On the End-Point Voltage of the Lead-Acid Storage Cell.

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The terminal voltage of a lead-acid storage cell falls, gradually, in the course of discharge and finally the discharge must be terminated at the proper value of the voltage, which is called the end-point voltage of the cell. Abolition of the end-point voltage is said to result in the formation of crystalline lead sulphate in the active material of the plates, and reduces the capacity and life of the electrodes.

Vinal(1), Lyndon(2), and Nakamura(3) studied the relations between the end-point voltage and the discharge hour rate of the cell. The following experiments have been undertaken on this subject.

Table 1.

t_0-t (min.)	e (volt)	C (%)
$t_0=275$	2.038	100
274	1.960	99.6
273	1.962	99.3
272	1.966	98.8
269	1.968	97.8
264	1.968	96.1
259	1.968	94.2
254	1.970	92.4
249	1.966	90.6
234	1.962	85.2
219	1.960	79.6
199	1.958	72.4
179	1.948	65.2
149	1.940	54.2
119	1.928	43.3
89	1.920	32.2
59	1.900	21.4
29	1.866	10.6
14	1.838	5.1
9	1.816	3.3
4	1.770	1.5
3	1.756	1.1
2	1.722	0.7
1	1.642	0.4
0	1.480	

Experimental. The cells under examination were connected in series and several cycles of charge and discharge were made by the constant currents of 1.5 amp., 2.0 amp., 2.5 amp., and 3.0 amp. The end-point voltage was taken at about 1.3 volts, while that specified by the maker of the cells was 1.8 volts. As such discharge will cause the formation of crystalline lead sulphate in the active material, the cell was charged as soon as possible after the discharge had been terminated.

One example of change of the terminal voltage with time is tabulated in Table 1. In this table t_0 denotes the total time of discharge and t the time at which the terminal voltage is e. The values of C is defined as follow:

$$C=\frac{t_0-t}{t_0}\times 100\,.$$

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(1) Vinal, "Storage batteries," (1924), 177.

(2) Lyndon, "Storage battery engineering," (1911), 91.

(3) Nakamura, *Bull. Dept. Railways, Govt. Japan,* **18** (1930), 1–26.

The values of $t_0 - t$ in the table will be proportional to the remaining capacity of the cell provided the discharge is undertaken at a constant current. Consequently, the value of C indicates the percentage ratio of the remaining capacity to the total capacity of the cell.

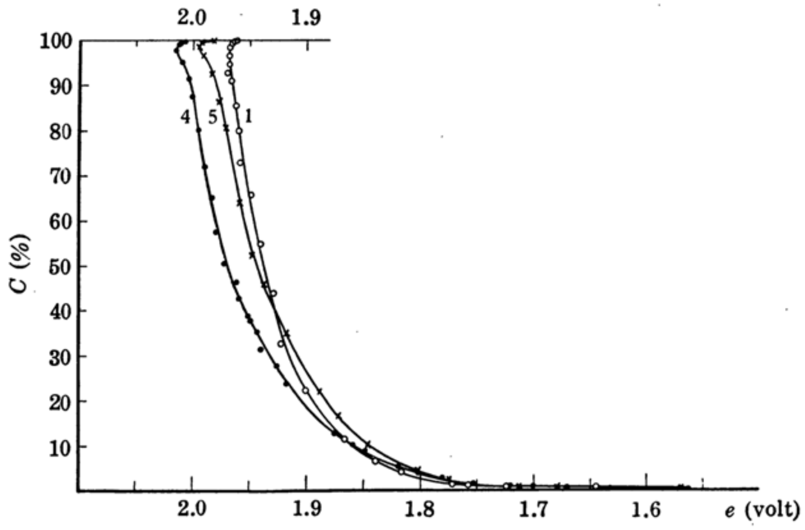

Fig. 1.

The relation between C and e on the three different types of the cells are represented in Fig. 1. As seen from Fig. 1, the terminal voltage of the cell No. 4 is higher than the others in the early stage of the discharge but it falls rather quickly. The terminal voltage of the cell No. 1 is lower at first but it falls slowly and finally takes the highest value among the three, when C falls to about 10. The cell No. 5 shows an intermediate value until C falls to about 40, and becomes the lowest when it falls under 40.

The discharge capacities of these three cells are shown in Table 2.

Table 2. (2.0 amp. discharge)

Cell No.	Discharge hours	Discharge capacity
1	4 h. 36 m.	9.2 a.h.
4	6 41	13.4
5	4 18	8.6

From the above results we see that the terminal voltage e of the cell having the larger capacity is not always higher than that of the cell having the smaller capacity, the value of C being the same. It may be an interesting fact that the C-e curve shows some characteristic nature of the cell.

The C-e curves obtained by different discharge currents on the cells of the same type are shown in Fig. 2. The curves correspond to the discharge current of 1.5 and 3 amp. As is seen from this figure the terminal voltage is higher in the case of a weaker discharge current than the case of stronger

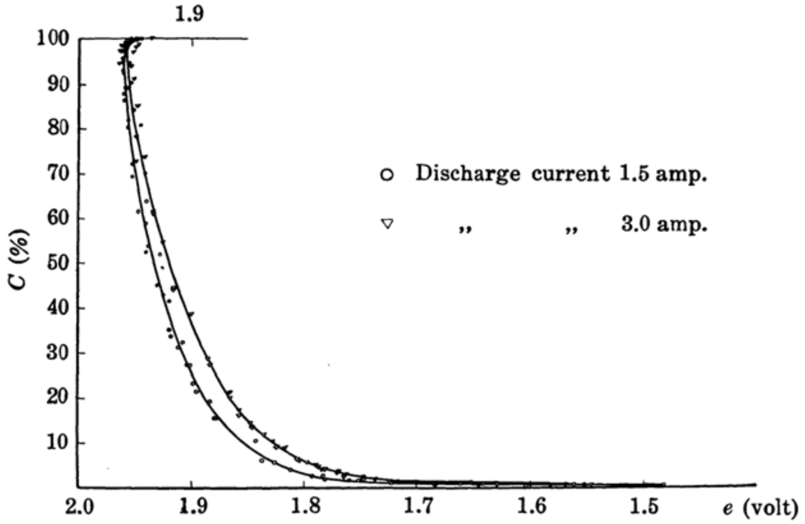

Fig. 2.

discharge current provided the value of C is the same. Consequently, if there be a definite value of C at which the formation of the crystalline lead sulphate occurs, the end-point voltage in the case of a smaller discharge current must be taken higher than in the case of a larger discharge current.

Now the values of $\log C$ and $\log e$ are delineated in Fig. 3, Fig. 4, Fig. 5, and Fig. 6. These figures correspond to the data obtained by the discharge currents of 1.5, 2.0, 2.5, and 3.0 amperes, respectively.

As seen from these figures the relation between $\log C$ and $\log e$ is almost linear in the upper part of the figures, while the curves are concave to the C axis at the lower part. We see, moreover, that the linear part becomes the more predominate in the case of the higher discharge current. The linear part of the curves may be represented by the following formula:

$$\log C = m \log e + \log k \qquad (1),$$

where m and k are the constants. This equation can be transformed into the following forms:

$$C = k\, e^{m} \quad (2) \qquad \text{or} \qquad e = K\, C^{n} \quad (3), \qquad \text{where } n = 1/m.$$

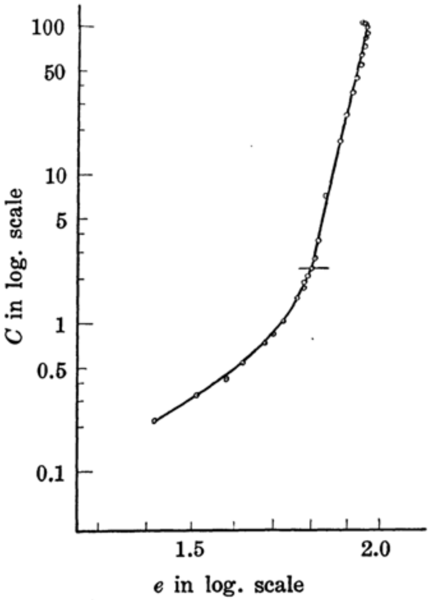

Fig. 3. Discharge current 1.5 amp.

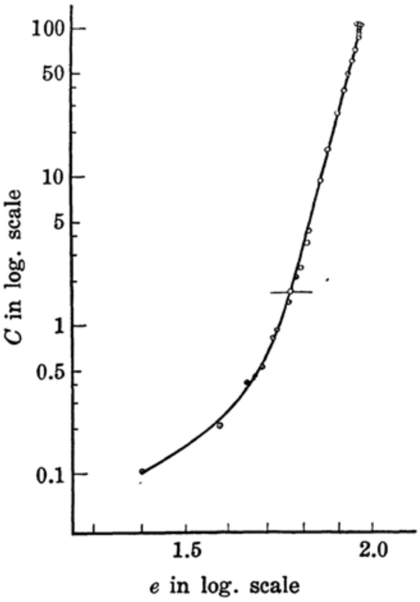

Fig. 4. Discharge current 2.0 amp.

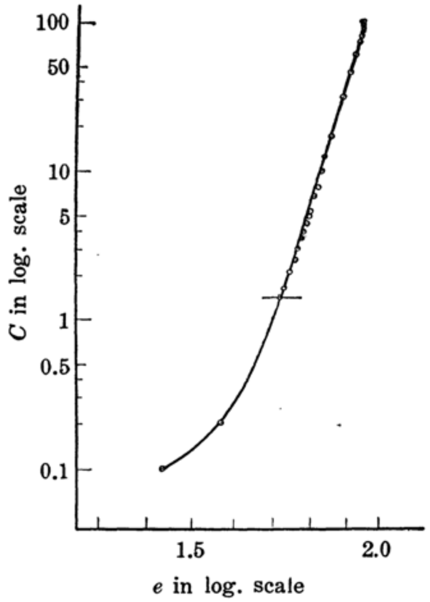

Fig. 5. Discharge current 2.5 amp.

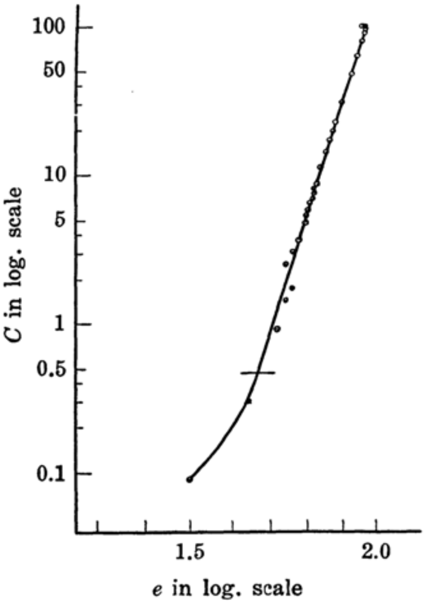

Fig. 6. Discharge current 3.0 amp.

From equation (3) it follows that the terminal voltage e of the cell is proportional to the n-th power of the percentage of the remaining active material out of the total active material, which should be consumed at the end of the discharge. Namely, the terminal voltage of the cell may be said to be proportional to the n-th power of the concentration of remaining active material in the plate.

It was known that the terminal voltage of the cell can be represented by the following equations:

$$e = E + IW \quad \text{in charge;} \qquad \text{and} \qquad e = E - IW \quad \text{in discharge,}$$

where E is the electromotive force of the cell in volts, I the charge and discharge current in amperes, and W the internal resistance in ohms. The internal resistance of the cell is said to be very small except at the end of the discharge. It follows that the variation of the terminal voltage of the cell in the discharging state is mainly due to the variation of E by polarization. The polarization caused by the variation of the concentration of sulphuric acid at the electrode will be the most important factor. But the existence of the relation (3) shows that the variation of the value of C has some relation to the variation of e. The examination of the nature of the cell in the course of discharge may be made from this point of view.

As soon as the discharge is begun, the consumption of sulphuric acid at the electrodes is expected, and there occurs the reduction of the concentration of acid in the pores of the electrodes. The change of concentration of the acid will bring about the fall of terminal voltage by polarization. After a while sulphuric acid will diffuse into the pores from outside the electrodes, until finally the supply and the consumption of the acid become stationary. At this stage the chief cause which effects the fall of terminal voltage may be considered to be the variation of C within the active material of the plates. At the end of the discharge the pores of the plates are clogged by the lead sulphate which has formed during the course of discharge. Consequently, the supply of the acid into the pores may be interrupted and there occurs a sudden fall of the terminal voltage. The linear relation between $\log C$ and $\log e$ can no more be seen in this stage of the discharge. The fact that the curvature of the lower part of the $\log C$-$\log e$ curve becomes more gradual as the discharge current becomes large is the result of the gradual fall of the terminal voltage due to the steep concentration gradient between the electrolytes in and out of the pores produced by the superficial functioning of the plate.

From the above considerations, the ranges where the relation (3) holds between C and e may be the most favourable condition of the plates, for the value of e varies according to the polarization due to the variation of the strength of acid and that of the value of C, these two being in equilibrium.

It follows that the value of e, where the relation (1) does no more hold between C and e may be the most reasonable end-point voltage of the cell.

Table 3.

No. of the cell	Discharge current 1.5 amp.		Discharge current 2.0 amp.		Discharge current 2.5 amp.		Discharge current 3.0 amp.	
	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)
No. 1	1.55	1.785	1.30	1.752	1.00	1.720	1.03	1.708
No. 2	1.91	1.784	1.47	1.757	1.50	1.745	1.20	1.715
No. 3	1.46	1.758	1.45	1.753	1.25	1.734	0.77	1.689
Mean	1.64	1.776	1.41	1.754	1.25	1.733	1.00	1.704

The values of C and e thus obtained by the diagrams, Fig. 3—Fig. 6 as examples, are tabulated in Table 3. The values of C and e tabulatad here are the mean values of nine discharges for one value of discharge current. In Fig. 7 these values of e are plotted against the discharge hour rate of the cell. The reasonable end-point voltage of the cell at 6-hour rate of discharge may be considered to be 1.784 volts.

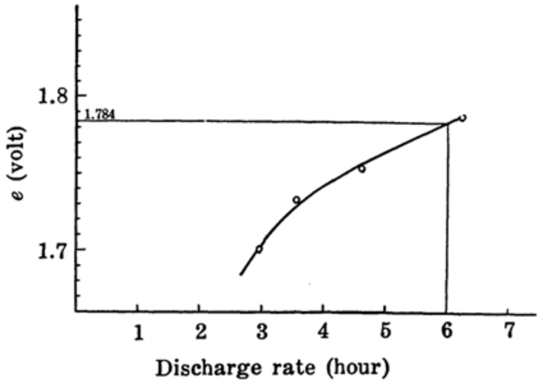

Fig. 7.

The equation (3) is analogous in form to Freundlich's formula for adsorption: $x = \alpha D^{\frac{1}{a}}$, where x denotes the amount of the solute adsorbed by 1 gram of the adsorbent, D the concentration of the solution in equilibrium with the adsorbent, and α and a are constants. If it be an ideal solution this formula coincides with Henry's partition law, and the value a becomes unity. By analogy the value of n in equation (3) may be considered to indicate the state of dispersion of the active material in the plate. If the active material of the plate forms a homogeneous solid solution with $PbSO_4$ the value of n in the equation (3) may become unity. In this case (3) will be transformed into the following form: $e = KC$. Namely, the terminal voltage of the cell is directly proportional to the concentration of the remaining active material in the plate. If the active material of the plate be colloidally dispersed into $PbSO_4$, e will be proportional to the n-th power of C. And if the active material of the plate behaves as a mere mass of PbO_2 or Pb, the value of n in the equation (3) will become naught, and the equation will takes the form: $e = \text{const.}$ In this case the terminal voltage of the cell only depends upon the active material used in the plate and will become quite independent of the concentration of the remaining active material.

As the results of above-mentioned analogy between the equation (3) and Freundlich's formula, the value of n in the equation (3) may be considered to represent the structural features of the plate.

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