A predictive model of the reliabilities and the distributions of the acid concentrations, open-circuit voltages and capacities of valve-regulated lead/acid batteries during storage

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Abstract

A model is presented which can be used to determine the distribution of voltages, acid concentrations and capacities of stored, valve-regulated (or sealed) lead/acid (VRLA) batteries with absorptive glass mats (AGM). Data taken on the self-discharge of six-cell, flat plate batteries are used to test the model. The actual capacities of cells stored at room temperature for up to two years correlate closely with capacities predicted by the model from measured open-circuit voltages. The model may also be used to predict capacities and voltages of cells stored at any temperature from data taken at only three temperatures.

Keywords: Lead/acid batteries; Capacity; Valve-regulated lead/acid batteries; Open-circuit voltages; Acid concentration

1. Introduction

The storage life of lead/acid batteries is limited by self-discharge processes which reduce the acid concentration and open-circuit voltage (OCV) over time. Since higher ambient temperatures accelerate these processes significantly, storage life is presently limited to a practical maximum of six months. Batteries which are not recharged within this time period are considered out of warranty and must be returned from the field for recycling at considerable expense. Although batteries stored at room temperature may have a storage life of up to one year, they are still out of specification after six months.

A predictive model has been developed which uses OCV rather than storage time to determine battery state-of-charge and rechargeability. The advantage of this approach is that it is independent of the temperature profile during storage and is relatively insensitive to the battery temperature. Voltages can easily be measured in the field with inexpensive equipment. Using the model presented below, acceptable voltage ranges can be determined. For greater accuracy, these can be corrected to account for the measured battery temperature. In addition, the distribution of voltages and acceptable storage time can be predicted for any absorptive glass mat (AGM)

valve-regulated lead/acid battery (VRLA) design from a minimal number of measurements.

Use of this method will prevent return and recycling of usable batteries. Such a tool can be used to better control inventories and to monitor batteries shipped to overseas applications where in-transit storage times are longer.

2. Theory

The relationship between the measured OCV of a lead/acid cell and the acid activity, a_a, is given by the Nernst equation

$$V = V_o + 2.303(RT/F)(\log a_a - \log a_w) \tag{1}$$

for the double sulfate reaction

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \tag{2}$$

Because lead, lead dioxide and lead sulfate are all solids having low solubilities, the activities of these substances are unity. The activity of water, a_w, cannot be assumed to be unity as is often done for dilute solutions, but accurate values have been reported as a function of acid activity and temperature [1]. At 25 °C, the absolute temperature T is 298.15 K. The value of R, the gas constant, is 8.3144 J/(mol K); F, the Faraday constant, is 96 485 C/mol. The standard cell poten-

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tial, V_o, is 2.048 V at 25 °C. Published temperature coefficients allow correction of the OCV from 0 to 60 °C at acid concentrations from 0.1 to 13.877 M [1].

Bullock and McClelland [2] reported that the self-discharge process in cylindrical AGM VRLA cells is pseudo-first-order with respect to the acid concentration. The kinetic equation for a pseudo-first-order reaction may be written as

$$\ln a_a - \ln(a_a)_o = -kt \tag{3}$$

where t is the time, k is the rate constant, a_a is the acid activity at time t and $(a_a)_o$ is the initial acid activity. According to this equation, a plot of $\ln a_a$ versus t should be linear with a slope of $-k$. Activities are used in this calculation instead of concentrations because of the high initial acid concentration (about 40 wt.%) and the wide concentration range covered during the shelf-life of the cell.

Below a $\ln a_a$ of about -3, which corresponds to an OCV of about 2, the plots are linear. The slope remains the same throughout the remaining shelf-life of the cell even though the concentration of the sulfuric acid changes by three orders of magnitude. Bullock and McClelland [2] evaluated the slopes of the lines by the method of least squares and reported

that the correlations were excellent, with beta coefficients varying between 0.996 and 0.999.

The activity and concentration of sulfuric acid are related by the equation

$$a_a = 4\gamma_\pm^3 m^3 \tag{4}$$

where $\gamma_\pm$ is the mean ionic activity coefficient and m is the acid molality.

Data from Ref. [1] at 25 °C were fitted to a third-order polynomial equation to obtain the relationship shown in Fig. 1 between log a_a and the OCV

$$\log a_a = -22.963153 - 5.21367V + 13.711436V^2$$
$$- 2.790766V^3 \tag{5}$$

and the relationship shown in Fig. 2 between the acid molality, m, and the OCV

$$m = 517.8557 - 729.8575V + 331.772V^2$$
$$- 47.832189V^3 \tag{6}$$

Bullock and McClelland [3] used the Nernst Eq. (1) to derive equations for the state-of-charge of the cell

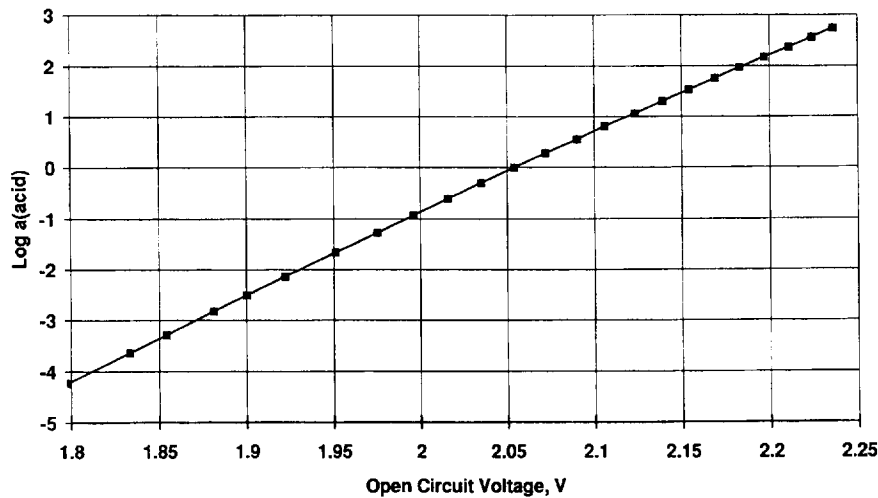$$\% \text{ state-of-charge} = (c_r - c_i)/c_r \times 100 \tag{7}$$
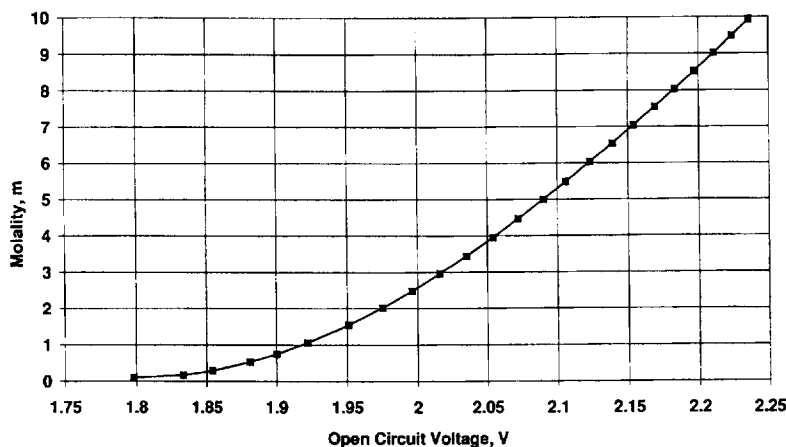

Fig. 1. Log a_a vs. OCV.

Fig. 2. OCV vs. molality.

where c_r is the nominal rated capacity, c_1 is the capacity lost by self-discharge, and

$$c_1 = \frac{v_i\rho_i(98.08P_im_f - 98.08m_f \times 10^2 + P_i \times 10^3)}{98.08 \times 0.6722 \times 10^2 m_f + 3.6594 \times 10^5} \quad (8)$$

where v_i is the initial electrolyte volume in cm^3, ρ_i is the initial density of electrolyte in g/cm^3, P_i is the initial weight (see Eq. (6)).

The OCV of the lead/acid battery decays linearly with time because the relationship between the OCV and log a_a is nearly linear. The calculations can thus be simplified by using the measured OCV directly, rather than calculating from the log a_a, to determine the initial voltage. Thus

$$V(t) = V_i - k't \quad (9)$$

and

$$dV(t)/dt = -k' \quad (10)$$

A linear regression analysis of each curve is used to determine the slope. Extrapolation of these lines back to zero days is used to determine the average initial voltage, V_i. From this voltage, the initial acid molality can be calculated using Eq. (6). The initial wt.% acid P_i and density ρ_i can be determined from this initial molality.

Bro and Levy [4] have published equations for predicting the distributions and reliabilities of the capacities of primary batteries based on the assumption that the capacity decays exponentially with time. In AGM VRLA batteries, since the acid activity decays exponentially with time, a similar approach can be used.

We assume a single-valued, initial acid activity, calculated from V_i (see Eq. (9)) and a normally-distributed rate constant, k (see Eq. (3)) which is independent of the initial acid activity. In other words, the slope of the ln a_a versus t curve is not a function of the initial acid concentration.

The normal distribution of the rate constant is given by the equation

$$f_k(k) = [\sigma_k \sqrt(2\pi)]^{-1}\exp[-(k - \mu_k)^2/(2\sigma_k^2)] \quad (11)$$

where $f_k(k)$ is the probability density function of the rate constant, σ_k is the estimated standard deviation and μ_k is the mean of the rate constant, k. We may then calculate the acid activity from values of k at a given storage time, t, to determine the probability density function of a. As shown above, the OCVs and residual capacities can then be calculated from the acid activities.

Frequently, it is desirable to know how long a set of batteries can be stored before they must be recharged. The model presented above can be used to answer this question. First, however, a criterion for recharge must be established. The reliability of a set of batteries stored for a given time, t, may then be predicted. The reliability, $R(a_s,t)$ is the fraction of the battery population with capacities above the established criterion at any given time, t. $F_a(a_s)$, the probability that the random variable a_a has a value equal to or less than a_s, is called the cumulative distribution function.

The integral of the $f_k(k)$ versus a curve is set equal to unity. The reliability, $R(a_s,t)$ is then the fraction of the population defined by the integral from a_s to a_{max} where a_s is the established failure criterion. A plot of reliability versus time shows the failure rate of the battery population during storage.

As previously shown by McClelland and Bullock [2], the Arrhenius equation may be used to obtain the activation energy of the self-discharge process from slopes of the log activity versus time curves measured at three or more temperatures

$$\ln \mu_k = \ln A - E_a/(RT)$$

where A is the Arrhenius constant, and E_a is the activation energy. Once E_a is determined from a slope of a ln μ_k versus $1/T$ plot by a linear regression analysis, it may then be used to predict the acid concentrations, voltages and capacities of cells stored at other temperatures. Thus, the model given above can be used to predict the performance of cells stored under a variety of conditions from OCVs measured at only three temperatures.

In this paper, we have used the model described above to study the self-discharge process in six-cell VRLA batteries with electrolyte immobilized in AGMs.

3. Experimental

Fig. 3 shows the IR-40 (KS23815) battery used in the study. Eight IR-40 batteries stored on open circuit for 35 days were given an equalizing charge at 14.1 V per battery (2.35 V/cell) for seven days. The batteries were then allowed to
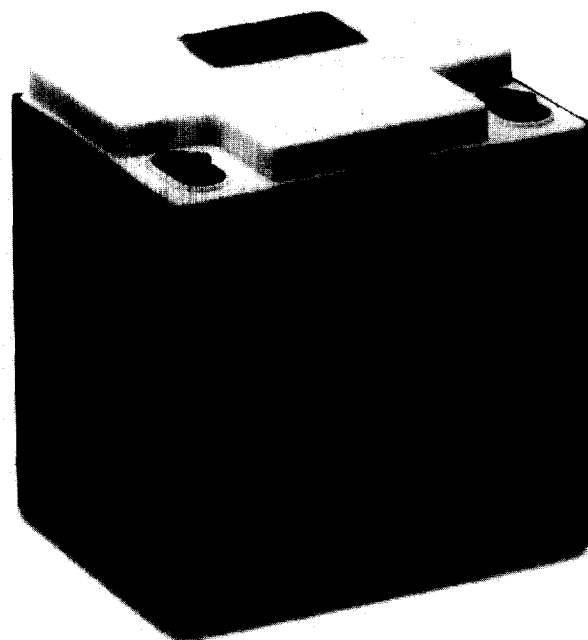

Fig. 3. Sealed rechargeable lead/acid battery. Specifications: model IR-40/40C; nominal voltage 12 V; nominal capacity 36 Ah (10 h rate); depth 5.125 in (13.02 cm); width 8.25 in (20.96 cm); height 7.00 in (17.78 cm); weight 32 lbs (14.40 kg); internal resistance of charged battery 8.0 mΩ.
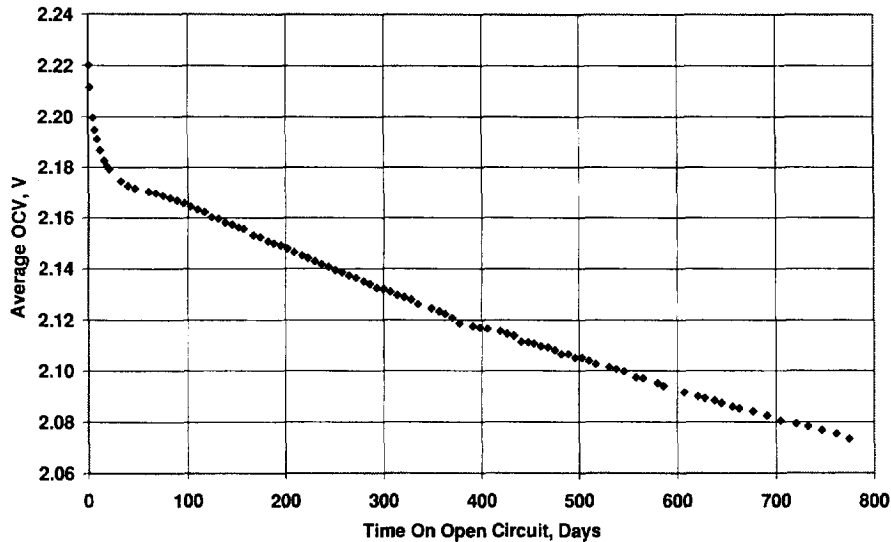
Fig. 4. Average OCV vs. storage time.

self-discharge at room ambient conditions of 22 ± 3 °C. The batteries were not discharged prior to the open-circuit interval and were estimated to be at 95% of rated capacity at time zero. Open-circuit potentials and ambient temperatures were recorded periodically. The range of OCVs was not more than 20 mV at every point in this study. Cell voltages were calculated by dividing the battery OCV by 6.

After 337 days, four of the batteries were individually discharged at the $C/10$ rate (3.6 A), where C is the capacity in Ah, to an end voltage of 10.5 V per battery (1.75 V/cell). Two of the remaining four batteries were similarly discharged after 547 days on open circuit, and the final two batteries were discharged after 775 days on open circuit at 22 ± 3 °C. The capacities were temperature corrected to 25 °C using a 0.63%/°C correction factor.

The first group of four batteries was recharged in parallel at 14.1 V per battery for 19 days and then discharged again at the $C/10$ rate to 10.5 V per battery. The two remaining two-battery groups were discharged three additional times at the $C/10$ rate after being subjected to a variety of recharges as follows:

1. recharge between discharge 1 and 2 = 24 h at 13.8 V (maximum) and 23.6 A (maximum);
2. recharge between discharge 2 and 3 = 168 h at 13.8 V (maximum) and 3.6 A (maximum), and
3. recharge between discharge 3 and 4 = 130% of discharge #3 Ah at 1.8 A plus 24 h at 13.8 V.

4. Results and discussion

Fig. 4 shows the mean of the OCVs versus time at 22 ± 3 °C for each of eight batteries stored up to 337 days, for the four batteries stored from 337 to 547 days, and for the two batteries stored from 548 to 775 days. As expected, the OCV decays linearly with time. A linear regression analysis of each

of the OCV versus time curves for the eight batteries stored up to 337 days was used to determine the mean of the slope, k', and its estimated standard deviation. Extrapolation of these lines back to zero days was used to determine an average initial voltage (see Eq. (9)). The average voltage V_i was 2.181 with an estimated standard deviation of 2.69×10^{-4}. The average slope, k', was 1.643×10^{-4} V/day with estimated standard deviation of 2.54×10^{-6} V/day.

Fig. 5 shows the $\ln a_a$ versus storage time curve for the eight batteries. The slopes of these curves can also be used to extrapolate back to zero time to determine the initial state of the battery. Once $(a_a)_o$ is determined, the initial voltage can be calculated. The slope of each curve is the rate constant of the self-discharge process.

The discharge data given in Table 1 show that after 337 days on open circuit, a four-battery mean of 80.1% of rated capacity was available. The range from low to high was 79.5
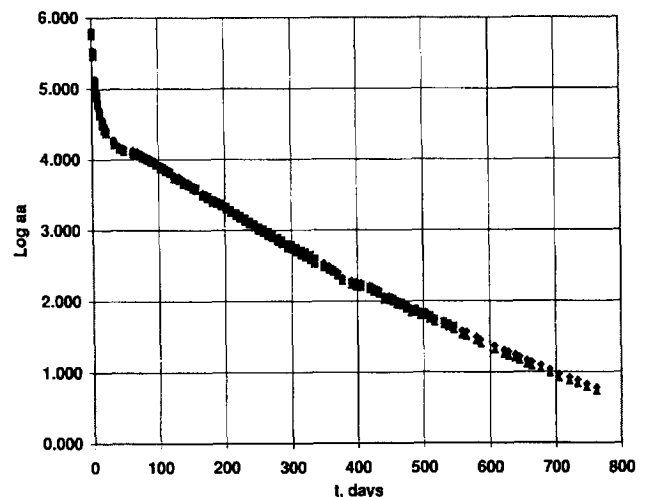

Fig. 5. Log a_a vs. t for IR40 batteries.

Table 1

Comparison of actual and predicted capacities of IR40 battery based on Bullock-McClelland model

Days on open circuit	337	547	775
Average discharge capacity (%)	80.1	67.2	57.0
Capacity from OCV (%)	78.6	66.5	54.7
Capacity predicted from slope of ln a_a vs. t curve (%)		65.1	53.3
Capacity predicted from slope of OCV vs. t curve (%)		62.2	45.8

Table 2

IR40 battery performance after extended open circuit stand % Ah capacity

Days open circuit	337	547	775
Discharge #1 (%)	80.1	67.2	57.0
Discharge #2 (%)	104.5	91.0	86.5
Discharge #3 (%)		97.9	98.8
Discharge #4 (%)		97.5	96.4

to 80.8% with an estimated standard deviation of 0.56. After 547 and 775 days on open circuit, the measured capacities were 67.2% (67.1–67.3%) and 57.0% (56.9–57.1%), respectively.

The % remaining capacities shown in line 3 of Table 1 as a function of time were calculated using Eqs. (7) and (8).

The mean capacities calculated from the OCVs measured just before the first discharge are all slightly lower but are within 2% of the actual measured cell capacities: 78.6% with an estimated standard deviation of 0.44 at 337 days, 66.5% at 547 days and 54.7% at 775 days.

A disadvantage of studying the self-discharge process at room temperature and below is the very long time required to complete the measurements. We therefore looked at the accuracy of predicting capacities at 547 and 775 days using
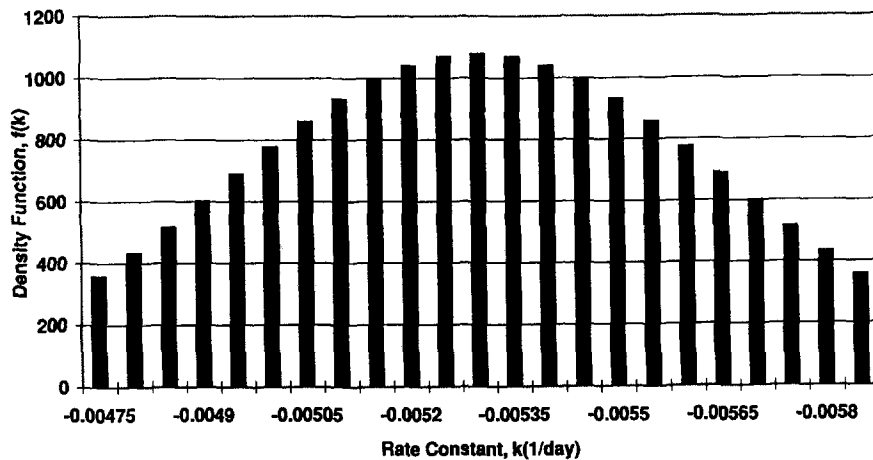

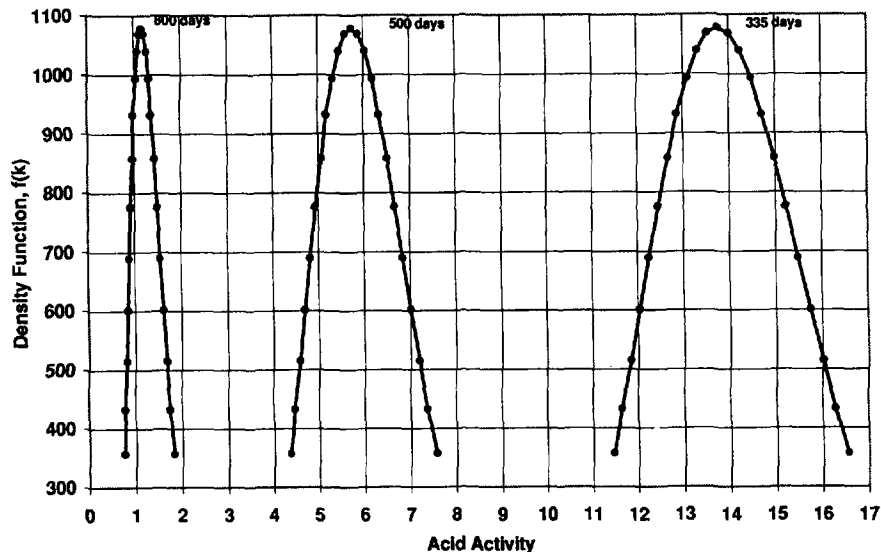Fig. 6. Probability density function of self-discharge rate constant.

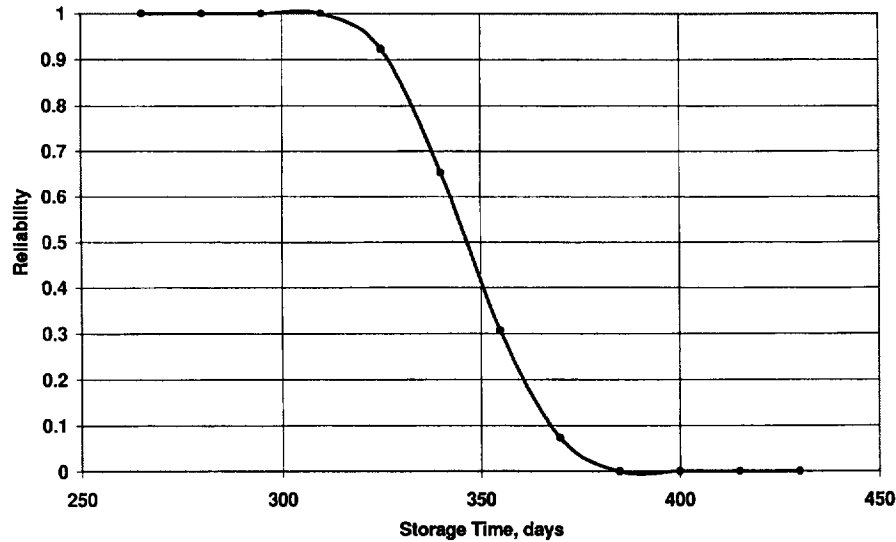Fig. 7. Distribution of acid activity as a function of storage time.

Fig. 8. Predicted failure rate of IR40 battery population.

both initial values and the slopes determined from either the log activity versus time or the OCV versus time curves measured up to 337 days. The linear portion of the curve from which the slope is determined is reached at about 2.17 V after 50–60 days of storage. As shown in Table 1, use of the log activity versus time curves gave the better values: 65.1% at 547 days and 53.3% at 775 days. The OCV versus time curves provide a direct graphical method of predicting the OCV as a function of storage time without doing extensive calculations but with somewhat less accuracy. When the slopes of the OCV versus time curves were used, the predicted mean % remaining capacities were 62.2% at 547 days and 45.8% at 775 days.

The effect of the storage interval on recoverable capacity was also examined. Table 2 summarizes the discharge/recharge activity for the three groups stored for different intervals. The four batteries on open circuit for 337 days were recharged at 14.1 V per battery at room temperature for 19 days and then were discharged again at $C/10$ to 10.5 V/battery. The capacities ranged from 103.6–105.1% of rated capacity, indicating full recovery within 3 weeks at 2.35 V/cell.

The batteries on open circuit for 547 days were recharged at 13.8 V (2.30 V/cell) with a 3.6 A maximum for 24 h and then were discharged again at $C/10$. The batteries delivered an average of 91.0% (90.2–91.7%) of rated capacity. A third discharge was performed after a 168-h, 13.8 V recharge followed by a 24-h, 13.8 V recharge and yielded an average of 97.9% (97.1–98.6%) of rated capacity. A fourth discharge after a 130%, 1.8 A recharge followed by a 24-h, 13.8 V float charge delivered an average of 97.5% (96.6–98.3%) of rated capacity.

The two batteries on open circuit for 775 days were recharged and discharged as described above for the 547-day group. The average capacity was 86.5% (86.2%–86.7%) of rated capacity after the 24-h recharge, 98.8% (98.6–98.9%)

after the 168-h charge, and 96.4% (95.9–96.9%) after the 130% plus 1 day float recharge.

These data show that the self-discharge processes which occur in the VRLA batteries studied here are reversible and cause no permanent loss of the $C/10$ rated capacity for cells stored up to about one year at room temperature. Although some permanent capacity loss may result from open circuit storage longer than one year at 22 ± 3 °C, as indicated by less than 100% of rated capacity after four discharges, the degradation appears to be minimal.

Based on the limited data shown in Table 1, we have established that the IR40 battery may lose a few Ah of capacity permanently if allowed to self-discharge to a 67% state-of-charge. However, at 80% state-of-charge, the capacity lost by self-discharge is fully recovered by recharge. Therefore, a conservative minimum state-of-charge before recharge may be established as 80%. This value corresponds to a minimum acid activity, a_s, of 13.1555. The reliability of the IR40 battery population at any given storage time is determined using this criterion.

Fig. 6 shows the normal distribution for the self-discharge rate constants of the IR40 battery at room temperature. The corresponding distribution of the acid activities is shown in Fig. 7 at three storage times. Because each acid activity corresponds to a single OCV and state-of-charge, the distributions of these values will be the similar to those shown in Fig. 7.

The reliability of the batteries is shown in Fig. 8. The IR40 battery shows a narrow distribution of failures, where failure is defined as 80% state-of-charge. These failures occur close to the 337 day storage time where the first discharge measurement was made. Further evaluation of the failure criteria may establish an even lower acceptable state-of-charge and thus further extend the shelf life. Experiments at higher temperatures can be used to predict shelf life for any storage temperature profile.

References

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