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POLARIZATION STUDIES OF THE LEAD-ACID STORAGE CELL

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CONTENTS

| | |
|---|----|
| Abstract | ii |
| Problem Status | ii |
| Authorization | ii |
| INTRODUCTION | 1 |
| THEORY | 1 |
| EXPERIMENTAL WORK | 5 |
| DATA | 7 |
| DISCUSSION | 9 |
| SUMMARY | 15 |
| REFERENCES | 17 |
| APPENDIX A - Short-Circuit Currents from Submarine Cells | 18 |
| APPENDIX B - Calculation of Steady-State Terminal Voltage Vs. Current in an Electrochemical System Involving Resistance Only | 20 |

ABSTRACT

Submarine cells of type MAQ-71 and MAW-76C were discharged through resistance-inductance series circuits. Cell voltage and discharge current were measured with time up to two minutes. Positive and negative single-electrode potentials were also measured.

Two voltage-decay periods were found at the start of the discharge. The first was large and rapid and corresponds electrically to a constant potential discharging through an R-L circuit, enabling internal resistance to be determined uncomplicated by other polarization phenomena. The small slow secondary decay was found to be confined substantially to the positive plate, and is explained as a decrease in ΔF for the electrochemical reaction resulting from the production of water and consequent dilution of the electrolyte at the plate-solution interface. The polarization was treated theoretically from the standpoint of condenser charge and discharge, and it is concluded that such theory does not apply.

The magnitude of the secondary voltage decay depends on the amount of discharge, independent of rate over the range measured, so that a simple alternative method of determining the resistance of these cells is possible.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C05-17
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POLARIZATION STUDIES OF THE LEAD-ACID STORAGE CELL

INTRODUCTION

In the past, it has been desirable for various reasons ^{1,2,3,4,5} to measure the internal resistance and other electrical characteristics of lead-acid storage batteries. Measurement of these quantities has been uncertain because they appear to be more or less inextricably lumped in with a quantity which is referred to in electrochemistry in a general way as "polarization." It is the purpose of this report to discuss the concepts involved and to indicate by means of theory and experimental data, that specifically for the lead-acid cell and for some other electrochemical systems by inference, both the electrical and the electrochemical pictures may be quite uncomplicated and readily interpreted in mutually satisfactory terms.

THEORY

The maximum available energy which can be obtained from an electrolytic cell is given by the free energy change, ΔF , for the chemical reaction concerned. It is related to the electrical energy by the equation

$$\Delta F = -n F E$$

where E is the voltage which can be supplied by the system, n is the electron change for the reaction and F is the Faraday constant. Presumably, E can be calculated from ΔF only when no current is being drawn, i. e., when the cell is on open-circuit. In this condition, E will be referred to as the open-circuit-voltage (OCV). The maximum energy is never actually obtained outside the cell, except possibly at very low currents, because some work must always be done inside the cell, if only against internal resistance. Consequently, ΔF will be divided between inside and outside work. The voltage measured at the cell terminals, in a working cell, is the energy available for outside work, while the OCV minus the terminal voltage is presumably the energy used for doing work inside the cell. This latter quantity is the polarization voltage for a working cell, it is the quantity of interest because it limits the useful work which can be done by the cell. It is generally considered to be made up of internal resistance and a term or terms involving concentration changes of ions and other reactants or products at or near the electrode-solution interface. In this connection, perhaps it may be stated that ΔF is a function of the activities of reactants and products involved in the electrochemical reaction.

When a battery is discharged through a nearly pure resistance, the voltage at the terminals varies with time ^{1,6} in the fashion shown in Fig. 1. Similar curves have been obtained frequently for single electrodes. ^{6,7,8} It has been attempted to represent the equivalent electrical circuit of the battery at each electrode in the way shown in Fig. 2,

where A and B are capacitance-resistance combinations corresponding to the Helmholtz layer (or diffuse double layer) and to concentration polarization, respectively. R_s is the solution resistance between the electrodes. It is evident that this representation is not adequate for the battery plate because if the resistance which shunts condenser A is of relatively low value then it will discharge while the battery is standing on open circuit and the condenser will not be able to furnish energy when the battery is connected across an external resistance. On the other hand, if this is considered to be the equivalent circuit on discharge, then the capacitance should discharge to zero voltage in a relatively short time through R_s and the external circuit. In fact, it does not; the voltage decreases more or less logarithmically to a value at which current continues to flow at a constant rate with no additional voltage decay. The physical impossibility of treating concentration polarization as a capacitance, as in portion B of the proposed circuit, will be treated later in the discussion section. Variations of this equivalent circuit have also been considered for electrochemical systems in general.⁹

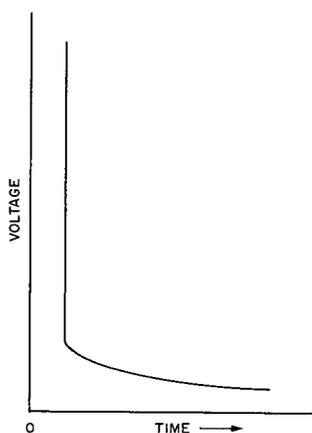
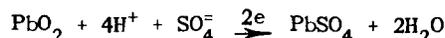


Fig. 1. Experimental polarization curves

Equivalent circuits such as shown in Fig. 2 imply two paths for the discharge of the condenser when the external circuit is made. This is probably the case, but the resistance shunting the Helmholtz layer condenser is so high that for all practical purposes it is an open circuit. This may reasonably be deduced from a consideration of the electrochemical reactions involved. For this purpose, the positive plate of the lead-acid cell will be used as a model.

When a positive plate is placed in the electrolyte, the following electrochemical reaction can occur



This is the reaction which takes place at the positive plate when the cell is discharged. In this instance, however, the reaction causes a positive charge to be placed on the grid of the plate, because the electrons for the reaction must come from the grid. A negative charge arises in solution because more positive ions than negative are used up in the reaction.

The reaction proceeds until its tendency to occur is balanced by the refusal of the grid to give up more electrons. The result is that a condenser is formed such as illustrated in Fig. 3. The voltage of this condenser is given by the free energy change for the reaction. This picture of the condenser formation has utilized nothing more than the simple Helmholtz concept of the manner in which an electrode gets its charge.

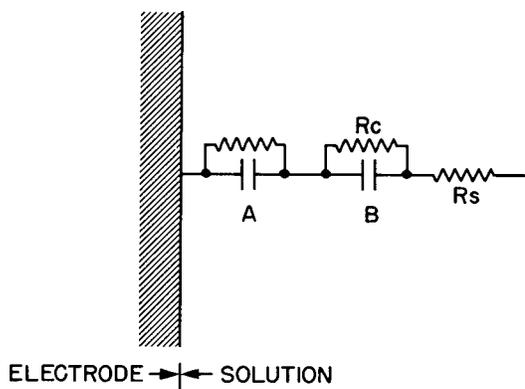


Fig. 2. An electrical representation of a working electrode

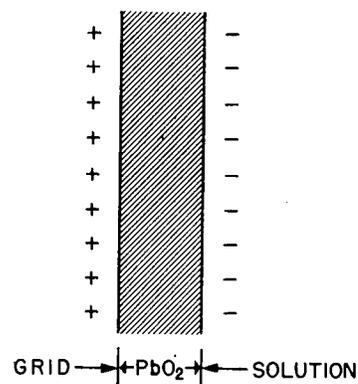


Fig. 3. The electrical condition at the positive plate

Now consider how the condenser may discharge. Obviously, it can discharge if electrons can be supplied to the grid and if the negative charge in solution at the interface could be used up by reaction or drift off into solution. This actually tends to occur on stand at a very low rate by corrosion of the grid, where the grid itself furnishes the electrons by reacting with the electrolyte to form PbSO_4 and PbO . Evidently the excess negative charge is also removed by the self-discharge reaction (as SO_4^- in PbSO_4 , or by production of H^+ in the formation of PbO). However, the self-discharge reaction does not discharge the condenser because the cell-discharge reaction can go forward to keep the condenser charged up. The latter discharge can proceed at very great rates as is evident from the rate at which current can be drawn from a lead-acid cell. This situation may be represented electrically as shown in Fig. 4 where the condenser represents the charge across the Helmholtz layer. It is shown to be discharging through a resistance which represents the resistance to corrosion of the grid, but in addition charge is being supplied by a source of emf which represents the cell-discharge reaction. It supplies the condenser through a resistance ($R?$) which is so noted because its value is questionable and may even approach zero.

Now consider what would happen when a negative plate is put into the solution and the two plates are connected through an external resistance. Then, a new path is supplied for the reaction which discharges the condenser across the Helmholtz layer of the positive plate because the positive plate grid is connected to the negative plate through the external resistance, and the reaction $\text{Pb} \rightarrow \text{PbSO}_4 + 2e$ can now occur at that plate instead of at the positive grid so that electrons may be supplied for the discharge of the positive plate of the condenser through the external resistance. Again, the negative charge in the solution will tend to be removed by reaction of SO_4^- with PbO_2 and by migration of SO_4^- to and reaction at the negative plate. But the condenser discharge does not go to zero because the electrochemical reaction proceeds in a forward direction to keep the condenser charged. If the negative plate were to be made very large, so that its potential change would be negligible, then the positive-plate condenser discharge could proceed at a rate limited only by the resistance of the path through the solution, the plates, and the external resistance. Indeed, the discharge is materially assisted by the potential of the negative plate which exists in series with and adds to that of the positive plate condenser, so that charge is driven in the total circuit by the sum of the two voltages. And so it can be seen that the effect of adding a negative plate and an external circuit is to supply a new path for the discharge of the positive plate condenser and to add an extra potential to help drive current around the new path.

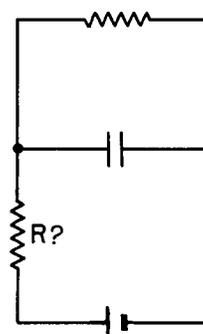


Fig. 4. An electrical representation of the self-discharging positive plate

The new situation may be represented by the electrical circuit shown in Fig. 5, where R_0 is the external resistance, R_p is the electrical resistance of the metallic plates and grids, R_s is the solution path resistance, and V_T is the voltage measured across the cell terminals. Evidently, R_p and R_s can be summed up in R_I , the internal resistance of the cell.

The discharge characteristics of this cell are obvious; the voltage at V_T will be, initially, the voltage of the two plates minus IR_I . As the discharge progresses, the voltage of the condenser will fall off as current flows in the outside circuit and this voltage decay will be reflected in a decreased voltage at V_T . The decay will continue until current supplied by the positive-plate half-cell (i. e., the electrochemical reaction) equals the external current, at which time the positive-plate voltage and the cell voltage become stable. The equation for the change in voltage across the condenser with time (dE_c/dt) is easily derived to be

$$C \frac{dE_c}{dt} = - \frac{(R?) + R_I + R_0}{(R?) (R_I + R_0)} E_c + \text{const} \quad (1)$$

where C is the capacity of the positive-plate condenser, and the constant is a function of the positive- and negative-plate voltages and $(R?)$, R_I , and R_o . According to this equation dE_c/dt is a linear function of E_c with a negative slope equal to $(R?) + R_o + R_I/C(R?) (R_I + R_o)$ so that by measuring the change in voltage as a function of voltage the value of C could be determined if the values of the several R 's were known. However, it is important to note that if $(R?)$ is zero the above equation does not apply and any change in voltage is a function of the emf characteristics of the positive plate and is not a function of the characteristics of the condenser, so that even though C may be present and have a real value, its value could not be determined from the voltage decay data.

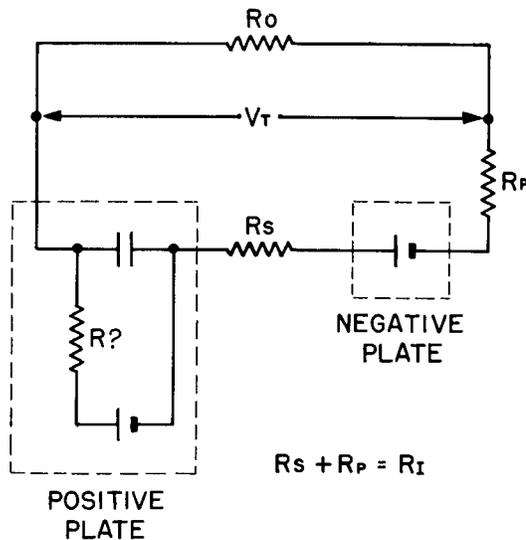


Fig. 5. An electrical representation of the working cell

It can also be shown that

$$C \frac{dV_T}{dt} = - \frac{(R?) + R_I + R_o}{(R?) (R_I + R_o)} V_T + \text{const} \quad (2)$$

and if no change in negative-plate voltage is included, the characteristics of the positive-plate decay determine those for the whole cell and C could be determined by measuring the proper quantities at the cell terminals.

In similar fashion the equations:

$$\log_{10} \left(- \frac{dE_c}{dt} \right) = - \frac{(R?) + R_I + R_o}{2.3C(R?) (R_I + R_o)} t + \text{const} \quad (3)$$

$$\log_{10} \left(- \frac{dV_T}{dt} \right) = - \frac{(R?) + R_I + R_o}{2.3C(R?) (R_I + R_o)} t + \text{const} \quad (4)$$

can be derived so that C could be determined by plotting $\log (-dV_T/dt)$ vs. t , if the various R 's are known.

It is evident that plots of V_T vs. t would resemble the curve shown in Fig. 1, if $(R?) \neq 0$ so that the proposed circuit could be equivalent.

Now let an inductance be introduced in series in the external circuit, as shown in Fig. 6. Then the mathematical situation is more complex, because the transient voltage condition becomes a function of C , R , and L and a second order differential equation of the form

$$\frac{d^2 E_c}{dt^2} + A \frac{dE_c}{dt} + B E_c + C = 0 \quad (5)$$

is involved. In this case, instead of falling off, the current builds up with time, and dE_c/dt will be slowed down. dV_T/dt is changed considerably also. There is no immediate drop in V_T corresponding to IR_I because I starts at zero and builds up with time. All the initial energy is contained in the term $L dI/dt$, so that V_T will start at the open-circuit value and fall away smoothly with time. However, dE_c/dt and dV_T/dt are not linear functions of E_c and V_T because they are also functions of $d^2 E_c/dt^2$ and $d^2 V_T/dt^2$, the magnitudes of which are not constant with either t or V_T .

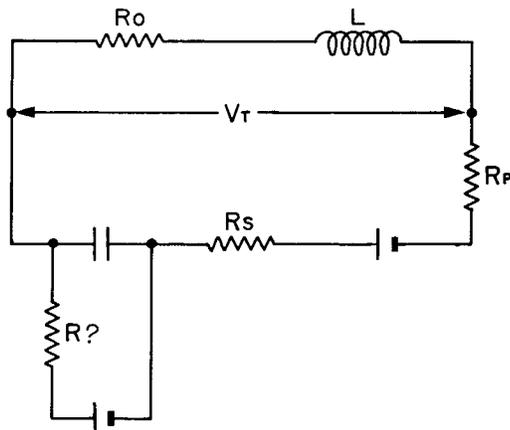


Fig. 6.- An electrical representation of the working cell, inductance added to the external circuit

If $(R?) \rightarrow 0$ or $C \rightarrow \infty$, then a constant potential would be driving the discharge. E_c would not change with time, but dV_T/dt would become a function of V_T or t according to the equations:

$$\frac{dV_T}{dt} = -\frac{(R_I + R_o)}{L} V_T + \text{const} \quad (6)$$

and

$$\log_{10} \left(-\frac{dV_T}{dt} \right) = -\frac{(R_I + R_o)}{2.3L} t + \text{const} \quad (7)$$

where the constants are functions of R_I , R_o , L and the open-circuit voltage. Evidently, dV_T/dt is linear with V_T and $\log_{10}(-dV_T/dt)$ is linear with t . The respective slopes are

$$-\frac{R_o + R_I}{L} \quad \text{and} \quad -\frac{R_o + R_I}{2.3L}$$

EXPERIMENTAL WORK

The experimental work consisted in discharging a fully charged MAQ-71 or MAW-76C submarine cell through resistances of known values from about 1000 μohms to about 30 μohms for times up to two minutes, while cell voltage and voltage across a known resistance (current) were recorded as a function of time. The resistances consisted of a one-inch stranded copper cable or lengths of these in parallel, or a short heavy brass tube with a resistance of 1.4×10^{-6} ohms. The resistances were measured by running currents of about 100 amperes through them and measuring their voltage drop with a type K potentiometer.

The switching arrangement and the arrangement of the external resistances are shown in Fig. 7. The heavy six-bladed knife switch, A, is used for opening the circuit. In parallel with this a fuse was usually placed, so that opening the switch threw the load on the fuse, which burnt out to break the circuit. The circuit was closed by driving the wedge switch B into its seat in the mounting. It was designed to make the circuit as quickly and completely as possible. All mechanically contracting parts were silver-plated to reduce contact resistance. Under best conditions, after polishing all contacts, the total resistance of the switch mounting could be reduced to about 15-20 μohms .

The procedure for making a run was as follows. The cell was charged to full gassing and then allowed to sit on open circuit until the voltage became steady, usually overnight. The shunt resistance was clamped into place on the switch mounting with both switches open and its resistance was measured. Voltage connections were made to the recording instruments from the proper places in the discharge circuit. The knife switch was closed and the wedge slammed home. Current was allowed to flow for times up to two minutes, the circuit broken, and the cell put on charge to get it ready for another run.

The early work in these series of experiments was done with the MAQ-71 cell and a Hathaway Oscillograph - Type S8-A. The cell voltage was recorded across the tops of the terminals outside the cell, and an attempt was made to measure current by measuring the voltage drop across the external shunt. Reference to Fig. 7 will show that the external resistance, the switch mounting, and the top of the cell form a closed loop for the current path, which means an inductance was present in series with the resistance. Furthermore, since a large portion of this inductance is included in the external shunt, current could not be measured in it until $dI/dt \rightarrow 0$. Actually, this could be corrected for by analysis of the data, if so desired. The value of the inductance was enough to delay current rise appreciably

because the resistance values were so low. In addition, however, a smaller portion of the inductance was included in the cell voltage measurement at the tops of the terminals and this fact made the resultant data for the transient voltage condition practically impossible to interpret quantitatively; so a new set of discharges was run at a later time using the MAW-76C cell.

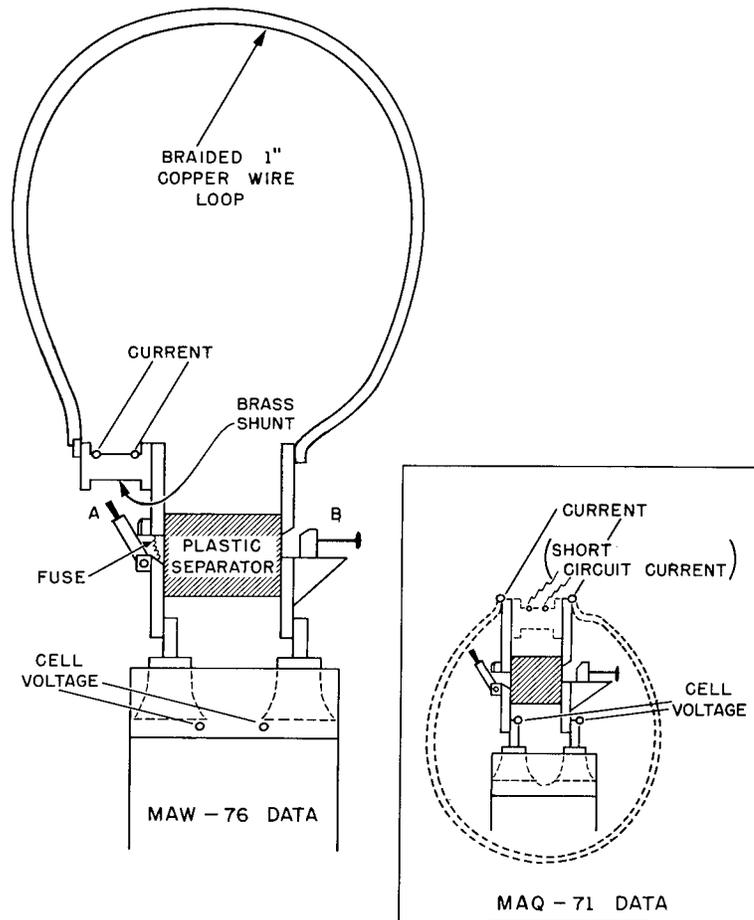


Fig. 7. End-on view of the cell top and switch

From the circuit geometry and indications from the analysis of the data obtained with the MAQ-71 cell, it was thought that the troublesome inductance portion included in the cell voltage measurement could be eliminated by measuring the cell voltage at the tops of the plates next to the top of the electrolyte. A few preliminary experiments showed that this estimation of the situation was correct, and in the new series of discharges with the MAW-76C cell the cell-voltage connections were so located.

Single-electrode potential measurements were made in each series. Those made in the first series of discharges suffered from the same trouble as the cell-voltage measurements, because the connections to either plate were made at the cell terminals. In the second set connections to the plates were made at the tops of the plates near the electrolyte level, as were the cell-voltage connections. The reference electrode was a fully charged positive or negative plate from a small cell placed in the electrolyte in the top of the cell, insulated from the plates themselves. Currents drawn for measuring the single-electrode potentials were too small to polarize the reference electrodes.

For measuring current in the second set of data, the potential drop was measured across the short brass cylinder ($1.4 \times 10^{-6} \Omega$ resistance) in series with the inductance loop. In this way, substantially all the inductance contribution was eliminated from the current data. Also a larger, approximately constant, inductance loop was used in arranging the external circuit. A Brush Recorder, Type BL-202, was used in place of the Hathaway Oscillograph. With either recorder, time could be established to within ± 0.002 second, which was of sufficient precision because the initial transient existed for times of 0.04 to 0.1 second or more depending on the L/R ratio.

DATA

Data are quoted for both series of discharges but for the MAQ-71 set it is used only after the first transient voltage condition has passed, when $L \frac{di}{dt}$ is zero and the current and cell voltage measurements become accurate. Figure 8 shows the cell-terminal voltages at various rates for the MAQ-71 cell over the time interval 1-130 seconds. Figure 9 shows the transient voltage data from 0-0.14 second for discharge number 9 of Fig. 8.

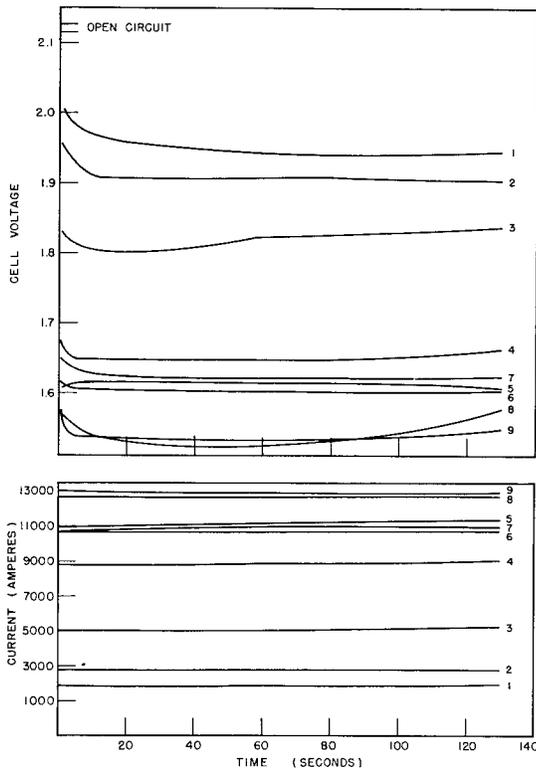


Fig. 8. Voltage and current vs. time; MAQ-71 cell.

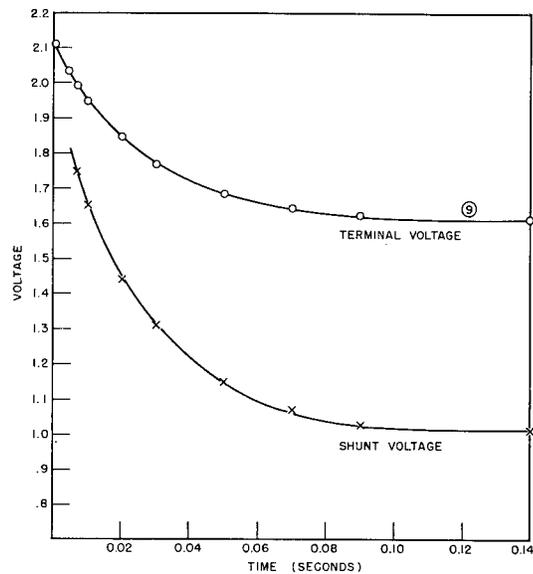


Fig. 9. Voltages across cell terminals and external shunt; MAQ-71 cell; $77.4 \mu\Omega$ external resistance.

Figures 10 and 11 show the voltage decay (measured at the tops of the plates) and current rise (measured across the short brass tube) curves for the MAW-76C cell, shorted through external resistances of 171, 193, 354, and 624 microhms. Figure 12 shows the change in voltage at the tops of the plates of the cell and the single electrode potentials of the positive and negative plates. These were measured during a separate run with the same external resistance as Run No. 4 of Figs. 10 and 11.

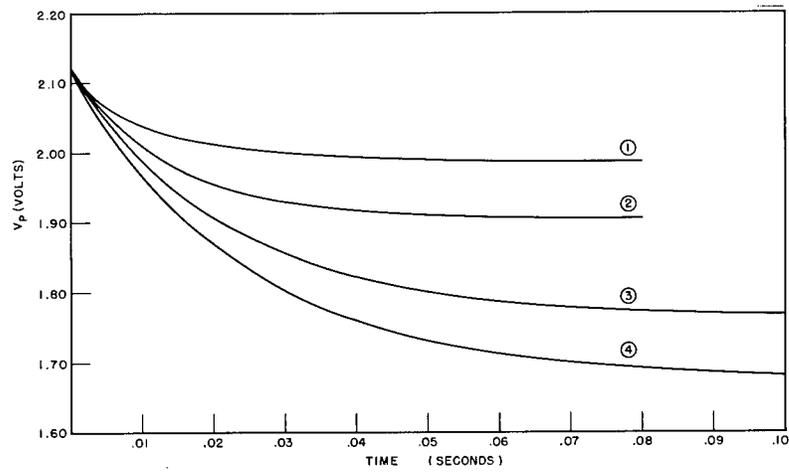


Fig. 10. Cell voltage vs. time; MAW-76C cell

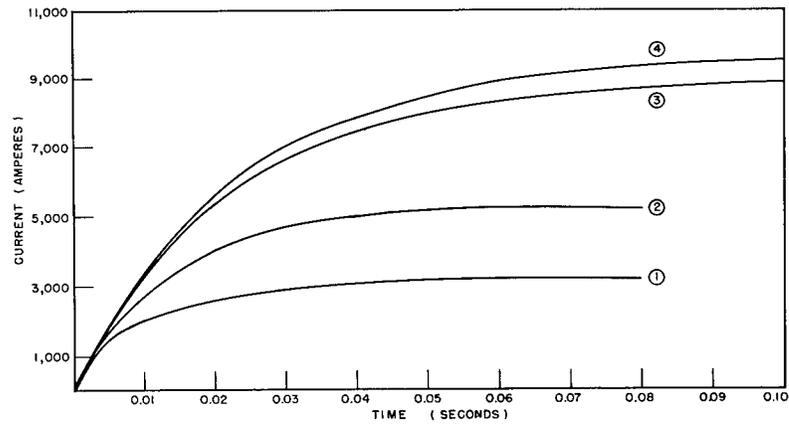


Fig. 11. Current vs. time; MAW-76C cell

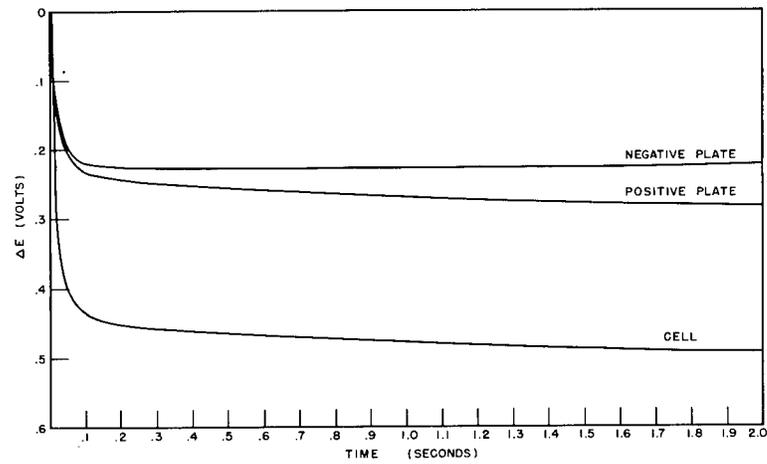


Fig. 12. Voltage changes for cell, negative, and positive plates vs. time; MAW-76C cell

All the MAW-76C cell data were taken from recorder traces from two runs which always duplicated exactly when the tracings were superimposed.

DISCUSSION

The slopes of the voltage-time curves (Fig. 10) were measured up to times of 0.1 second and plotted against cell voltage and time in Figs. 13 and 14. Because the latter curves are linear, Eqs. 6 and 7 adequately describe the discharge over this transient period, that is to say, this portion of the discharge is represented by a constant potential which drives current through an R-L series circuit. Consequently, the voltage drop of the cell at any time over this period by its corresponding current at that time. This has been done with the data of Fig. 10, curves 1 and 2 at 0.08 second and curves 3 and 4 at 0.1 second; and the values obtained are 42.2, 41.0, 40.0, and 48.5 x 10⁻⁶ ohms, respectively. Several values measured over the whole range for each run give the internal resistance for the fully charged MAW-76C cell, measured across the tops of the plates, to be (42.2 ± 2.3) x 10⁻⁶ ohms. The resistance of the cell from the tops of the plates to the tops of the outside terminals was measured during current flow to be 10 x 10⁻⁶ ohms; therefore, the internal resistance of this cell was (52.2 ± 2.3) x 10⁻⁶ ohms.

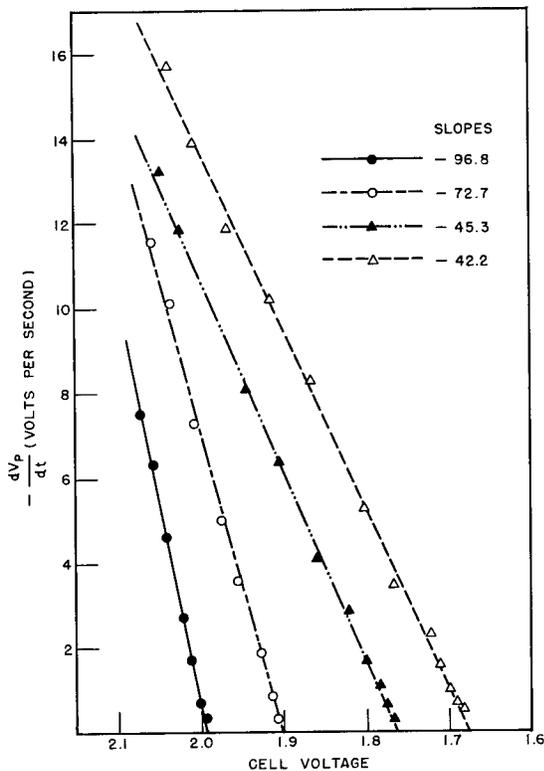


Fig. 13. $-\frac{dV_p}{dt}$ vs. cell voltage; MAW-76C cell

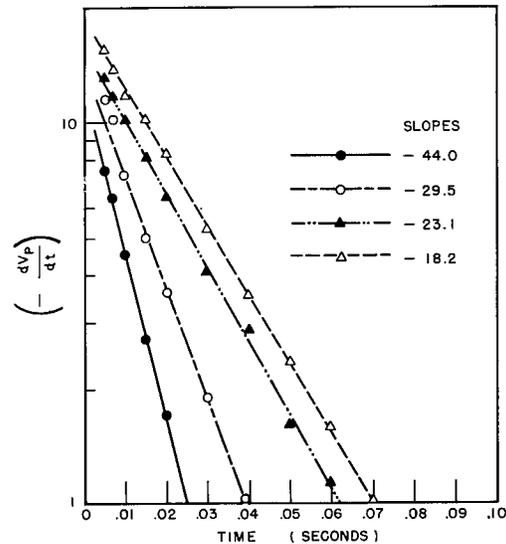


Fig. 14. $\log \left(-\frac{dV_p}{dt} \right)$ vs. time; MAW-76C cell

Knowing the value of R_I , the inductance of these circuits can be calculated from the slopes of the $-\frac{dV_p}{dt}$ vs. V_p and $\log \left(-\frac{dV_p}{dt} \right)$ vs. t curves. (V_p denotes cell voltage measured at the tops of the plates.) The results of these calculations are shown in Table 1. With the help of a nomograph¹⁰ for a one-turn loop, it was estimated that these loops should have inductances of 5-8 x 10⁻⁶ h, in good agreement with the experimental values.

TABLE 1
Inductance of External Circuits

| Run No. | Total R | Inductance from Slopes of: | |
|---------|-----------------------------|--------------------------------|--------------------------------|
| | | Fig. 13 | Fig. 14 |
| 1 | $680 \times 10^{-8} \Omega$ | $7.0 \times 10^{-6} \text{ h}$ | $6.7 \times 10^{-6} \text{ h}$ |
| 2 | 410 | 5.6 | 6.0 |
| 3 | 249 | 5.5 | 4.7 |
| 4 | 227 | 5.3 | 5.4 |

The conclusion of theoretical interest to be drawn from these results is that either $(R?)$ of Fig. 6 approaches zero or that C is so large that the current flowing does not result in appreciable discharge during the time necessary for the inductance field to be established. To attempt to distinguish between these two possibilities the data for the slower secondary decay illustrated in Fig. 12 must be examined.

First, it is evident that the negative plate is acting substantially as the constant-potential source considered in the theory, even when over 9000 amperes are being drawn, because, as has been shown, the initial decay period corresponds to a constant potential; after that the negative plate voltage decays to the extent of less than 0.01 volt in about 0.05 second. The combined secondary voltage decay amounts to about 0.05 volt in 2 seconds; this is confined entirely to the positive plate after 0.25 second and is comparatively a very slow process. Consequently, the secondary voltage decay may be represented by the circuit shown in Fig. 4, if $(R?) \neq 0$, and Eq. 1 would be applicable.*

The data for the slow decay of the positive plate voltage was expanded (Fig. 15), a smooth curve drawn through the points, and values of dE_c/dt determined as a function of potential. When the secondary voltage decay becomes zero, the maximum possible value of $(R?)$ can be found from the total voltage change over the secondary decay period, and the current flowing. It is $0.08/9000 \approx 9 \times 10^{-6}$ ohms.

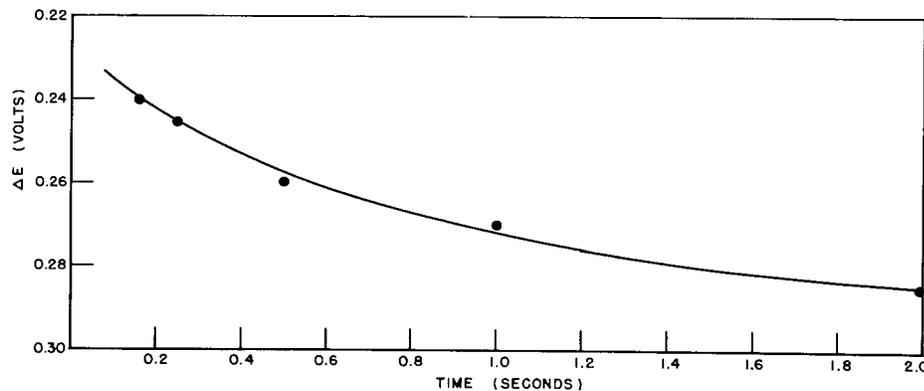


Fig. 15. Change in positive plate voltage from Fig. 12, ΔE scale expanded

* Actually, because the circuit is described accurately by the discharge of a condenser through the R-L circuit, the inductance is still in the circuit. However, the maximum value of dI/dt at the start of this decay period was measured to be minus 1270 amperes per second so that the maximum value of $L dI/dt$ is -0.005 volt per second. This is small in comparison with the measured value of dV_p/dt of 0.086 volt per second. Furthermore, since $L dI/dt$ decreases rapidly with time, Eq. 1 would become a good approximation at the longer times.

Using this value and $R_0 + R_1 = 227 \times 10^{-6}$, from the slope of the dE_c/dt vs. V curve (Fig. 16), the value of C would be estimated to be 116,000 farads.

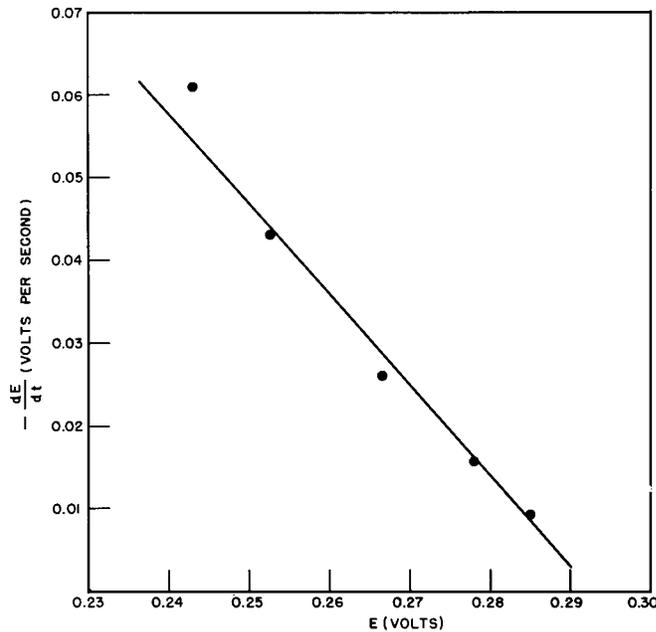


Fig. 16. $-\frac{dE}{dt}$ vs. E from Fig. 15

This cell has a gross positive plate area of 69,000 sq cm. If it may be assumed that the true area of the plates is 1000 times this value* and that the value for the dielectric constant is 4, then C may be estimated to be

$$C = \frac{0.0885 \times 10^{-12} \times 4 \times 69,000 \times 1000}{2 \times 10^{-8}} = 1,200 \text{ farads}$$

The value calculated from the slow decay would be unreasonably high on this basis. Furthermore, the value of $(R?)$ also seems to be unreasonably high, because if $(R?)$ represents the resistance of the PbO_2 active material between the grid and the solution, then it should have a maximum value

$$(R?) = \frac{10^{-5} \times 0.5}{0.69 \times 10^5} = 0.73 \times 10^{-10} \Omega$$

On this basis, it would appear that the slow decay involved in this work is not governed by the decay of an electrical capacitance associated with the Helmholtz or diffuse double layer. Neither does it correspond to the build up or decay of an electrical capacitance associated with the concentration polarization term, because such a capacitance should have a value of the same order as or lower than that calculated for the Helmholtz layer, i. e., the thickness term would be so much larger since concentration polarization is considered to extend out into solution to distances well over 100 Å°. Consequently, it may be considered that $(R?) \rightarrow 0$, that the voltage decay measured is not a function of the

* A rough estimate from particle size measurements indicates 700 to 3600 times. (Manual of Storage Battery Testing Equipment and Procedure, Eagle-Pitcher Lead Co., Joplin, Missouri, 1939 revision.)

electrical capacitance of the system, and that C cannot be measured by this method. The secondary voltage decay is to be regarded as a variable positive-plate voltage, and the equivalent circuit is that illustrated in Fig. 17.

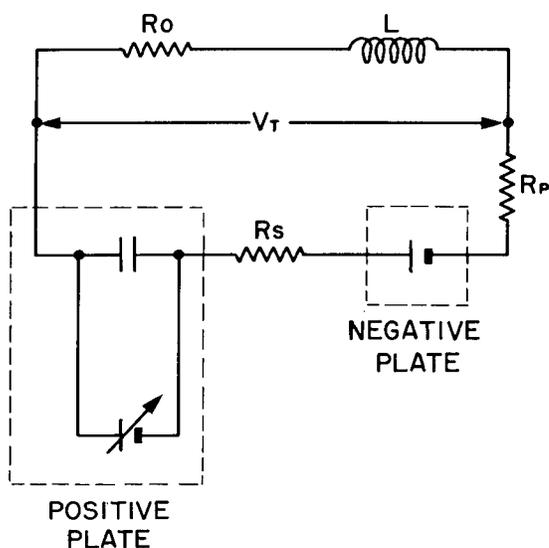


Fig. 17. The equivalent circuit of a working cell

This variable positive plate voltage actually corresponds to a change in the free energy available from the electrochemical reaction at the positive plate, and the reason for it is not hard to find when it is considered that the reaction is flooding the Helmholtz layer with water. The water would have to diffuse away as fast as it is formed in order for the reaction to go forward without a reduction in ΔF . Furthermore, it may not be considered that the water production really corresponds to an increase in R_s , due to dilution, rather than a change in ΔF , because the amount of water produced in two seconds is calculated for the current of run No. 4 to be 3.6 grams. If this were spread over an area equal to the estimated true area of the positive plate, the thickness of the layer would be $3.6/6.9 \times 10^7 = 5.2 \times 10^{-8}$ cm. If this were treated as a layer of pure water, its resistance would be

$$R = \frac{10^7 \times 5.2 \times 10^{-8}}{6.9 \times 10^7} = 0.76 \times 10^{-8} \Omega$$

and at 9200 amperes the contribution to IR_s from this source would be 0.00007 volt, whereas the measured voltage change (Fig. 12) is 0.05 volt. Actually, the resistance of this layer must be very much less than that calculated, because of diffusion and because it must contain ions carried in by the potential field.

The possibility of the slow decay being the result of a capacitance charge or discharge has been eliminated on the basis of calculations, the quantitative factors of which are open to argument - i. e., the true area, the value of the dielectric constant, and the distance of separation of the plates are not exactly known. However, it is possible to eliminate the capacitance on more definite grounds. Figure 16 shows that dV_p/dt is not a linear function of V_p (even though a line was drawn through the points to enable an estimate of C), so Eq. (1) for the discharge of the Helmholtz layer, cannot represent the data because it does not have the proper form. Furthermore, as was mentioned earlier, the circuit B of Fig. 2 cannot represent the setting up of a concentration polarization, because the charging process for such a condenser would be described by the relation

$$\frac{dE_B}{dt} = - \frac{R_C + R_T}{C_B R_C R_T} E_B + \text{const} \quad (8)$$

where E_B would be the voltage across the condenser representing the concentration polarization, C_B its capacity, R_C its shunting resistance, and R_T the total resistance in the remainder of the circuit. The equation results from reducing a second order differential equation of the type

$$\frac{d^2 E_B}{dt^2} + A \frac{dE_B}{dt} = 0$$

to first order. So again, the equation describing the charging of this capacitance is not of the proper form. Also, R_C would have a very low value, so that C_B estimated from the slope would have an unreasonably high value.

Proceeding to a consideration of the concentration polarization and its mathematical consequences, evidently, water is being produced at a rate equal to the current flowing. It can diffuse away at a rate given by $k(c_w - c_o)$, where k is a constant including the diffusion constant and c_w and c_o are the respective concentrations of water at the interface of the working electrode and in the body of the solution. The equation for the change of concentration with time at the electrode surface is then:

$$\frac{dc_w}{dt} = I - kc_w + kc_o \tag{9}$$

where I is the discharge current. Then, assuming that the electrode potential is a function of the activity of water at the surface of the electrode and that this will be given by the Nernst equation, the activities corresponding to the positive plate potentials of Fig. 15 were obtained from the data of Harned and Hamer¹¹ to be those shown in the accompanying table.

TABLE 2
Positive Plate Potential Vs. Activity of Water

| t | E | a_{H_2O} |
|------|--------|------------|
| 0.14 | -0.238 | 0.63 |
| 0.20 | -0.242 | 0.645 |
| 0.30 | -0.248 | 0.663 |
| 0.40 | -0.253 | 0.675 |
| 0.60 | -0.261 | 0.70 |
| 0.90 | -0.270 | 0.722 |
| 1.20 | -0.276 | 0.737 |
| 1.60 | -0.281 | 0.750 |
| 2.00 | -0.285 | 0.760 |

The activities were plotted as a function of time as shown in Fig. 18 and slopes obtained. Then the slopes were plotted against the water activity as shown in Fig. 19. The result is the linear relationship expressed in Eq. (9), at least over the first 0.8 second.

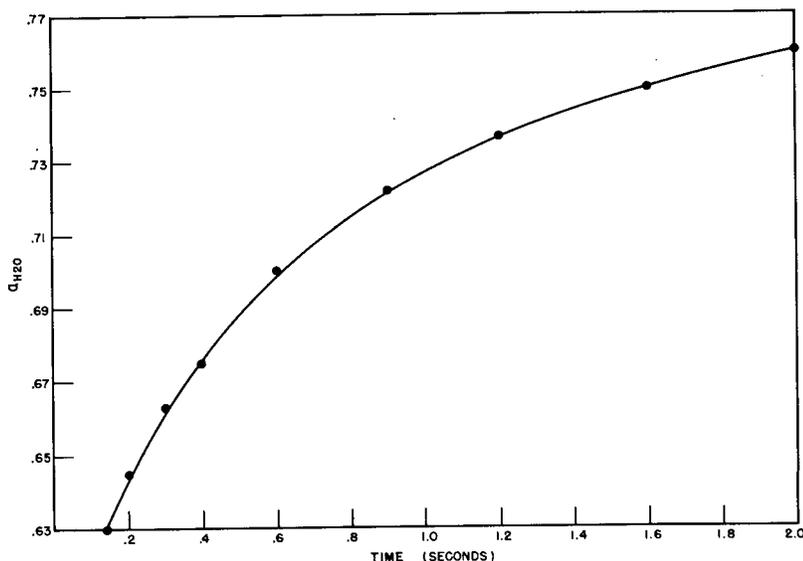


Fig. 18. H_2O activity vs. time

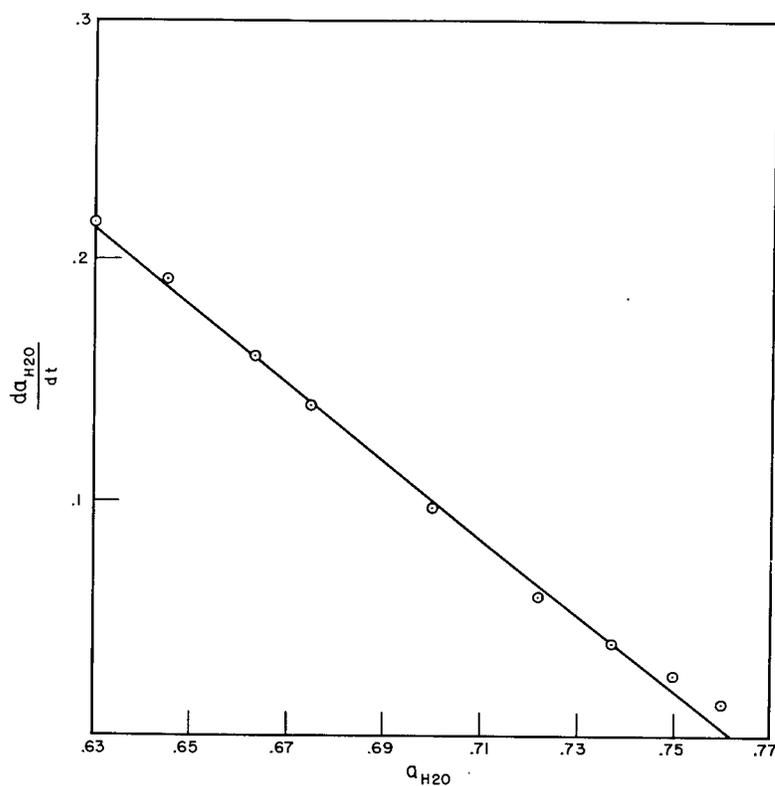


Fig. 19. $\frac{da_{H_2O}}{dt}$ vs. a_{H_2O}

So it may be concluded that the secondary decay curve does not represent the charge or discharge of a condenser, but concentration polarization at the positive plate established by the formation of water by the electrode reaction. A reduction of the specific gravity of the electrolyte from 1.280 to about 1.210 at the surface of the plate would be sufficient to produce a change in potential of 0.05 volt.

It should be noted that if the discharge of the cell represented by Fig. 17 were run through a pure resistance, then a curve of the type shown in Fig. 1 would be obtained because IR_I would be established instantaneously. The break between the IR_I drop and the concentration polarization should be sharp because of the slowness with which the concentration polarization is established in this system, and the IR_I portion could be accurately ascertained. This would be particularly true at low currents. In practice, however, some inductance effect is always included in the measurement, causing the IR_I portion of the drop to be less than infinite and to blend into the concentration polarization portion, so that more or less error is involved in establishing the IR_I portion. Such error should lead to somewhat low values of R_I .

The data for the MAQ-71 cell indicate still another simple method for obtaining the internal resistance of the cell. If Fig. 9 is referred to, it will be seen that the voltage across the external resistance becomes constant at about 0.1 second. At this time the measured voltages are accurate measurements of cell voltage and current because $dI/dt \rightarrow 0$. The discharge current is $1.02/77.4 \times 10^{-6} = 13,800$ amperes. The cell voltage has decreased by 0.494 volt and contains little or no concentration polarization, as established, and therefore the internal resistance is given by $0.494/13,800 = 35.8 \times 10^{-6}$ ohms. Now, if the data of Fig. 8 are used and the cell voltage is plotted against the current for constant amounts of discharge, the curves shown in Fig. 20 are obtained. These are very nearly linear and so it is indicated that the slopes represent a resistance. They are the same for

both curves and equal to 37.3×10^{-6} , a value in good agreement with that obtained from R_I from Fig. 9. The value of the intercept of the curves in Fig. 20 subtracted from the OCV (2.114) is the amount of concentration polarization established for the amounts of discharge concerned, regardless of rate. This shows that at currents of 2000 amperes and above the diffusion process is slow in comparison to the rate of formation of water, so that polarization depends substantially on the amount of water formed. Somewhere, at lower currents, these straight lines should fall away toward higher values of the intercept and should become closer and closer to the open-circuit voltage, as current is decreased and the diffusion process becomes more nearly able to keep up with the water-production process.

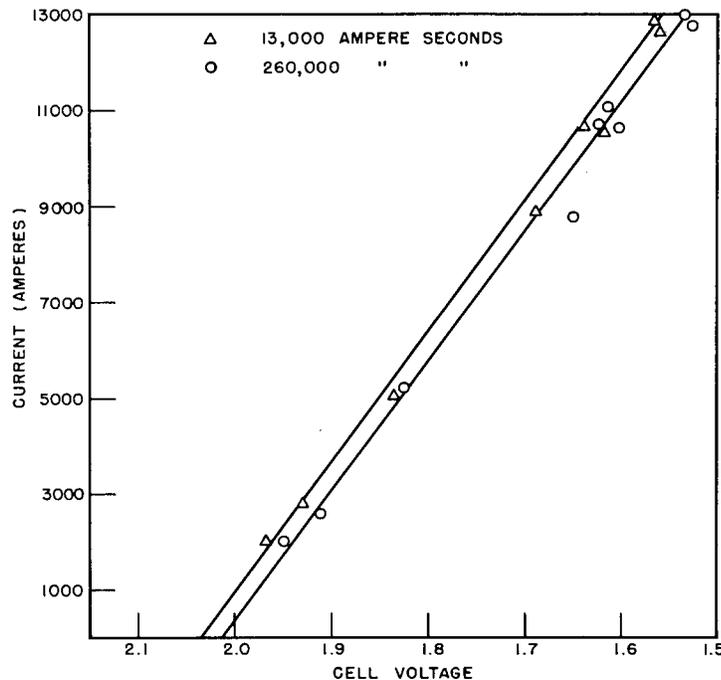


Fig. 20. Current vs. cell voltage at constant amount of discharge; MAQ-71 cell

This kind of data for establishing R_I could be obtained with an ammeter and a voltmeter. It is necessary simply to observe the voltage at different times over a few minutes of discharge at several constant rates and to plot the current-voltage relationship for equivalent amounts of discharge as was done for Fig. 20. The slope of the linear portion of the resulting curve is the value of the internal resistance of the cell for that condition of discharge.

SUMMARY

Two submarine cells of types MAQ-71 and MAW-76C were discharged through inductance-resistance series circuits of various values. The cell voltage and current flowing were measured vs. time up to two minutes.

The data for the MAW-76C cell were analyzed to show that the primary rapid cell-voltage and current transients are a function of a constant potential driving the discharge. This fact enables the cell polarization to be directly interpreted as the product of current and internal resistance dissociated from other polarization phenomena, which makes the internal resistance easily and accurately measurable.

There was found to be a subsequent, small, comparatively slow voltage decay which was shown to be located almost entirely at the positive plate up to current drains of 9000 amperes. Interpretation of this secondary decay in terms of discharge of an electrical condenser (associated with the Helmholtz, or the diffuse double layer, or even further out in solution) seems unreasonable. This decay is readily interpreted, qualitatively, to correspond to a real change in ΔF — the maximum energy the cell can produce — due to the production of water by the reaction at the positive plate and the consequent dilution of the electrolyte at the interface. The maximum energy the cell can produce at any time is completely accounted for as outside work and internal iR . Because cell voltage can be calculated from the concentration, according to the Nernst equation, the cell may be considered to be discharging reversibly.

It is indicated that diffusion of water away from the reaction site is slow compared to its rate of production at currents above at least 2000 amperes, which makes the resultant concentration polarization substantially dependent on the amount of water produced. Since this dependency results in a nearly constant amount of concentration polarization for equivalent amounts of discharge, over the current range measured, a simple alternative method of determining internal resistance is provided.

* * *

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* * *

APPENDIX A
Short-Circuit Currents from Submarine Cells

It is of interest to consider what values of short-circuit currents and current rise rates could be obtained with cells of these types. Zero resistance in the outside circuit can never be obtained, and there is a built-in inductance loop in cells of this type which cannot be done away with. This loop is bounded by the tops of the plates, by the shoulders, risers, and lugs, and by whatever shorting device is used across the lugs. If it can be assumed that the short is formed by a flat copper plate of resistance as low as, say, 5 microhms, then the maximum current that could be drawn in the absence of inductance would be given by dividing the open-circuit voltage by the sum of the internal and external resistances. For the MAQ-71 cell this would be

$$\frac{2.12}{(5 + 37) \times 10^{-6}} = 50,500 \text{ amperes}$$

and for the MAW-76C

$$\frac{2.12}{(5 + 52) \times 10^{-6}} = 37,000 \text{ amperes}$$

As concentration polarization becomes established, the cell voltages and the current would fall off rapidly to values in the neighborhood of 47,500 and 35,000 amperes. The inductance loop in the cell top can be estimated¹⁰ to have a value of about 0.08 microhenry. The time constants for the cells would be given by L/R to be: 0.08/42 and 0.08/57 or 0.0019 and 0.0014, so that values of I equal to 0.632 x (50,500 and 37,000) would be reached at these times. The short-circuit values (or slightly less) would be reached at times slightly longer.

In this connection, data may be shown for the case of an approximation to the short-circuit condition. Several discharges of the MAQ-71 cell were made with the brass cylinder arranged in the circuit as shown in Fig. 7. A typical set of data obtained for current rise, measured by the voltage drop across the brass cylinder, and cell voltage decay is shown in Fig. 21. The shunt voltage (current) becomes constant at 0.03 second and the current flowing is $0.048/1.4 \times 10^{-6} = 34,300$ amperes. The internal resistance is then calculated to be $1.50/34,300 = 43.7 \times 10^{-6}$ ohms. From values measured from the several runs the precision of the measurement for these high current conditions is $\pm 5 \times 10^{-6}$ ohms, so that this value may be considered to be in good agreement with those measured at the lower rates. The external resistance is $0.62/34,300 = 18.1 \times 10^{-6} \Omega$. The inductance may be calculated from the time constant, which is found from the current rise curve when $I = 0.632 I_{\max}$. This time is 0.06 second, so $L = tR = 0.006 \times (43.7 + 18.1) \times 10^{-6}$ or 0.37×10^{-6} henry. The nomograph¹⁰ indicates a value of 0.2-0.3 microhenry.

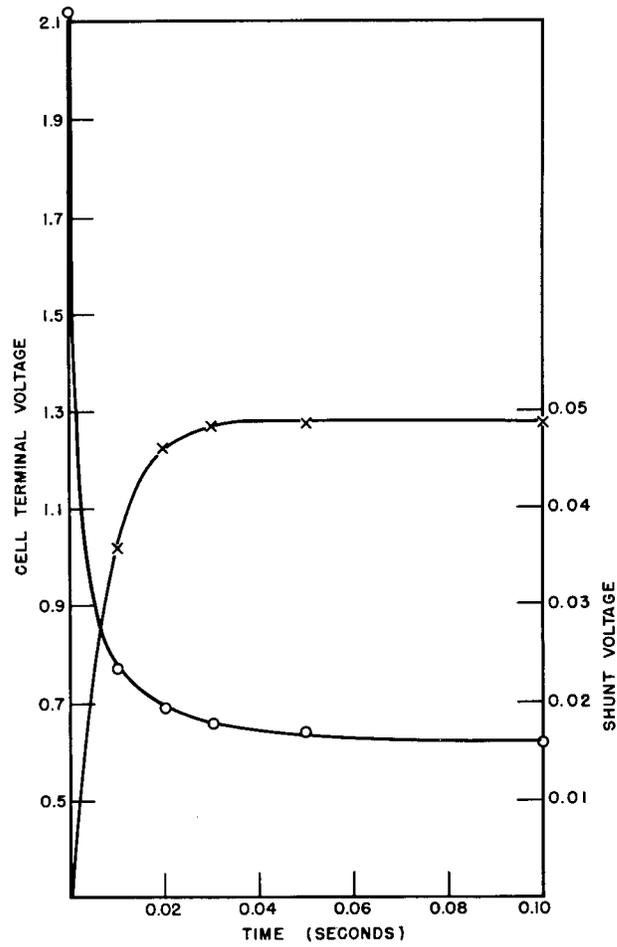


Fig. 21. Voltages across the cell terminals and the $1.4 \mu\Omega$ brass shunt; MAQ-71 cell

* * *

APPENDIX B
 Calculation of Steady-State Terminal Voltage Vs. Current
 in an Electrochemical System Involving Resistance Only

The system consists of two wires 100 cm long and 1 mm square immersed in an electrolyte separated by 1 cm. They are coated on three sides so that only one side is presented to the solution and they are so enclosed that current is constrained to flow in straight lines between them. They are capable of reacting with the solution electrochemically to furnish 2.00 volts on open circuit. The wires have a resistance of 0.0028 ohm per cm. The solution has a specific resistance such that the volume bounded by the sides of the cell and 1-cm length of the wires will have a resistance of 6.15 ohms.

Now let the resulting cell discharge through resistance of 1, 0.5, and 0.225 ohm and calculate the current in the resistors and the terminal voltage of the wires, assuming that the cell does work outside against the shorting resistance and inside against the resistances of the wires and the electrolyte. Concentration changes in the electrolyte are not allowed.

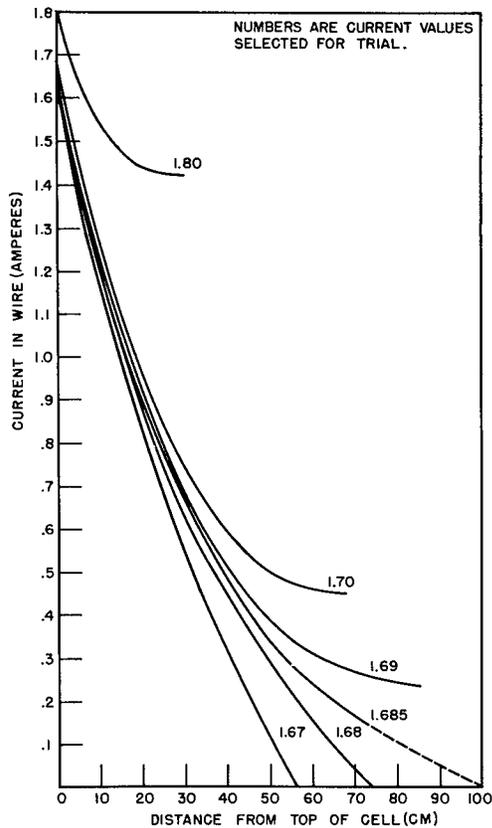


Fig. 22. Estimation of current in a cell having resistance only

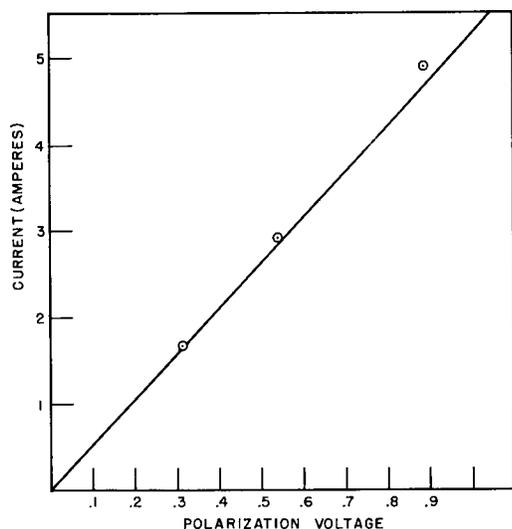


Fig. 23. Current vs. voltage for several values of external resistance

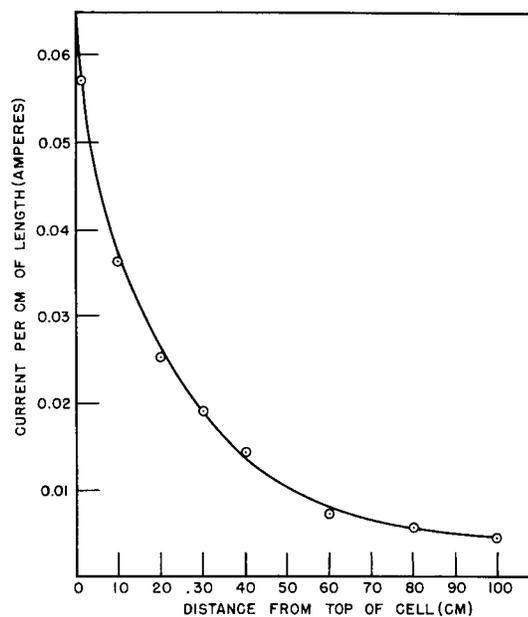


Fig. 24. Current distribution for Fig. 22

Assume some value of I for one of the outside resistances. Then the potential drop at the top of the wires is I times the outside resistance. If all this current flows through the top centimeter of the wires (which is not quite exact, but is not too far off as can be seen from the graphs included), the potential drop in the first centimeter of wire can be obtained, so the value of the potential difference across the wires at 1 cm below the top is determined. The average current through the top centimeter of solution will be approximated by the difference between the open-circuit voltage and the average of the values of potential difference across the wires at the top and at 1 cm from the top. This current is subtracted from I and the process repeated cm by cm down the wires. If the assumed value of current is too high, it will be found that current will be flowing in the wire at some distance from the bottom, but there will be no potential left to drive current through the solution. If the assumed value is too low, current stops flowing in the wire, but there is potential difference left to drive the current through the solution. Obviously both of these situations are impossible, and so, in this fashion, a series of approximations is made until a value of current in the shorting resistance is obtained which results in current and potential coming out right at the bottom of the cell.

By this means, 1.685 was determined to be the current through an outside resistor of 1 ohm. The several estimates of current made are illustrated graphically in Fig. 22. Currents estimated for resistors of 0.5 and 0.225 ohm were 2.91 and 4.90. The currents are plotted against the terminal voltage in Fig. 23. It can be seen that the resulting curve is slightly concave toward the current axis. Internal resistance calculated from the values of current and voltage in order of increasing polarization are 0.189, 0.186, and 0.182. This would seem to be due to more efficient distribution of the current density at the higher values of current drain. The current in the solution to 1-cm lengths of the wires is plotted as a function of distance along the wire in Fig. 24 for the data of the curve marked 1.685 of Fig. 22.

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