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NRL Report 5908

THEORETICAL DESIGN OF PRIMARY AND SECONDARY CELLS

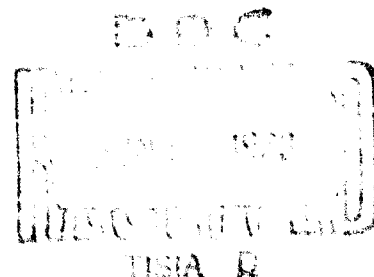
PART III - BATTERY DISCHARGE EQUATION

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PREVIOUS REPORTS IN THIS SERIES

"Part I - Effect of Polarization and Internal Resistance on Current Density Distribution," C. M. Shephard, NRL Report 5211, Dec. 29, 1958

"Part II - Effect of Polarization and Internal Resistance on Cell Characteristics and Cell Design," C. M. Shephard, NRL Report 5212, Dec. 30, 1958

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ABSTRACT

An equation has been derived describing a complete battery discharge for the case when the current density distribution is uniform. The battery potential during discharge is given as a function of time, current density, polarization, internal resistance, and other factors. This equation will be used as a base for deriving the more general case where the current density over the face of the electrodes is uneven. This equation has a number of practical applications. It can be used to describe battery charges and discharges, capacities, power evolution, and predict capacities on the basis of limited data. The equation can be applied to the charging of batteries by changing the signs of some of the terms in the equation.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

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THEORETICAL DESIGN OF PRIMARY AND SECONDARY CELLS

PART III - BATTERY DISCHARGE EQUATION

INTRODUCTION

An ultimate goal in the Laboratories battery program is to determine procedures for designing batteries having optimum properties such as minimum weight or volume. The derivation of a battery discharge equation, which gives the cell potential during discharge as a function of discharge time, current density, and certain other factors, has been included as part of the series of studies to reach this goal. This equation can be used to describe battery charging and discharging, capacities, to predict capacities, and as a basis for deriving the equations that describe the discharge of a battery through constant resistance.

If the potential drop in the grids of a battery during discharge is relatively high compared to the potential drop in the electrolyte, the current density will be unevenly distributed and will be much higher at the top than at the bottom of the electrode. The current density distribution over the face of the electrode as well as other cell characteristics has been determined mathematically for linear, logarithmic, cubic, and other types of polarization.* An example of what can occur has been plotted (Fig. 1) where the ratio of the actual current density to the average current density is shown as a function of the fractional electrode height where 0 represents the bottom of the electrode, 0.5 is the mid-point, and 1.0 is the top of the electrode. The dotted line represents the case where the current density is uniform over the face of the electrode. This ideal condition is approached closely by most batteries. In certain cases an appreciable deviation from this ideal distribution may occur. This condition is most often encountered in tall batteries or in batteries where optimum characteristics are being sought. In the curve in Fig. 1 the current density at the top of the electrode is four times the average current density and at the bottom of the electrode is about 1/7 of the average current density. This condition would hold true only at the beginning of the discharge, whenever we are dealing with porous electrodes, because the high current density at the top of the electrode causes the active material to be used up at a faster rate than average. The uneven distribution of unused active material that results would affect the current density distribution and tend to make it more even. If optimum cell properties are to be obtained, a mathematical analysis is needed of the cell characteristics throughout a complete discharge. One of the bases for such an analysis is given in this report, in which the potential of a battery during discharge is determined for the ideal case where the current density distribution over the face of the electrode is uniform.

MATHEMATICAL ANALYSIS

Basic Assumptions

The mathematical analysis given here is based on the assumption that the following conditions are applicable:

*C. M. Shepherd, "Theoretical Design of Primary and Secondary Cells. Part I - Effect of Polarization and Internal Resistance on Current Density Distribution," NRL Report 5211, December 29, 1958.

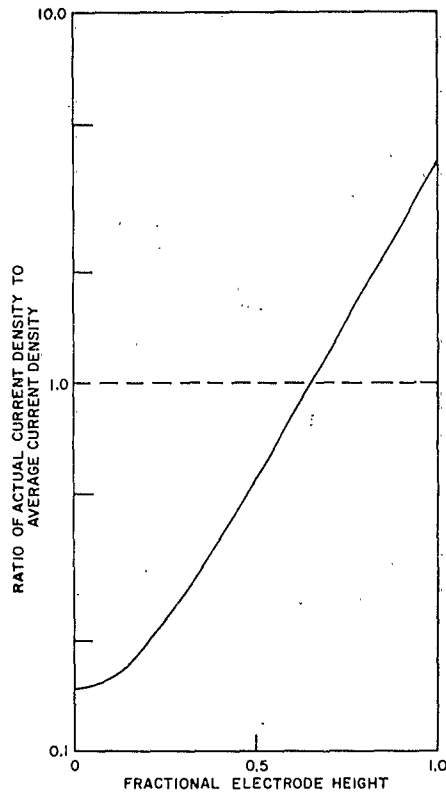


Fig. 1 - Example of uneven current density distribution

1. The anode and/or cathode have porous active materials.
2. The electrodes and electrolyte are homogeneous.
3. The electrodes are parallel.
4. The current density is uniformly distributed over the face of the electrode, as it is, approximately, in most batteries.
5. The distance between the electrodes and the cell case is small compared to the width of the electrodes and the amount that the electrolyte extends above the electrodes is small compared to the height of the electrode. Under these conditions, end effects on the current density distribution are negligible.
6. The temperature is constant.
7. The internal resistance is constant.
8. The battery is discharged at a constant current.

9. The potential drop during discharge can be divided into three parts: (a) a potential drop occurring only in the initial portion of the discharge, (b) a potential drop due to internal resistance, and (c) a potential drop due to polarization.

10. The polarization is linear over the range of current densities covered in the battery discharge.

Definition of Terms

t = the time at any point during the discharge.

i = the apparent current density in amperes per unit area.

M = the amount of active material per unit area that is available for discharge purposes on the controlling electrode at the beginning of the discharge. It is not necessarily the total amount of active material per unit area.

Q = the available quantity of electricity per unit area and can be calculated by Faraday's law to be equal to kM where k is a constant.

M_1 = the amount of available active material per unit area, used up at time t . Consequently $kM_1 = it$.

t_d = the capacity of the battery in time when discharged at current density i .

K = the slope of the polarization curve.

- L = the internal resistance per unit area of the cell.
- W_t = total energy evolved at time t expressed in watt hours per unit area.
- E = the cell potential during discharge.
- E_s = a base potential that is constant in value.
- $E_f = E_s - Ki - Li$.
- E_f = the voltage at the end of the discharge.
- $k_2 = E_s - E_f$, a constant.
- A, B = empirical constants.
- i_{am} = the active-material current density.

The active-material current density at any time t during a discharge is defined by the two following conditions.

1. At the beginning of the discharge i_{am} equals the apparent current density i.
2. At any time t during the discharge, i_{am} is directly proportional to the amperes per gram of unused active material.

Thus, if 2/3 of the available active material has been consumed at some point during the discharge, 1/3 of the available active material is left and i_{am} is equal to 3i at that point.

The above two conditions define the active-material current density by the equation

$$i_{am} = \left(\frac{M}{M - M_1} \right) i \tag{1}$$

$$i_{am} = \left(\frac{kM}{kM - kM_1} \right) i \tag{2}$$

$$i_{am} = \left(\frac{Q}{Q - it} \right) i \tag{3}$$

$$i_{am} = (1 - it/Q)^{-1} i . \tag{4}$$

Derivation of Equation

If all factors other than polarization are omitted temporarily, then assumption 10 states that E, the cell potential during discharge, is a linear function of the active material current density. This relationship is shown in Fig. 2 as a solid line over the range of current densities that give a linear polarization. If this function is extrapolated to $i_{am} = 0$, the intercept is E_s . If the slope of the polarization straight line is K,

$$E = E_s - Ki_{am} . \tag{5}$$

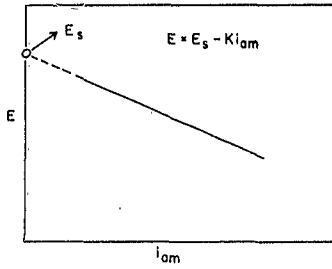


Fig. 2 - Effect of linear polarization on potential

Substituting Eq. (3) in Eq. (5),

$$E = E_s - K \left(\frac{Q}{Q - it} \right) i. \quad (6)$$

The term Li is subtracted to take care of the potential drop due to internal resistance and Eq. (6) becomes

$$E = E_s - K \left(\frac{Q}{Q - it} \right) i - Li. \quad (7)$$

When Eq. (7) is evaluated mathematically a set of curves is obtained, one of which is shown in Fig. 3 as a solid line which depicts the potential E as a function of the quantity of electricity it . However, there is a drop in potential at the beginning of a battery discharge that is not included in Eq. (7). This initial drop is more or less rapid and is shown in Fig. 3 as a dotted line. Consequently, another term must be added to correct for the difference in potential between the solid line potential, calculated from Eq. (7), and the dotted line that represents the actual discharge potential. It has been found experimentally that the expression $Ae^{-B it/Q}$, where A and B are empirical constants, gives an evaluation of the initial potential drop that is adequate in most situations. When this term is added to Eq. (7) the final equation

$$E = E_s - K \left(\frac{Q}{Q - it} \right) i - Li + Ae^{-B it/Q} \quad (8)$$

is obtained.

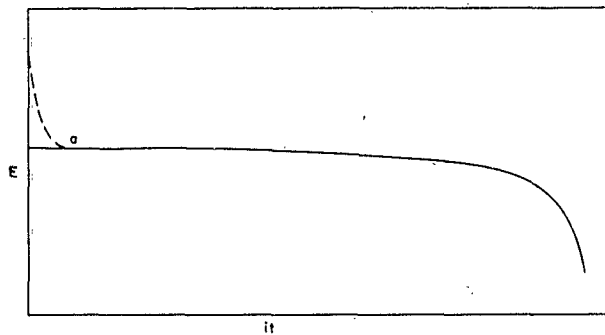


Fig. 3 - Battery discharge curve

If the basic assumptions were true and numerical values of E_s , K , Q , and L were known, Eq. (8) could be used to calculate the cell potential E as a function of discharge time t at various current densities i for those portions of the curves that lie to the right of the point a in Fig. 3. The portion of the curve that lies to the left of point a is generally of less importance. However, the location of point a can only be determined from actual discharge data. Moreover, the work involved in determining values of E_s , K , Q , and L would be large. Consequently, it would be easier and more accurate in most cases to determine discharge curves experimentally, than it would be to attempt to calculate them by use of Eq. (8).

However, Eq. (8) can be used to great advantage by fitting it to actual discharge data and determining numerically the empirical values of E_s , K , Q , L , A , and B . The resultant equation describes a set of experimentally determined discharge curves made at various current densities by giving the potential E as a function of the time t , the current density i , and the numerically calculated values of E_s , K , Q , L , A , and B . Such an equation gives an accurate description of the battery discharge and can be used to describe energy evolution, cell capacity, and also to predict cell capacities.

FITTING THE EQUATION NUMERICALLY TO EXPERIMENTAL DATA

There are a good many approaches that can be used to determine the numerical values of E_s , K , Q , L , A , and B in Eq. (8) from experimental discharge data. Most of them are involved and time consuming. A method is desired that is simple, easily applied, and gives results that are reasonably accurate. The following approach was the most satisfactory of those tested.

The first case to be studied is that of fitting Eq. (8) to a single experimentally determined discharge curve shown as a solid line in Fig. 4. Three points are selected. Point 3 is slightly below the knee of the curve. Point 2 is somewhat to the left of the knee. Point 1 is farther back along the curve but not so far back that it lies to the left of point 2 and is caught in the initial part of the curve where the potential is dropping rapidly.

The potential at point 1 is indicated by substituting E_1 and it_1 for E and it , respectively in Eq. (8) which gives

$$E_1 = E_s - K \left(\frac{Q}{Q - it_1} \right) i - Li + A e^{-B it_1/Q} \quad (9)$$

Similarly for points 2 and 3

$$E_2 = E_s - K \left(\frac{Q}{Q - it_2} \right) i - Li + A e^{-B it_2/Q} \quad (10)$$

$$E_3 = E_s - K \left(\frac{Q}{Q - it_3} \right) i - Li + A e^{-B it_3/Q} \quad (11)$$

In nearly all cases the numerical value of $A e^{-B it/Q}$ decreases very rapidly as it is increased in value, and as a consequence its value at points 1, 2, and 3 becomes extremely small and is considered equal to zero.

Subtracting Eq. (10) from Eq. (9) gives

$$E_1 - E_2 = Ki \frac{Q(it_2 - it_1)}{(Q - it_2)(Q - it_1)} \quad (12)$$

Similarly, Eq. (11) is subtracted from Eq. (10)

$$E_2 - E_3 = Ki \frac{Q(it_3 - it_2)}{(Q - it_3)(Q - it_2)} \quad (13)$$

Dividing Eq. (12) by Eq. (13) gives

$$\frac{E_1 - E_2}{E_2 - E_3} = \frac{(it_2 - it_1)(Q - it_3)}{(it_3 - it_2)(Q - it_1)} \quad (14)$$

When numerical values of E and it are taken from the discharge data in Fig. 4 and substituted in Eq. (14), a linear equation in Q is obtained which is solved to give a numerical value of Q . By substituting this value of Q in Eqs. (12) or (13) and solving, a numerical value for K is obtained. When the numerical values of Q and K are substituted in Eqs. (9) and (10), remembering that the exponential terms are essentially zero, a numerical value for $E_s - Li$ is obtained. When these numerical values of $E_s - Li$, K , and Q are substituted in Eq. (8), omitting the final exponential term, E is obtained as a specific function of the quantity of electricity (it). If this value of E were plotted in Fig. 4, it would follow the dotted line to the left of a , and to the right of a , would approximate the solid line which represents the battery discharge. The difference in potential between the dotted and the solid line in most cases can be fitted approximately by the empirical term $Ae^{-B it/Q}$.

Equation (8) may also be fitted to discharges made at a number of current densities. A moderately high current density curve and a moderately low current density curve are selected from the available discharge curves and four points are selected on these curves as shown in Fig. 5. Points 3 and 4 are taken just below the knees of the curves and points 1 and 2 are taken near the beginning of the discharge but not so close as to be caught in the initial potential drop. Under these conditions the value of $Ae^{-B it/Q}$ is negligible and the potential at point 2 is

$$E_2 = E_s - K \left(\frac{Q}{Q - i_a t_2} \right) i_a - Li_a \quad (15)$$

where E_2 and $i_a t_2$ are the values of E and it .

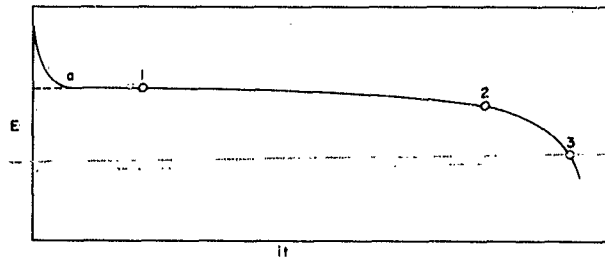


Fig. 4 - Fitting equation to a single discharge curve

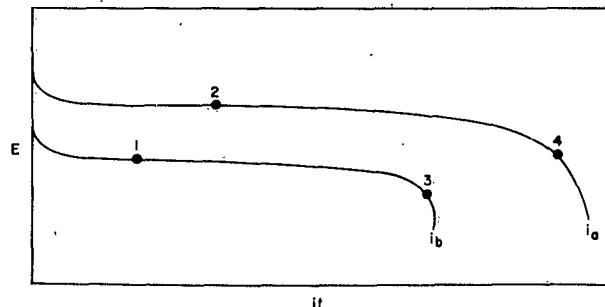


Fig. 5 - Fitting equation to discharge curves made at various current densities

Similarly for point 4

$$E_4 = E_s - K \left(\frac{Q}{Q - i_a t_4} \right) i_a - L i_a \quad (16)$$

Subtracting Eq. (16) from Eq. (15) gives

$$E_2 - E_4 = K i_a \left[\frac{Q(i_a t_4 - i_a t_2)}{(Q - i_a t_4)(Q - i_a t_2)} \right] \quad (17)$$

Similarly for points 1 and 3

$$E_1 - E_3 = K i_b \left[\frac{Q(i_b t_3 - i_b t_1)}{(Q - i_b t_3)(Q - i_b t_1)} \right] \quad (18)$$

Dividing Eq. (17) by Eq. (18) gives

$$\frac{E_2 - E_4}{E_1 - E_3} = \left(\frac{i_a}{i_b} \right) \left(\frac{i_a t_4 - i_a t_2}{i_b t_3 - i_b t_1} \right) \frac{(Q - i_b t_3)(Q - i_b t_1)}{(Q - i_a t_4)(Q - i_a t_2)} \quad (19)$$

When numerical values of E , i , and (it) are taken from the discharge data in Fig. 5 and substituted in Eq. (19), a quadratic equation in Q is obtained which is solved to give a numerical value of Q . By substituting this value of Q in Eqs. (17) or (18) and solving, a numerical value for K is obtained. When the numerical values of Q and K are substituted in Eq. (15) and a similar equation for E_1 , two simultaneous equations are obtained which may be solved to give numerical values for E_s and L . When these numerical values of E_s , L , K , and Q are substituted in Eq. (8), E is obtained as a specific function of current density and time (it) . The term $A e^{-B it/Q}$ is determined by difference.

Experimental discharge data from Edison, Ni-Cd, silver-zinc-alkaline, air depolarized-zinc-alkaline, lead acid, and dry cell batteries have been plotted as dashed lines in Figs. 6-11.

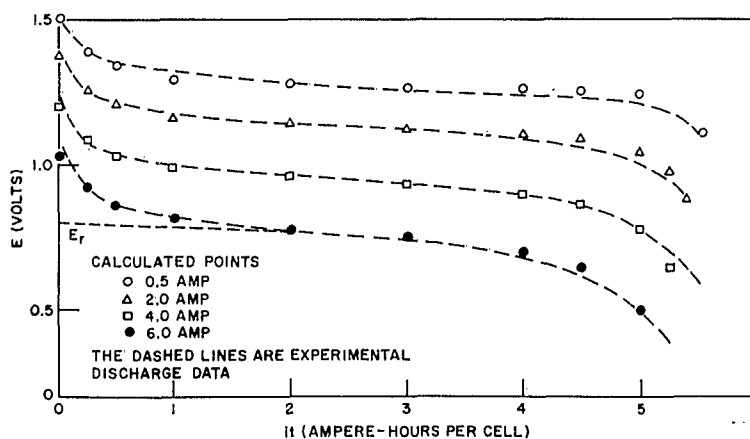


Fig. 6 - Comparison of the discharge data for an Edison cell with the calculated results from the equation

$$E = 1.320 - 0.00656 \left(\frac{1}{1 - 0.1766 \cdot it} \right) i = 0.0799 i + 0.228 e^{-2.608(it)}$$

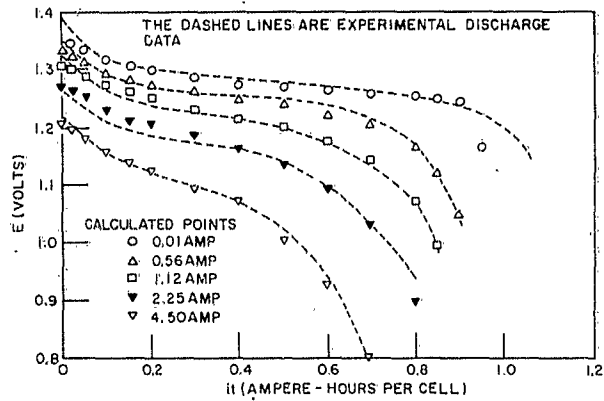


Fig. 7 - Comparison of the discharge data for a sealed Ni-Cd cell with the calculated results from the equation

$$E = 1.25 - 0.025 \left(\frac{1}{1 - 1.05 it} \right) i - 0.006 i + 0.095 e^{-3.83(it)}$$

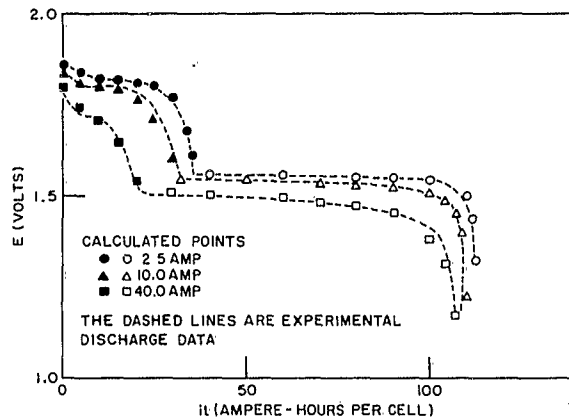


Fig. 8 - Comparison of the discharge data for a silver cell with the calculated results from the equation

$$E = \text{Either} \left[1.831 + 0.02 e^{-0.6(it)} - 0.00514 \left(\frac{1}{1 - 0.027 it} \right) i + 0.00388 i \right]$$

or

$$\left[1.5667 - 0.0004 \left(\frac{1}{1 - 0.00893 it} \right) i - 0.00067 i \right]$$

whichever is larger in value.

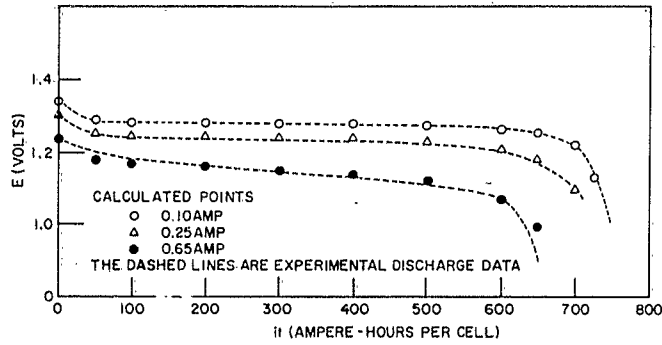


Fig. 9 - Comparison of the discharge data for air depolarized cells with the calculated results from the equation

$$E = 1.303 - 0.038 \left(\frac{1}{1 - 0.00135 it} \right) i - 0.168 i + 0.06 e^{-0.044(it)}$$

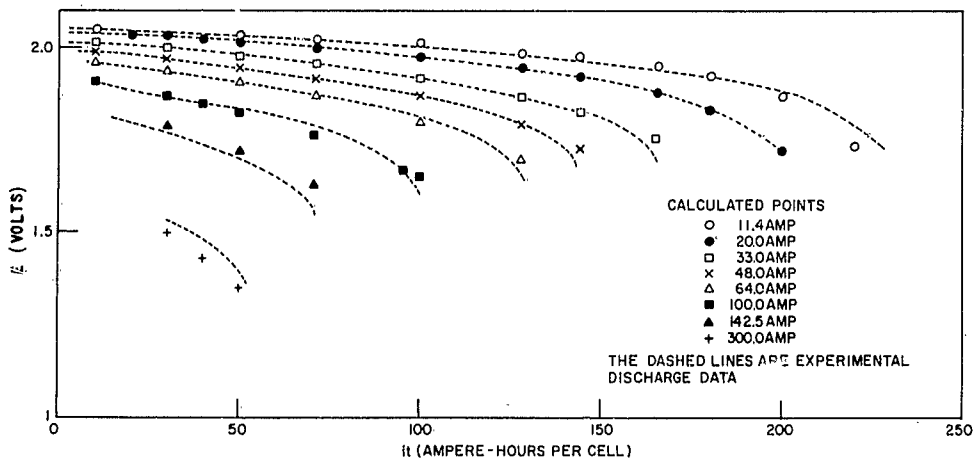


Fig. 10 - Comparison of the discharge data for a lead acid cell with the calculated results from the equation

$$E = 2.0615 - 0.004274 \left(\frac{1}{1 - 0.003918 it} \right) i + 0.002934 i$$

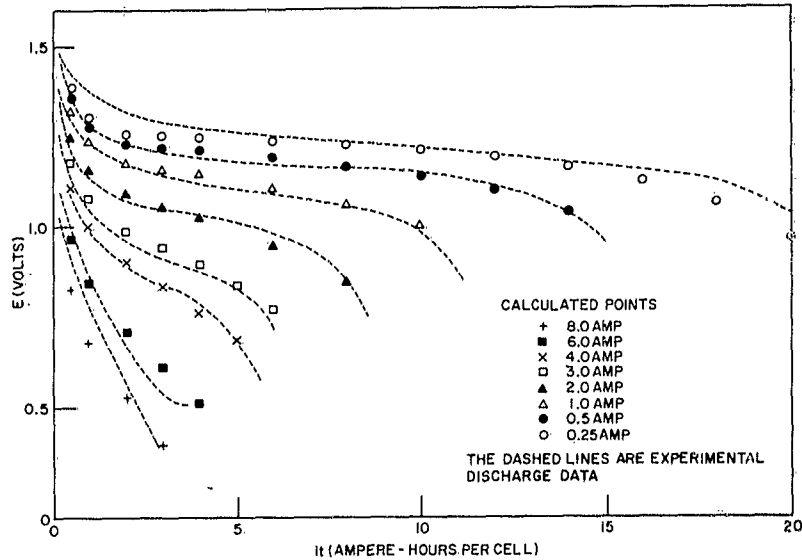


Fig. 11 - Comparison of the discharge data for No. 6 dry cells with the calculated results from the equation

$$E = 1.274 - 0.3343 \left(\frac{1}{1 - 0.039 \, it} \right) i + 0.269 \, i + 0.36 e^{-2.197(it)}$$

The potential E in volts is given as a function of the quantity of electricity in ampere hours per cell. The current density is given in amperes per cell. The points are calculated from the equations that were fitted numerically to each set of discharge curves by the method just described. It can be seen in each case that there is a good agreement between the experimental data and the fitted equation at every current density. No high current density or low current density curves were omitted. A few intermediate current-density discharge curves were deleted in Figs. 6 and 7 solely to maintain visual clarity in the graphs.

Equation (8) is being fitted to discharge data for a large number of various types of batteries in addition to those shown in Figs. 6-11.

EQUATION DESCRIBING BATTERY CHARGE

If the basic assumptions are assumed to be true during the charge of a battery, then the following equation would hold for the potential of a battery during charge:

$$E = E_s + K \left(\frac{Q}{Q - it} \right) i + Li - Ae^{-B \, it/Q} \quad (20)$$

Equation (20) can be obtained from Eq. (8) by reversing the signs of the last three terms.

Equation (20) has been fitted to the charge of a Ni-Cd cell in Fig. 12. The solid lines represent the actual data and the points are calculated from the equation.

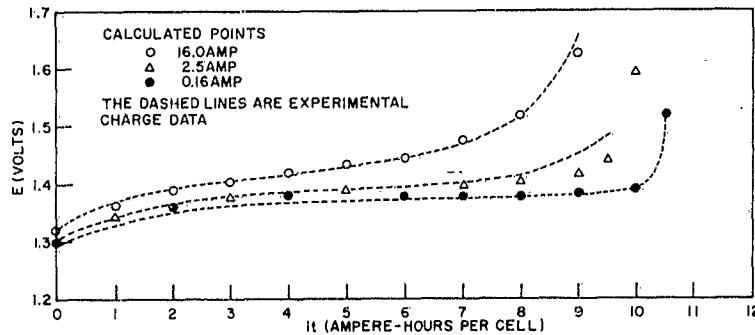


Fig. 12 - Comparison of the charge data of a Ni-Cd cell with the calculated results from the equation

$$E = 1.379 + 0.0024 \left(\frac{1}{1 - 0.095 it} \right) i - 0.00117 i - 0.08 e^{-0.693(it)}$$

ENERGY EVOLVED DURING DISCHARGE

The total energy W_t that has been evolved from the beginning of the discharge up to time t is defined by the equation

$$W_t = \int_0^t i E dt.$$

Substituting Eq. (8)

$$W_t = \int_0^t \left[E_s i - K \left(\frac{Q}{Q - it} \right) i^2 - Li^2 + Ai e^{-B it/Q} \right] dt \tag{21}$$

$$W_t = \left[E_s it + KQi \ln(Q - it) - Li^2 t - AQ/B e^{-B it/Q} \right]_0^t \tag{22}$$

$$W_t = E_s it - KQi \ln(1 - it/Q)^{-1} - Li^2 t + AQ/B (1 - e^{-B it/Q}). \tag{23}$$

If the constants from the equation describing the discharge of the Ni-Cd cell in Fig. 7 are substituted in Eq. (23), the total energy evolved at time t is found to be

$$W_t = 1.25 it - 0.0238 i \ln(1 - 1.05 it)^{-1} - 0.006 i^2 t + 0.0248 (1 - e^{-3.83 it}). \tag{24}$$

In Fig. 13, W_t in watt hours per cell has been plotted as a function of t in hours for various values of the cell current in amperes. The solid lines are obtained from calculations based on numerical integration of the actual discharge data. The points are calculated from Eq. (24). The agreement between the calculated and the measured results in such cases depends entirely upon how well Eq. (8) can be fitted to the original discharge data.

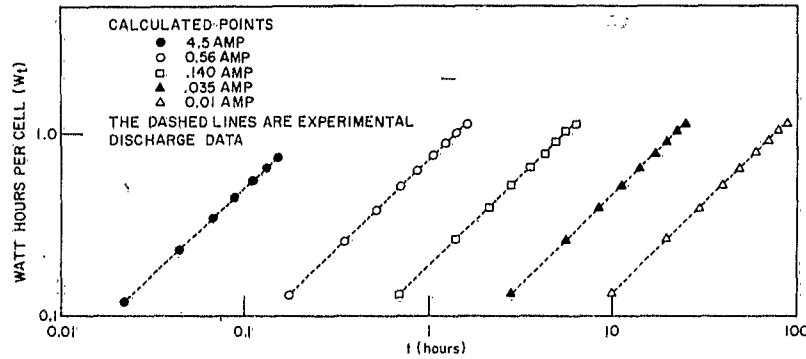


Fig. 13 - Calculated vs measured energy evolved during the discharge of a Ni-Cd cell

CELL CAPACITY

The discharge of a battery is considered to be terminated when the potential has dropped to a particular value which is called the cutoff voltage. A constant cutoff voltage for the various current density discharge curves can be used satisfactorily whenever the potential difference between the curves is small, as they are in Fig. 8.

When the potential difference between the discharge curves is large, as it is in Fig. 6, a constant cutoff voltage would not be satisfactory since a value low enough to take care of the 6.0-ampere curve, would be entirely too low for the 0.5-ampere curve. It would be desirable in such cases to have a cutoff voltage that decreased as the current density increased. This condition is achieved in the following manner. If the equation for the 6.0-ampere curve in Fig. 6 is plotted, omitting the final exponential term, a solid curve is obtained that approximates the actual discharge curve to the right of a value of it which is equal to approximately 2.0. When it is less than 2.0 a dotted line is obtained which intersects $it = 0$ at E_r . Values of E_r are obtained for each current density curve in a similar manner. The cutoff voltage on each discharge is taken to be some suitable, constant value, k_2 , such as 0.25 volt, below the value of E_r for that curve. This operation gives a value for the cutoff voltage that decreases as the current density increases. E_r may be determined mathematically by substituting $it = 0$ in Eq. (8) and omitting the exponential term

$$E_r = E_s - Ki - Li \quad (25)$$

At the end of the discharge, the exponential term in Eq. (8) is negligible in value and the final or cutoff voltage is

$$E_f = E_s - K \left(\frac{Q}{Q - it_d} \right) i - Li \quad (26)$$

where t_d is the capacity in time at the end of the discharge for the particular current density i .

Subtracting Eq. (26) from (25) gives

$$E_r - E_f = K \left(\frac{Q}{Q - it_d} \right) i - Ki \quad (27)$$

$$E_r - E_f = k_2$$

$$t_d = \frac{k_2 Q}{K i^2 + k_2 i} \tag{28}$$

$$i t_d = \frac{k_2 Q}{K i + k_2} \tag{29}$$

Equations (28) and (29) give the capacity in time t_d at any current density as a function of K and Q which are determined by fitting Eq. (8) to discharge data.

Capacities calculated from Eq. (28) or Eq. (29), have been plotted in Fig. 14 where the time in hours t_d is plotted against the current density i . The Ag' curve was taken from the first step in the discharge of the cell in Fig. 6 and the Ag curve was taken from the second step. All of the data in Fig. 14 was taken from Figs. 6-11. The axes had to be shifted in most cases to bring all the curves into one chart, and the figures in the x and y column in Fig. 14 are the quantities that must be multiplied times t_d and i , respectively to give the true values of the capacities and the current densities.

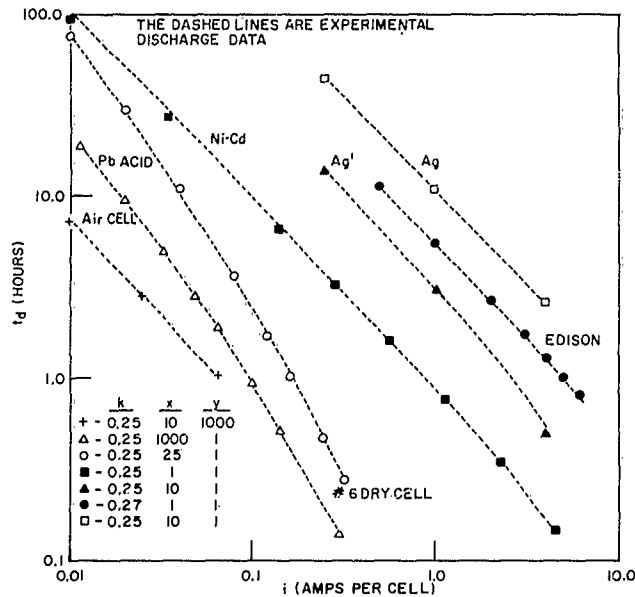


Fig. 14 - Comparison of calculated and measured capacities

PREDICTION OF CELL CAPACITIES

Equation (29) is a function of the two quantities K and Q . It was shown earlier that numerical values of K and Q can be calculated from the data in a single discharge curve made at a constant current density. Numerical values of E and (it) for three points on such a curve are substituted in Eqs. (12) and (14) and solved to give numerical values of K and Q . When these values are substituted in Eq. (29), it can then be solved to give the

capacity t_d in time at any current density i . Thus, the data from a single discharge curve at one current density can be used to predict capacities at other current densities.

The results of such predictions are shown in Fig. 15 which has been plotted in the same manner as Fig. 14. A good agreement is obtained in all cases between the predicted and the measured capacities.

A single current density curve was chosen for each battery, three points were selected on this curve, and the capacities were predicted through use of Eq. (28) or (29).

The variation in the predicted capacities was found to be small when the positions of the three selected points were varied or when a new discharge curve with a different current density was used. To avoid bias in the presentation, the predicted capacities shown in Fig. 15 are those obtained from the first calculation that was made. However, there are a number of definite limitations to the use of this method for predicting capacities. It is essentially an extrapolation technique and is subject to the errors and limitations found in extrapolation. Assume that all the true capacities were known and that they were plotted as a curve on log paper in the manner shown in Fig. 15. Very serious errors would be introduced if the current density that was chosen as a base for predicting capacities happened to lie on a point on this curve where the slope was steeper than approximately -1.4 . In the case of the dry cell, the lowest current density discharge curve was the only one that could be used safely as a base. Deviations may also occur in the predicted capacities at current densities that are more than five or six times that being used as a base for the predictions. The five highest current densities on the dry cell curve in Fig. 15 fall outside this limit and it can be seen that the difference between the predicted capacities and the measured capacities for each of these current densities is well above the average for the remainder of the data.

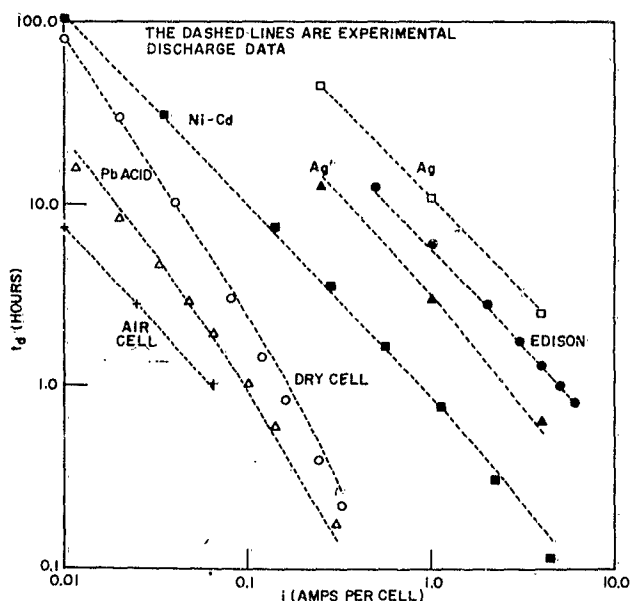


Fig. 15 - Comparison of measured cell capacities with capacities predicted from a single discharge curve

A more thorough mathematical and statistical analysis, covering a wide range of batteries and discharge conditions, is being contemplated in an attempt to determine as accurately as possible the limitations and the procedures involved in predicting cell capacities by this technique.

CONCLUSIONS

The potential E of a battery during discharge at constant current density is shown to be

$$E = E_s - K \left(\frac{Q}{Q - it} \right) - Li + Ae^{-B it/Q}$$

where E_s is a constant, K is the slope of the polarization curve, Q is the available quantity of electricity, L is the internal resistance, i is the current density, t is time and A and B are empirical constants.

This equation can be used to predict battery discharges or to describe them by fitting it to available discharge data. It can be used as a basis for deriving other equations which describe battery charging, characteristics of discharges made at constant resistance, power output, and capacities. It can also be used to predict capacities over a wide range of current densities from the data obtained in a single discharge curve made at a constant current density.

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