Float Conditions*

With $I_{0+}^0 = 7.5$ μA/Ah, $I_d^0 = -27.5$ μA/Ah, and $V_f = 2.170$ V/cell at 25°C, as I_{0-}^0 becomes more negative than the median -7.5 μA/Ah, η_+ increases and η_- approaches zero, reaching that point at $I_{0-}^0 = -247.0$ μA/Ah, where $I_f = 274.5$ μA/Ah and $\eta_+ = 109$ mV. As I_{0-}^0 becomes less negative, the reverse takes place, but before η_+ reaches 25 mV, $I_f - I_c$ becomes equal to $-I_d$. This takes place at $I_{0-}^0 = -0.934$ μA/Ah, with $I_f = 31.5$ μA/Ah, $\eta_+ = 39$ mV and $\eta_- = -69$ mV. Beyond this point, assuming $I_d = I_c - I_f$ which makes η_- independent of I_f , the positive polarization decreases, reaching 25 mV at $I_{0-}^0 = 0.689$ μA/Ah, with $I_f = 21.1$ μA/Ah and $\eta_- = -84$ mV. (η_+ goes to zero at $I_{0-}^0 = -0.408$ μA/Ah, with $I_f = 11.5$ μA/Ah and $\eta_- = -109$ mV.) In an otherwise median cell, then, the maximum range of I_{0-}^0 for adequate plate polarizations at 2.170 V/cell and 25°C is -0.689 to -247.0 μA/Ah, a range which could be considerably reduced under other float conditions.

IV. BATTERY BEHAVIOR; FLOAT CHARACTERISTICS OF BATTERIES OF TYPICAL LEAD-CALCIUM CELLS

The previous discussion of cells is obviously applicable to batteries provided they consist of identical cells at the same temperature. This is not usually the case because of normal variations in the manufacturing process, as indicated by the range of parameters given for the "typical" cell, and because of non-uniform temperatures under some conditions of use. The requirements for adequate plate maintenance remain the same ($\eta_+ > 25$ mV, $\eta_- < 0$), but the behavior of the cells in the battery during float now depends on the distribution of the battery polarization among the cells as well as on the distribution of the resulting cell polarizations between the plates. For an n cell battery,

$$nV_f - \sum_n V_{cell}^{o.c.} = \sum_n (\eta_+ - \eta_-), \qquad (17)$$

where V_f is the float voltage per cell and η_+ and η_- are given for the different cells by the appropriate versions of equations (15) and (16). The following results illustrate some situations of interest.

4.1 **12** *Cell Battery, Cells from Extremes of Normal Range Behavior, Standard (2.170 V/cell at 25°C) Float Conditions*

The lowest positive polarization in single cell float occurs for $I_{0+}^0 = 10$ μA/Ah, $I_{0-}^0 = -5$ μA/Ah, $I_d^0 = -20$ μA/Ah and the highest for $I_{0+}^0 = 5$ μA/Ah, $I_{0-}^0 = -10$ μA/Ah, $I_d^0 = -35$ μA/Ah.

(i) With 1 cell from the low η_+ group and 11 from the high η_+ group, $I_f = 55.7$ μA/Ah, the low η_+ cell has $\eta_+ = 50$ mV, $\eta_- = -94$ mV and the high η_+ cells have $\eta_+ = 71$ mV, $\eta_- = -35$ mV. All the plate polarizations are adequate and float operation should be satisfactory, with cell voltages of 2.205 V and 2.167 V.

(ii) With 6 cells from each group, $I_f = 49.9$ μA/Ah, the low η_+ cells have $\eta_+ = 46$ mV, $\eta_- = -85$ mV, and the high η_+ cells have $\eta_+ = 67$ mV, $\eta_- = -19$ mV. As before, the polarizations are adequate, with cell voltages of 2.192 V and 2.147 V.

(iii) With 11 cells from the low η_+ group and 1 from the high η_+ group, the standard float conditions do not provide proper maintenance of the negative in the high η_+ cell, and its polarization goes to zero. The float current, I_f, is 42.7 μA/Ah and in the low η_+ cells, $\eta_+ = 41$ mV and $\eta_- = -72$ mV, which are adequate and give cell voltages of 2.174 V. The high η_+ cell has $\eta_+ = 62$ mV and, with $\eta_- = 0$, the net negative discharge rate is $42.7 - 35 - 10 = -2.3$ μA/Ah at a cell voltage of 2.123 V. For satisfactory operation at 25°C, the float voltage must be increased to more than 2.176 V/cell, at which point the float current is 45.0 μA/Ah and the negative in the high η_+ cell is no longer discharging though its polarization is still zero.

4.2 12-Cell Battery, Median Cells, 2.170 V/cell with One Cell Hot

The median cells have $I_{0+}^0 = 7.5$ μA/Ah, $I_{0-}^0 = -7.5$ μA/Ah, and $I_d^0 = 27.5$ μA/Ah.

With 11 cells at 25°C (77°F) and 1 at 35°C (95°F), the polarization on the hot negative goes to zero. I_f is 53.3 μA/Ah and the 25°C cells have $\eta_+ = 57$ mV and $\eta_- = -59$ mV. In the 35°C cell, $\eta_+ = 26$ mV, which is marginal at best, and really neither set of plates is adequately maintained. The net negative discharge rate in the hot cell is -6.0 μA/Ah, here given by $I_e + I_{0-}$ because the rate of oxygen reduction at the negative is limited by the rate of oxygen generation at the positive under these conditions. This is, of course, a somewhat unlikely situation with regard to temperature but is of interest because individual median cells can be floated adequately even at 45°C.

V. DISCUSSION

While a good deal yet remains to be understood about the processes occurring in the lead-acid system, its behavior during overcharge can at least be formally described in terms of a limited number of experi-

mentally accessible parameters, some of which can be varied by design. These parameters determine the float characteristics and whether or not a cell or battery is capable of being satisfactorily maintained by a particular float condition, as has been discussed. It should be emphasized, perhaps, that in the present state of knowledge, these parameters must be determined experimentally in the assembled cell, modification of them by design is still largely an empirical business, and calculations of float capability must ultimately be verified by float tests.

Nevertheless, it is useful to consider the effects of variations in the parameters, for this gives some estimate of the permissible latitude in design, manufacture and use. For both cells and batteries consisting of identical cells maintained under identical conditions, it has been shown in the foregoing that satisfactory float operation can be expected for quite a range of characteristic parameters and float conditions.

On the other hand, for batteries which do not consist of identical cells which are identically maintained, there is far less latitude. Even certain combinations of what have here been termed "normal range" cells cannot be satisfactorily floated under standard conditions. Variations in temperature among otherwise identical cells can also lead to difficulty. While both these problems have long been recognized, it requires a quantitative treatment to specify the variability that can be tolerated. In general, satisfactory float operation is unlikely to be achieved without good uniformity among cells and their operating conditions.

Finally, there are quantities besides η_+ and η_- which may be of interest in characterizing cell conditions during float. One is the amount of float current being passed in excess of that required to keep the net negative discharge current equal to zero. This is given by $I_f + I_d + I_{0-}$. Another is what might be called the effective dc impedance of the negative, $\partial \eta_- / \partial I_f$, which is given by $b_- \log e/(I_f + I_d)$. These and others are easily calculated.

VI. ACKNOWLEDGMENTS

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