CAPACITY IN THE ALUMINUM CELL

By E. M. Dunham

Abstract

A new means of measuring the capacity of aluminum anode films is described in which the *solid* film capacity is measured without disconnection of the direct current used for film formation. The usual method of measurement has necessitated this disconnection and thus introduced an error in results due to the rapid recovery of the cell within the disconnection period. Results are obtained which verify the conclusions of A. L. Fitch and W. E. Meserve. It is found that the capacity of the solid film of oxide is inversely proportional to the quantity of electricity passed through the cell and that the resistance of the anode film in solid form is directly proportional to the quantity of electricity passed. If the film is composed of Al_2O_3 its resistivity and dielectric constant are about 1.5×10^{10} ohm cm and $7.7\mu f$/cm respectively. These values, because of the assumptions made in their calculation, are probably correct only in order of magnitude.

Introduction

THE phenomenon of anodic polarization and its application to the rectification of alternating currents has attracted many investigators and there is a marked difference of opinion as to its exact cause. In 1914 G. Schulze and R. Lindemann[1] put forward a view involving electronic processes in an exceedingly thin gas film on the surface of the anode metal. A short time later C. W. Greene[2] carried out measurements of the counter e.m.f. at extremely small intervals of time after charging and concluded that this e.m.f. alone was sufficient to cause the current reduction. A. L. Fitch[3] has proposed the theory of a double dielectric, one part of which changes with the time of open circuit and the other with the time of closed circuit. According to Schulze the film of oxide formed on the anode has a small resistance as compared to the gas layer while Fitch maintains that the solid film is the predominating factor after an appreciable time has elapsed during closed circuit. W. R. Mott[4] has done a great amount of work on this subject and states that the dielectric constant necessary to give his measured capacity values for the solid film would be extremely unreasonable.

Fischer[5] has found that the thickness of these solid films is of the order of 0.03 cm at 72 volts and that the capacity is about 0.15 μf/cm^2 at this voltage. He has also noted that as the film stands in solution on open circuit the capacity increases very rapidly with time becoming about ten times as great within a half hour.

[1] G. Schulze and R. Lindemann, Phys. Zeits. 254 (1914).
[2] C. W. Greene, Phys. Rev. **3**, 264 (1914).
[3] A. L. Fitch, Phys. Rev. **9**, 15 (1917).
[4] W. R. Mott, Elect. Chem. Ind. **2**, 352 (1904).
[5] Fischer, Zeits. f. Eleck. Chemie **10**, 869 (1904).

W. E. Meserve[6] has investigated the relation between time and current in the aluminum cell and the results are in good agreement with the theory proposed by Fitch.

The writer has investigated the capacity of the aluminum cell during closed circuit with the hope that some of the apparent lack of agreement might prove to be the result of misinterpretation of data. I believe that the data taken in this work show clearly that the formation of the solid anode film may be confined to a very simple criterion.

Experimental

The cell employed for making the investigation consisted of two aluminum wires immersed in sodium bicarbonate solution of fixed concentration. The cathode was made much smaller than the anode so that its capacity would be negligible in comparison. By use of the apparatus shown in Fig. 1 capacities as low as 0.001 μf could be measured to 10 percent accuracy by finding the resonance point of the vacuum tube wave meter and calculating

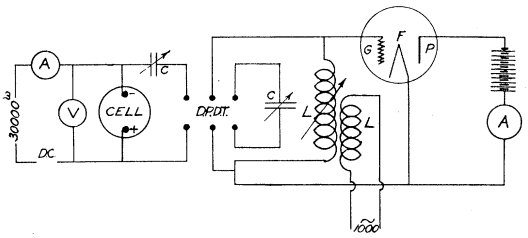

Fig. 1.

from the relation $\omega L = 1/\omega C$. The 30,000 ohm resistance is placed in series with the d.c. supply to insure a sharp resonance point when adjusting the wave meter. The 1000 cycle current was coupled to the resonant circuit so that a minimum of current was used. It may be seen at once that if the cell is to be studied under d.c. conditions any a.c. will have a detrimental effect on the anode film and must be kept as low as possible. Rawson meters reading to microamperes were used in the plate and cell circuits. The advantage of this type of apparatus lies in its ability to measure capacity without disconnection of the direct current supply and in the ease with which readings may be taken.

Difficulties encountered due to creeping of the solution and to the fluctuation of current, due to the formation of gas bubbles on the anode, were overcome by the application of insulating enamel to the upper part the electrodes and by very rapid rotation of the anode wire in solution. Maintenance of a high enough speed removed all observable traces of gas from the anode and the enamel proved to be impervious to the solution. There appeared to be no way of removing effects due to adsorption without the destruction of the film being studied. The results may contain, therefore, components due to this factor.

[6] W. E. Meserve, Phys. Rev. **30**, 215 (1927).

The data were taken in the following manner. The d.c. circuit was closed and a stop watch started simultaneously and at intervals of 300 seconds the direct current was read and the wave meter adjusted for resonance. The D.P.D.T. switch made the disconnection of the a.c. from the cell after the readings were obtained.

With the data obtained it was then possible to find the resistance of the film, the quantity of electricity passed through the cell, and the capacity of the film. Formation voltages of 30–60–90 and anode areas of 0.328–0.656–1.288 cm^2 were used in the work.

Results

By plotting E/I^2 against the time of closed circuit it was possible to compute the quantity of electricity passed through the cell since the slope of the resultant straight line has been shown by Meserve to be $2R/Q$. (In this

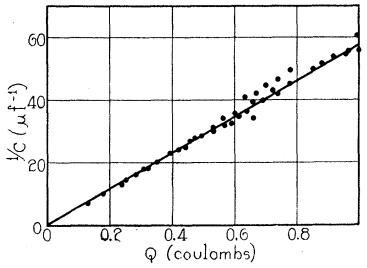

FIG. 2.

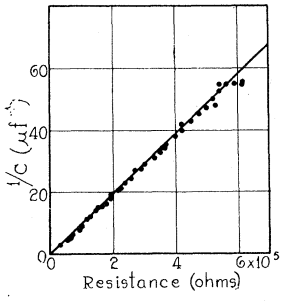

FIG. 3.

paper the following notation is used: E, voltage; I, current; R, resistance; C, capacity; p, resistivity; k, specific inductive capacity; Q, quantity; T, time.) To find the relation between the capacity of the cell and the quantity of electricity passed through it, Q was plotted against $1/C$ for the same area and three different voltages. This is shown in Fig. 2 and the result indicates that the capacity is inversely proportional to the quantity. The fact that three different voltages were used indicates that a change of voltage does not change the relation between C and Q below the breakdown point of the film.

The resistance was then plotted against the reciprocal of the capacity (Fig. 3) using the data for three voltages and three areas of anode. This relation is unmistakably linear and the conclusion is that the product of R and C is a constant equal to approximately 1.03×10^4 ohms-μf.

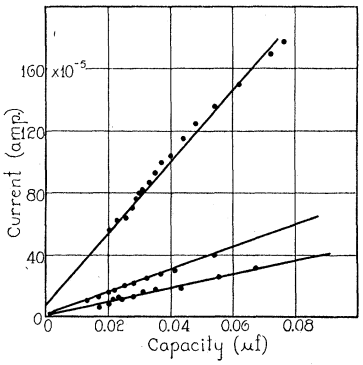

FIG. 4.

It would appear from these results that the capacity is directly proportional to the current passing through the cell at any given time providing the voltage is constant. To verify this I was plotted against C and the results are shown in Fig. 4 and bear out the preceding reasoning. Data for these curves were obtained with an anode area of 0.328 cm^2 and voltages of 30, 60 and 90.

The direct relation between capacity and time is shown in Fig. 5 and indicates that the capacity keeps dropping lower and lower with time but never reaches a steady state unless the film dissolves as fast as it is formed at some point.

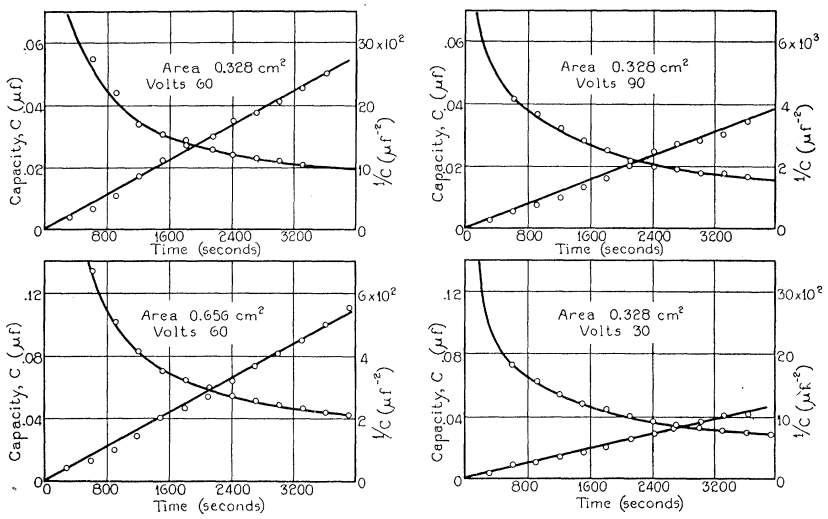

FIG. 5.

It would seem that the anomalous behavior of the aluminum cell had resolved itself into fairly simple form once the disturbing effects of creeping, surface effect, and gas accumulation are removed. The solid film seems to contribute the bulk of the resistance after some time has elapsed and the gas film only serves to resist the current at the outset due to its polarizing effect. Meserve has shown that over 95 percent of the gas goes into combination with the aluminum to form the solid film under d.c. conditions so that if the density of the film could be accurately determined in some way it would be possible to calculate the specific resistance and specific inductive capacity of the solid film. Assuming the film to be composed of Al_2O_3 of density 4 gm/cm^3, values for p and k as found from the data of this work would be 1.5×10^{10} ohm-cm and 7.7 μf/cm respectively.

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