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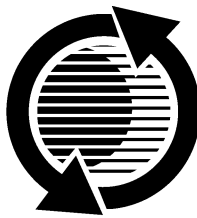
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ABSTRACT

The US Army has recently transitioned to using "maintenance free" batteries in its ground vehicles to increase the over-all vehicle readiness. Using lead-calcium alloy grids in place of the "reduced maintenance" design decreases water loss. This loss of water is known to be a measure of the battery self discharge. In this study, the charging of SLI batteries was examined over a range of operating temperatures as a means for characterizing the self-discharge rate as a function of battery voltage and temperature. The battery response was modeled analytically. Current activities are directed toward achieving a better description of the battery self-discharge over extreme environmental conditions.

INTRODUCTION

The self-discharge of lead-acid starting, lighting and ignition (SLI) batteries is a major factor influencing vehicle readiness. The reason for this is that military vehicles tend to be stored for extended periods of time before being brought back into service. These long periods allow sufficient self-discharge to take place resulting in a high probability that the vehicle will fail to start. Since self-discharge is a naturally occurring phenomena in lead-acid batteries, there exists a need for developing a better understanding of this effect and

for generating some quantitative methods for predicting its consequences [1].

DISCUSSION

Although lead acid battery self-discharge data is available from various battery manufacturers, it tends to be at best a semi-quantitative estimate of the extent of

the process. An exception is the data provided by the Exide Corporation for a Group 34 battery.

Table 1. Data taken from a group 34 battery rated at 625 CCA – 120 min rated capacity (66 amp-hrs at C/20)

Temperature degrees F	Charging Voltage (V)	Ca Alloy ma	1.6% Sb ma	2.6%Sb ma
32	13.8	1	6	10
	14.4	15	24	28
	15.0	19	30	48
	15.6	28	54	96
75	13.8	22	32	48
	14.4	29	62	110
	15.0	51	150	316
	15.6	106	232	480
104	13.2	10	16	23
	13.8	32	76	111
	14.4	80	202	331
	15.0	144	314	628
140	13.2	64	122	180
	13.8	144	300	480
	14.4	270	600	1200
	15.0	434	777	1500

This carefully performed study correlates the measured steady state current as a function of applied battery voltage, temperature and antimony concentration in the positive grids. The negative grids were of a calcium alloy construction.

As a first thought, it appears reasonable to assume that the steady state current under a particular selection of variables should be that current which compensates for the self -discharge of the battery. Other experimental work (not shown here), supports this supposition. This steady state current can be shown to correspond quantitatively to the gas evolution rate taking place at the

electrodes. This was the starting point for pursuing the investigation of the self-discharge of these batteries.

The data shown in Table 1 appears as “messy” data in a statistical sense [2]. Figure 1 shows a plot of a part of the data given in Table 1.

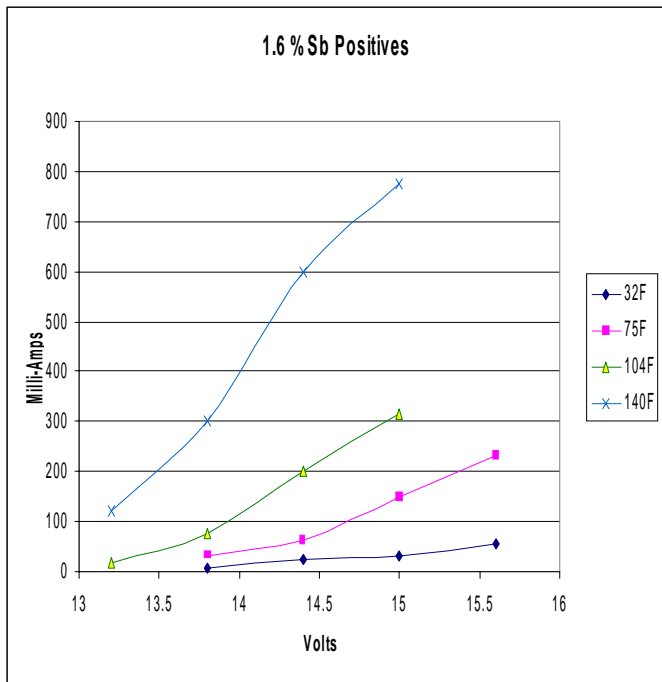


Figure 1. Actual steady state self-discharge currents.

Similar effects are observed after plotting the remaining data in that table. In all, there appears a distinct exponential trend in the data. Using a logarithmic transform, the exponential model was linearized. Using multiple linear regression methods, the entire data set was correlated as:

$$\ln I(ma) = -17.2 + 1.23 \cdot E + 0.035 \cdot T + 0.530 \cdot (\%Sb)$$

The independent variables appearing in the equation as it is written, are the result of the analysis of the data from Table 1 and represents the best fit for that data. Figure 2 shows the “cleaned-up” data for a particular set of parameters. These estimates are based on the trend exhibited by the entire data set.

At this point, one might leap to the conclusion that attributes the messiness of the data to experimental errors in the measurements. This appears not to be the case. In the discussion that follows, the messiness of the data itself is considered the significant aspect.

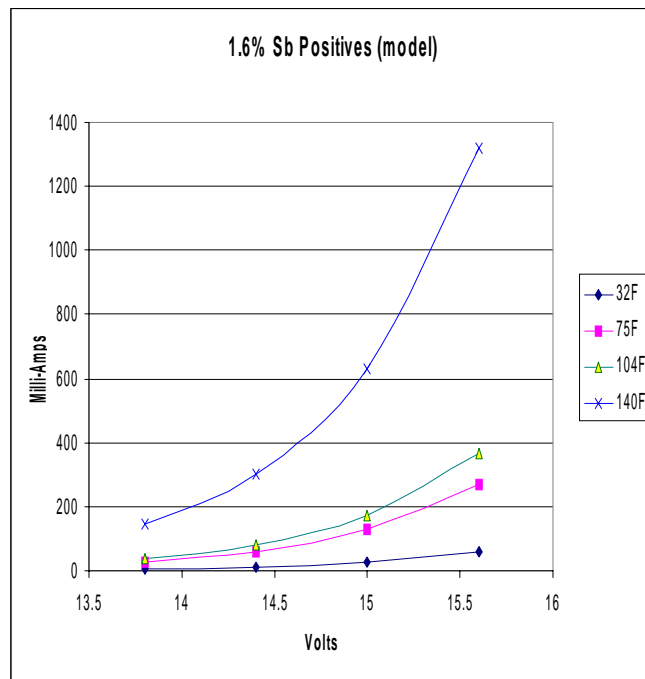


Figure 2. Self-discharge estimates based on an exponential statistical model.

Following this steady state current measurement approach, a set of measurements was made of military grade lead-acid batteries known as the 6T-series. The designations are not the important issue here. The 6TL battery is a reduced maintenance design having calcium alloy negative grids and 2.6 weight-percent antimony alloy positives. The 6TLFP is a transitional “maintenance free” battery and the 6TMF is the final version of that “maintenance free” design. Specifically, the positive grids in those designs are molded from the calcium alloy.

A set of measurements was made on these batteries as follows. A conditioning cycle was performed on each new battery. The batteries were discharged to 12.0 volts. They were then charged beginning at 12.5 volts for 24 hours and the steady state current measured. The charging voltage was then increased by 0.5 volts and the current measured again. This sequence was repeated until the steady state current was measured at 15.5 volts. The test temperature was then incremented by 20 degrees Fahrenheit and the entire sequence repeated. The testing covered the domain of 50 to 150 degrees Fahrenheit inclusively.

The measured data showed the same general exponential trend with deviations that appeared consistently. A typical example is shown in Figure 3.

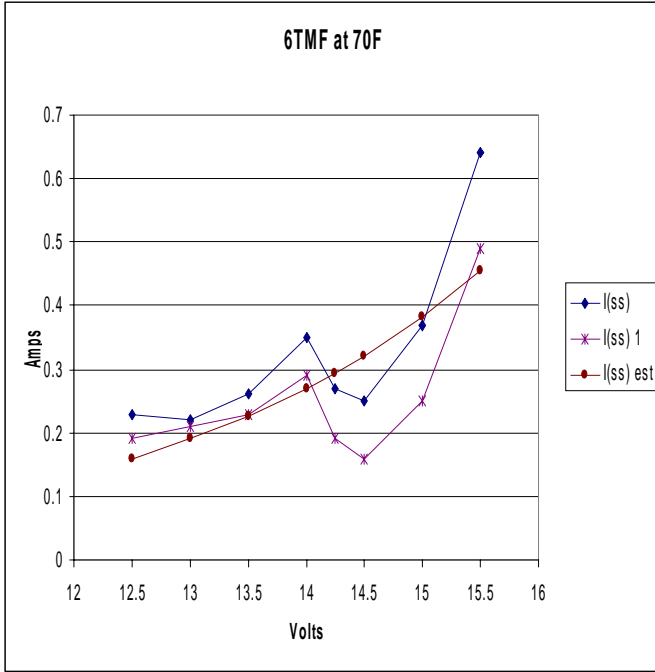


Figure 3. Self-discharge of 6TMF lead-acid battery.

The figure shows a peculiar maximum in the overall trend. The data represents the measurements made on two 6TMF batteries. The estimates are also shown based on the regression model based on the entire data set for this battery type:

$$\ln I(\text{amps}) = -7.15 + 0.349 \cdot E + 0.0136 \cdot T$$

where the voltage data domain is 12.5 to 15.5 volts and temperature domain is given above.

Again, the failure of the data to appear in the anticipated manner became the issue of concern. This led to an attempt at a physical modeling of the constant voltage charging of lead acid batteries.

The charging of a lead acid battery at constant voltage, where the applied voltage is sufficient to drive the overall electrochemical reaction to completion, is very similar to the mass transfer model published by J.J. Lingane [3] for a Constant Potential Electrolysis. The difference is that Lingane's model involves a depletion of the electroactive species at the electrode interface caused by a net ion flux moving toward the working electrode. In the case of the lead acid battery during charging, the net reaction product flux is away from the electrodes. The model for the constant voltage electrolysis occurring in a lead acid battery is slightly more complex. However, the physical picture tends to be instructive.

CV DERIVATION – The time dependent current (i_t) observed during a constant voltage charging is given by Faraday's Law as:

$$i_t = nF \left(\frac{dN}{dt} \right) \quad (1)$$

where n is the number of electron equivalents per mole of the electrode reaction, F is the Faraday and N is the number of moles reacted. The diffusional mass transfer between the electrode surface and the bulk solution can be described by Fick's Second Law of diffusion.

$$\left(\frac{dN}{dt} \right) = DA \left(\frac{dC}{dx} \right) \quad (2)$$

D is the diffusion coefficient, C is the concentration and A is the electrode area. Combining equation (1) and (2) gives:

$$i_t = nFAD \left(\frac{dC}{dx} \right) \quad (3)$$

In the case of convective flow, a boundary layer exists that can be approximated as a Helmholtz boundary layer:

$$\frac{dC}{dx} = \frac{C - C_0}{\delta} \quad (4)$$

where δ is the boundary layer thickness. Combining equation (3) and (4) gives:

$$i_t = nFAD \left(\frac{C - C_0}{\delta} \right) \quad (5)$$

At steady state, the number of moles of electroactive material produced at the surface equals that entering the bulk solution:

$$\left(\frac{dN_{\text{surface}}}{dt} \right) = \left(\frac{dN_{\text{bulk}}}{dt} \right) \quad (6)$$

Since,

$$N = CV$$

Faraday's Law can be written as:

$$i_t = nFV \left(\frac{dC}{dt} \right) \quad (7)$$

when substituted into equation (5):

$$\frac{dC}{dt} = -\frac{DA}{V\delta} (C - C_0) \quad (8)$$

Note that a negative sign has appeared in the equation. This is the consequence of using scalar notation in the derivation. This sign change is necessary because the time derivative of concentration is a negative quantity. Solving this differential equation begins as follows:

$$\int_a^C \frac{dC}{C-C_0} = -\int_{t_1}^t \frac{DA}{V\delta} dt \quad (9)$$

where a is the sulfuric acid concentration in the bulk solution at time t_1 . The initial and boundary conditions require some commentary. C_0 is the concentration at the electrode interface at the applied charging voltage. Under normal charging conditions, the applied voltage is about 14.2 volts and at this polarization, the concentration of sulfuric acid can achieve its maximum value, i.e., that of concentrated sulfuric acid (~18M). C_0 can be taken as being a constant. The value of t_1 corresponds to the time during the constant voltage charging process when mass transfer is diffusion controlled through an established boundary layer. Prior to that time, the sulfuric acid is produced in quantities in excess of that which can be removed by diffusion through a boundary layer. In effect, the sulfuric acid flows downward off the electrode producing it. This flow condition is inconsistent with a stable boundary layer because the sulfuric acid flows outward from the surface and then downward because of its higher density as compared to the bulk electrolyte. The earliest time for the possible creation of a stable diffusive boundary layer is t_1 . It is also to be noted that $a < C_0$.

The solution to equation (9) is:

$$\ln \frac{C-C_0}{a-C_0} = \ln \frac{C_0-C}{C_0-a} = -\frac{DA}{V\delta} (t-t_1) \quad (10)$$

or

$$\ln(C_0-C) = \ln(C_0-a) - \frac{DA}{V\delta} (t-t_1) \quad (11)$$

Since for equation (5),

$$\ln(i_t) = \ln\left(\frac{nFAD}{\delta}\right) + \ln(C_0-C) \quad (12)$$

then

$$\ln(i_t) = \ln\left(\frac{nFAD}{\delta}\right) + \ln(C_0-a) - \frac{DA}{V\delta} (t-t_1) \quad (13)$$

or

$$\ln(i_t) = \ln\left(\frac{nFAD}{\delta}(C_0-a)\right) - \frac{DA}{V\delta} (t-t_1) \quad (14)$$

If the current efficiency is less than 100% and the inefficiency component is known, then:

$$\ln(i_t - I(\text{kinetic})) = \ln\left(\frac{nFAD}{\delta}(C_0-a)\right) - \frac{DA}{V\delta} (t-t_1) \quad (15)$$

This is, $I(\text{kinetic})$ is a function of applied voltage and temperature. It is also a function of the aging of the battery but at any particular time, the conditions of the constant voltage charging $I(\text{kinetic})$ has a constant value.

So, a plot of $\ln(i_t - I(\text{kinetic}))$ vs. t should show a linear segment in the interval $[t_1, t]$ that goes to minus infinity as t increases in magnitude.

Here is a typical measurement based on this analysis.

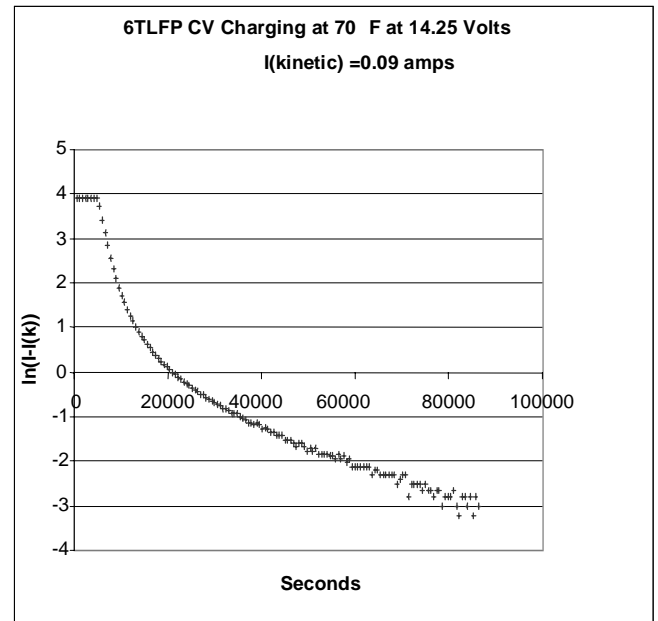


Figure 4. Corrected constant voltage charging curve.

A comment is in order regarding the effect of electric field migration effects that are to be expected under these experimental conditions. It is known that concentration changes are created by the influence of an applied electric field between the electrodes [4]. The present case specifies the concentration gradient between the bulk solution and the electrode surface. The bulk solution concentration is unaffected by the electric field because the ions moving out of any particular volume element in that field are replaced by those entering it. The surface concentrations specified in this model for both electrodes are those of a saturated solution. This establishes that the concentrations have achieved their maximum steady state value and they are unaffected (in terms of the saturation condition) by the existing electric field. The effect of the migration effects would then be expected to be found in the diffusion layer. There the assumed linear concentration gradient would very likely exhibit non-linear deviations. The influence of these deviations should not affect the steady state condition. This was experimentally confirmed. However, it would be expected that an attempt to calculate the specific values of the

parameters composing the coefficients would show deviations from their established values. A way of handling these deviations is to accept the value of the diffusion coefficient as an “effective” quantity.

Using the method established by the derivation presented above, the steady state current at 14.25 volts is compared with that estimated from the constant voltage charging curve. Three determinations for each approach are shown in Figure 5.

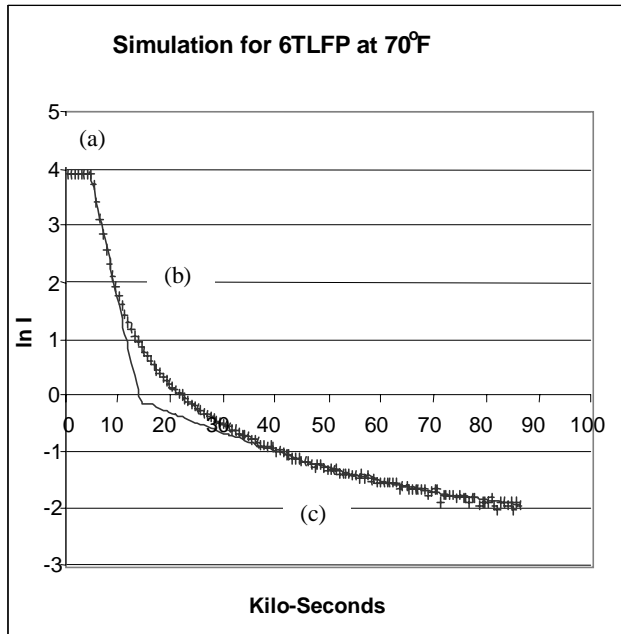


Figure 5. Comparison of measurements from CV model and steady state measurements.

It is to be noted that the CV charge estimation follows the steady state measurement but it is slightly smaller in magnitude. This is attributable to the fact that the steady state current was measured after 24 hours and actually constitutes an estimation of the asymptotic limit as it is being approached. Whereas the estimate made from the CV charge curve is that limit.

Figure 6 shows a simulation of the CV charging of a lead acid battery based on the proposed model and the actual CV curve.

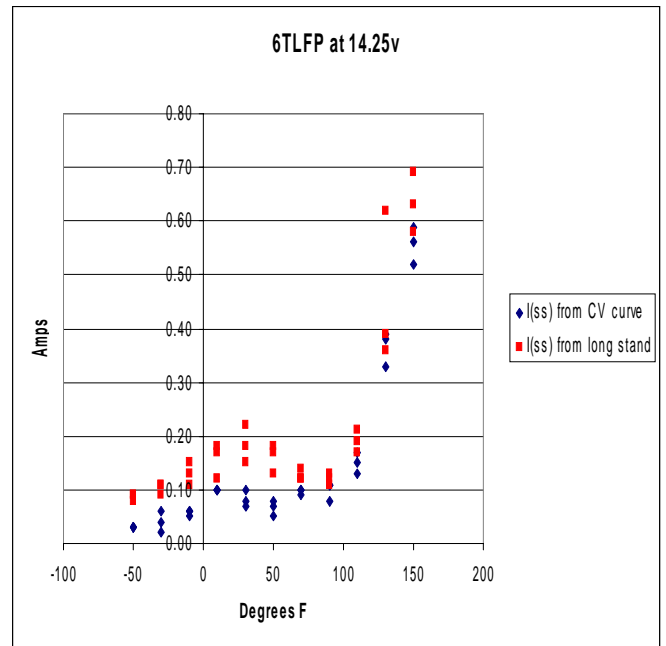


Figure 6. Comparison of actual versus modeled CV charging.

The regions of interest in the simulation (starting at the extreme left) are: (a) the flat constant voltage segment that is the limit caused by the maximum output of the power supply used to make the measurement; (b) that segment where the concentrated sulfuric acid flows out of the pores of the electrode and flows downward along the electrode interface; (c) the third segment represents the region where a diffusional mass transport through a boundary layer is sufficient to provide the mass transfer of the sulfuric acid away from the interface. This latter segment shows a curvature which is caused by the superimposed effect of the steady state self-discharge current. The deviation between the simulation and the actual curve can be rationalized by considering them as changes in the boundary layer thickness in the electrolysis model. The flow of sulfuric acid in the first segment does not permit the boundary layer required in segment (b) to exist. The reason is that the sulfuric acid flow is normal to the surface. The deviation would then be the transition to a stabilized boundary layer required in segment (b). This dynamic stabilization is not considered in the model. The model assumes that the transition is instantaneous. The semi-log plot exaggerates the deviation. Figure 7 shows the more conventional representation of the measurement and simulation.

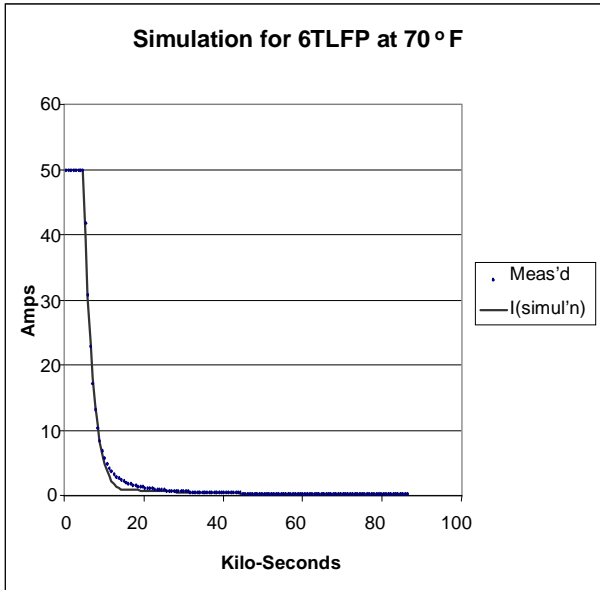


Figure 7. Another comparison of an actual CV charging versus the modeled charging.

Thus far the assumption was made that the steady state current measured as previously discussed represents the self-discharge of the battery. Consequently it was of interest to examine this estimate with the self-discharge of batteries that stand quiescently; i.e., having no exteriorly supplied current. Figure 8 shows the decay of the open circuit voltage of a lead acid battery as a function of time at different temperatures.

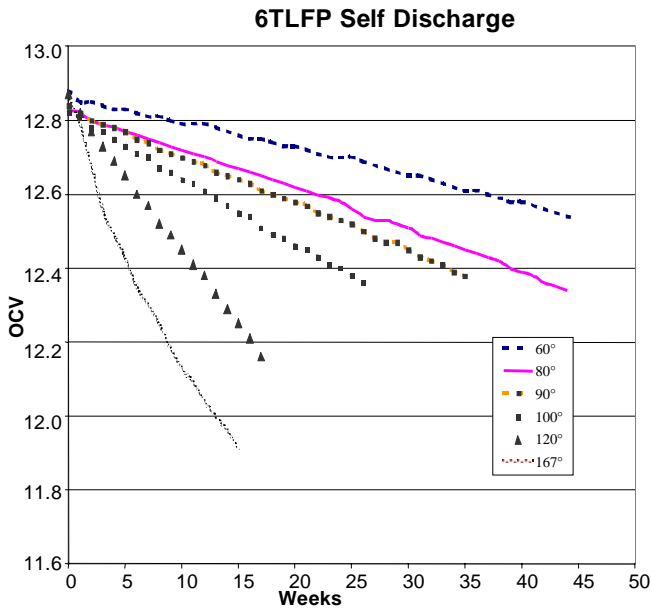


Figure 8. Quiescent self-discharge curves.

A casual inspection of this data indicates that if the self-discharge current estimates made from the steady state current measurements were operating, the open circuit voltages could never be maintained for the periods of time shown in this figure. Consequently, an attempt was

made to estimate the self-discharge currents for the battery whose performance is shown in Figure 8.

The approach to making this estimate uses the observation that the curves are essentially flat. By taking the slope of these lines as being equal to the slope existing at the midpoint of the discharge curve that analysis becomes straightforward.

INFLECTION POINT ANALYSIS – For the model

$$E = a + b \ln \left(\frac{Q - it}{it} \right) \quad (16)$$

Taking the derivative

$$\frac{dE}{dt} = -biQ \left(\frac{1}{(Q - it)it} \right) \quad (17)$$

At the inflection point

$$it = \frac{Q}{2} \quad (18)$$

then:

$$\frac{dE}{dt} = -biQ \left(\frac{1}{\left(Q - \frac{Q}{2} \right) \frac{Q}{2}} \right) \quad (19)$$

so

$$\left(\frac{dE}{dt} \right) = -\frac{4bi}{Q} \quad (20)$$

where i is the average self-discharge current observed at the voltage corresponding to the mid-point of the discharge curve.

The value of the constant, b , is determined by fitting the constant current discharge curve of a battery to the form of equation 16. That is, by plotting the applied voltage vs. $\ln((Q-it)/it)$, the slope is the quantity being sought. Calculating the value of I obtained from the quiescent condition with the steady state current measurements determined at approximately the midpoint voltage of the discharge of this battery, the comparison is shown in Table 2.

Clearly, the self-discharge currents determined by the steady state current measurements are over an order of magnitude larger than those existing in quiescently self-discharging lead-acid batteries.

Table 2. Comparison of the dynamic versus the quiescent estimates of battery self discharge.

Temperature degrees F	Using an Applied 12 v ma	Open Circuit Voltage ma
60	117	4.4
80	153	5.8
90	176	6.3
100	201	8.3
120	264	16.5
167	501	18.7

To attempt a justification for this apparent discrepancy requires that one appeal to the simulation model discussed above. It would appear that a dynamic condition exists during the steady state current measurements. That is, work is being done on the system and a convective mass transfer boundary layer is established and maintained. In the quiescent self-discharging situation, one can speculate that stable linear diffusion condition prevails where the boundary layer is limited by the internal geometry of the battery plates and separator. A linear diffusion process is a much less efficient mass transport mechanism as compared to a stable boundary layer resulting from a convective fluid flow.

Returning to the messiness of the original data, it is understandable that a boundary layer based on fluid flows caused by natural convection is not a way to achieve a well-defined (geometrically stable) boundary layer. The turbulent conditions should be chaotic and, consequently, measurements made under these conditions can be reliable only within the limits of variance of these chaotic conditions.

CONCLUSION

The self-discharge of lead acid batteries was shown to be affected by battery voltage, temperature, antimony alloy concentration and the prevailing mass transfer mode. Another factor that affects the self-discharge rate that was not investigated in this study is battery aging. The aging effect has long been known and is attributed to re-crystallization and the consequent build-up of impurity surface concentrations having a low over-potential for gas evolution. These factors create a complex response characteristic for battery self-discharge. Predictability of self-discharge has to be understood within these constraints in order to make meaningful prediction of state of charge after the passage of time. Estimates of the extent of self-discharge either require a control of the existing conditions or allowance for appropriate uncertainty factors that would be reflected in the error of the estimate.

On the positive side, the lead-acid battery appears capable of changing its mass transfer mode depending on the applied current. This observation suggests that current and voltage pulsing if applied at the proper intensity should induce interfacial stirring. The effect of pulsing at lead acid battery electrodes was documented by Lam [5]. These stirring effects may provide a mechanistic understanding of the reported experimental results.

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