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SOME CURRENT-TIME RELATIONS IN THE ALUMINUM CELL

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ABSTRACT

The relation between current and time in an aluminum cell with the aluminum as anode and with d.c. applied voltage has been investigated. Apparatus and methods for obtaining data are described whereby many of the difficulties which have in the past hindered observers in obtaining consistent results have been overcome. The results obtained are in agreement with the theory of Guthe as modified by Fitch. After the lapse of a certain time (t_0), which was found to be about 300 seconds, from the moment of applying the voltage, the dependence of current on voltage conforms to the relation $E/i^2=Ct+D$. From this is deduced a linear relationship between E/i and quantity of electricity passing through the cell, ($E/i-E/i_0=Cq/2$). The slope, $Cq/2$, is in the nature of a resistance and assuming that it represents the resistance of the oxide layer, the thickness and resistivity (3.403×10^{12} ohm cm) of the layer are computed. The data obtained show that the slopes of these lines vary inversely with the square of the anode area, which checks with the theory. Results obtained by Günther-Schulze with tantalum are compared and are shown to check the theory. After a short time of closed circuit the opposition to the flow of current when the aluminum is the anode is shown to be due primarily to the ohmic resistance of the solid layer which increases in value with time of closed circuit.

INTRODUCTION

AS A result of his work with the aluminum cell in an attempt to explain its rectifying action, Guthe[1] proposed the oxide-gasfilm theory. According to this theory a solid oxide or hydroxide film is formed on the anode which increases in thickness with the passage of current, and a thin film of gas is formed on this solid layer which further increases the resistance of the cell. The action of rectification is attributed to the ease with which free electrons which are present on the surface of the anode can penetrate the oxide and gas layer and traverse the electrolyte to the cathode, whereas the heavier cations are more or less completely held up by the film.

On the basis of this theory, Fitch,[2] while investigating the counter-electromotive force of the cell, showed that some permanent change must take place in the cell, for the current does not attain a steady minimum value but constantly drops lower and lower. His experimental results agreed very closely with a formula derived on the assumption that the thickness of the gas layer decreases with the time of open circuit. The increase in thickness of the solid layer results in an increase in the resistance of the combined layer and after a comparatively short time this is by far the predominating effect, thus explaining the slow diminution of current with time. As a result of this work it was concluded that any cell will function as a rectifier if a passage of current will cause a stable oxide film of high resistance

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[1] Guthe, Phys. Rev. **15**, 327 (1902).

[2] A. L. Fitch, Phys. Rev. **9**, 15 (1917).

to be formed on the anode and if the electrolyte is such as to liberate oxygen on electrolysis. This is in accord with the results of Graetz and Pollak[3] and also with the results of Günther-Schulze.

Günther-Schulze[4] has proposed a modification of the above theory in which he ascribes the valve effect to the gas film only. Smits,[5] after discussing the assumptions made in the theories advanced, arrived at the conclusion that the explanations are not sufficient to meet all the facts; such as for instance that amalgamated aluminum shows no rectifying effect.

Various metals have been used, aluminum probably being the most common, but later investigation has shown that many other metals possess the same property to a greater or less degree, notably tantalum. Electrolytes most commonly employed are the alums, carbonates, and phosphates. In view of the importance of the problem it seemed desirable to repeat and extend the measurements, and, by more refined methods of procedure, to determine if a careful study of the cell with the aluminum as the anode will not throw some additional light on the theory of its rectifying action.

APPARATUS AND METHOD

The cell employed for making the tests consisted of two electrodes, one of aluminum and the other of platinum, immersed in a 20% solution of sodium bicarbonate. The aluminum electrode was in the form of 99.8% pure, 0.102 cm diam. wire cut to the desired length. The cathode consisted of platinum foil of about 1 sq cm area, welded to a platinum wire which was

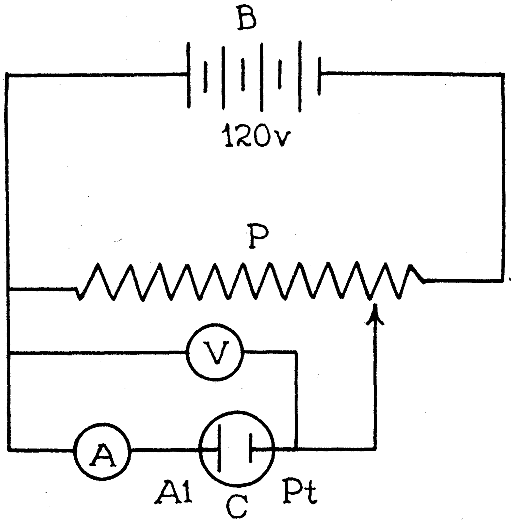

Fig. 1. Diagram of connections; *A*, Rawson multimeter; *C*, aluminum cell; *V*, Weston voltmeter; *P*, potentiometer rheostat.

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[3] Pollak, Elec. Zeits. **25**, 359.

[4] A. Günther-Schulze, Phys. Zeits. **22**, 146 (1921).

[5] A. Smits, Adak. Amst. 876 (1921).

sealed through the end of a glass tube. Platinum was chosen for this electrode in order to eliminate any reaction with the gas evolved at its surface. Changes in effective area due to the electrolyte's creeping up on the platinum wire were prevented by keeping the platinum-glass seal below the surface of the electrolyte at all times. For a variable source of voltage, a 3000 ohm potentiometer rheostat was connected across the terminals of a storage battery of 120 volts. A Rawson Multimeter was connected in series with the cell and a Weston voltmeter was connected in parallel with the cell and Multimeter.

Because of two factors, namely, the effect of surface tension in varying the effective area of the aluminum electrode, and second, the exposing of new areas to the action of the electrolyte by the breaking off of large bubbles of gas which form and adhere to the surface of the aluminum, considerable difficulty was at first experienced in obtaining consistent results. A coating of shellac was applied to the electrode where it entered the electrolyte but it was observed that after a time the liquid attacked the coating thereby rendering it ineffective. A black enamel such as is used for enamelling metal articles, which adheres very closely and which presents a very hard surface when dry, proved entirely satisfactory if two coats were applied. The resistance of this coating was sufficiently high so that any current which might pass through it was so small as to cause no deflection of the meter at 120 volts. To overcome the second difficulty, the bubbles were kept wiped off the aluminum by means of two camel's hair brushes so placed that they completely surrounded it. These brushes were driven by a small adjustable speed motor through a cam and vertical shaft. With this arrangement the brushes could be made to move up and down over the electrode at any desired speed and thus kept bubbles of gas from collecting on its surface.

RESULTS

Observations were made of the relation between current i and time t of closed circuit for different areas of aluminum anode and for different values of applied potential E. The results indicate that a relation of the form

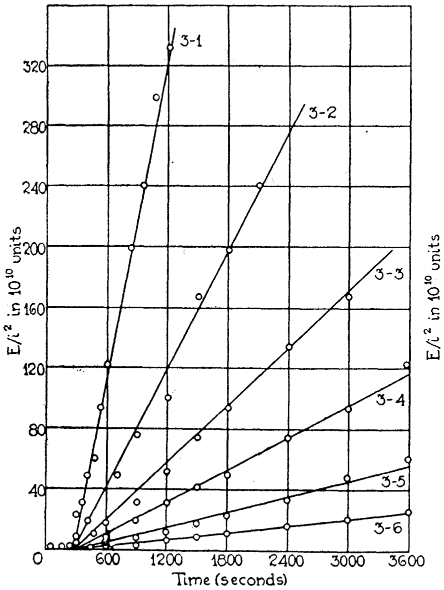
$$E/i^2=Ct+D. \tag{1}$$

correlates the data fairly well provided t is not less than about 300 sec. In this expression the slope C depends on the area of the anode. The extent to which this relation is satisfied is illustrated in Figs. 2 and 3. In Fig. 2 is plotted the variation of E/i^2 with time for a constant potential of 60 volts and for various areas of aluminum anode. It will be noted that the points lie nearly on straight lines whose slopes vary with the anode area. In Fig. 3 the anode area is constant (0.652 sq cm) while the potential is given values of 20, 60, 100, and 120 volts. The points lie fairly well on a single straight line.

The significance of Eq. (1) is most clearly brought out as follows. Transposing

$$i=(E/C)^{1/2}(t+a)^{-1/2}$$

where $a = D/C$. Multiplying this expression by dt and integrating between two instants t_0 and t (over range of time for which (1) is valid), gives the quantity of electricity q which has passed through the cell between these instants.



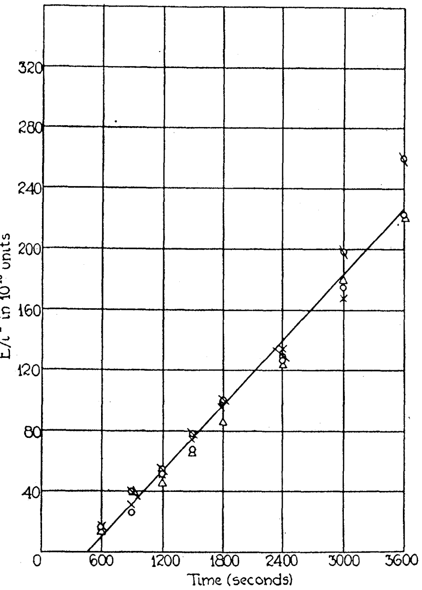


Fig. 2. E/i^2 plotted against time of closed circuit for different areas of aluminum anode. Numbers refer to those of column 2, Table I. 20% N sodium bicarbonate solution. 60 volts between electrodes. Temperature, 20°C.

Fig. 3. E/i^2 plotted against time of closed circuit to show the effect of various impressed voltages with a constant anode area. 20% N solution of sodium bicarbonate and anode area of 0.652 sq cm. Temperature, 20°C.

$$q = \int_{t_0}^{t} i dt = \frac{2E}{C}\left(\frac{1}{i} - \frac{1}{i_0}\right)$$

Rearranging, this becomes

$$E/i - E/i_0 = Cq/2 \tag{2}$$

We may regard E/i as the resistance of the cell at any instant. Hence (2) becomes

$$R - R_0 = Cq/2$$

This indicates that the resistance of the cell, after a time of about 300 sec, increases linearly with the quantity of electricity which has passed through it.

If this increase in resistance $Cq/2$ be assumed to be due to a solid layer of uniform thickness it may be written as $\rho T/A$ where ρ is the specific resistance of the solid, T its thickness and A its area. If this layer is formed by electrolytic action its mass M may be expressed as Kq where K is the electrochemical equivalent of the substance formed. Its mass is also ATd where d is its density. We thus find that the constant C of Eq. (1) has the value given by

$$C=2\rho K/A^2d,$$

which indicates that the slopes of the lines in Fig. 2 should vary inversely as A^2. To see how nearly this prediction is satisfied, we multiply the slopes in each case by the square of the corresponding areas. The results are presented in Table I. It will be noted that the products are reasonably constant.

TABLE I

Area aluminum (sq cm)	Line of Fig. 2	Slope $\left(\frac{\text{volts}}{\text{amp}^2\ \text{sec}}\right)$	Area$^2\times$Slope $\left(\frac{\text{volts cm}^4}{\text{amp}^2\ \text{sec}}\right)$
.330	3–1	35.3×10^8	3.85×10^8
.491	3–2	12.8	3.08
.652	3–3	6.6	2.81
.973	3–4	3.5	3.32
1.293	3–5	1.7	2.88
1.940	3–6	0.76	2.86
			Mean 3.13×10^8

The E/i^2 intercepts of the lines in Fig. 2 also vary inversely as A^2, however the reason for their negative value is not apparent.

The complete equation for the lines of Fig. 2 becomes on using the mean values of slope and intercept as obtained from all the data,

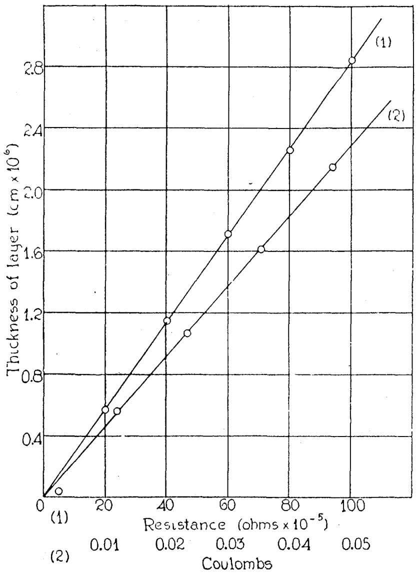
$$E/i^2=3.02\times10^8t/A^2-11.49\times10^{10}/A^2. \tag{3}$$

Likewise Eq. (2) becomes

$$E/i-2.09\times10^8=1.51\times10^8q/A^2 \tag{4}$$

If the solid layer formed on the anode be aluminum oxide, Al_2O_3, its resistivity may be computed and its thickness for various times of closed circuit may be determined from the relation $r=\rho T/A$. The mass of oxygen liberated at the anode is given by $(.829\times10^{-4})q$ grams. If the liberated oxygen all unites with aluminum to form oxide, the mass of oxide will be given by $1.77\times10^{-4}q$ grams. Using this value for K in the expression for the slope and solving for ρ, its value is found to be 3.403×10^{12} ohm-cm. For sake of comparison it may be noted that the resistivity of glass is 9×10^{13} at 20°C and that the value for varnish is 2×10^{12}. This shows that the resistivity of the assumed oxide layer is of the same order of magnitude as that of some of the best dielectrics. The thickness of the layer for various times of closed circuit are plotted in Fig. 4.

In the computation of the specific resistance of the oxide layer it was assumed that all of the oxygen liberated at the anode combined with aluminum to form oxide. To obtain some idea as to the amount of gas which actually does combine with aluminum, the following test was made. Two cells were made up using U tubes having side tube connections near the top. In one of these cells two platinum electrodes were placed in a sodium bicarbonate solution of the same concentration as that used in the previous work while in the other tube an aluminum and a platinum electrode were placed in the same kind of electrolyte. These two cells were connected in series electrically with the aluminum as anode in the second cell. With this arrangement the same volume of gas is formed at each anode. Connection was made to the side tube above each anode by means of rubber tubing to two long horizontal glass tubes which were fastened to the tops of two meter sticks. These two tubes, when containing a drop of water served to measure the volume of gas given off at the two anodes. The results when using an aluminum anode of 32.6 sq cm on closed circuit for 900 seconds are shown in Fig. 5. The curvature in the line for aluminum is probably due to the time lag of the gas because of the small diameter of the measuring tube. These results show that about 96% of the liberated oxygen combines with aluminum.



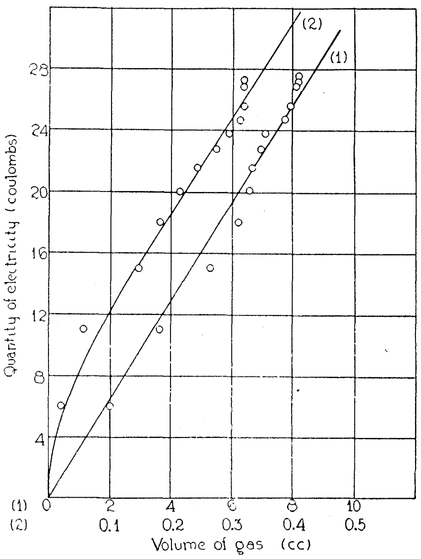


Fig. 4. Linear variation of thickness of solid layer with quantity of electricity which has passed through the cell, and with resistance of the cell.

Fig. 5. Quantity of electricity plotted against volume of gas given off at the anode to show relative magnitude for aluminum and platinum anodes. (1), platinum, diam. of measuring tube .34 cm (2), aluminum, diam of measuring tube, .0767 cm. Temperature 20°C. 20% N solution of sodium bicarbonate.

The results obtained by Günther-Schulze[4] with tantalum were plotted in accordance with the theory given in this paper in Fig. 6. It is interesting to note that the results obtained with tantalum are in agreement with this theory, but one outstanding difference is that the $\frac{E}{i^2}$ intercept is positive instead of negative.

The results of this investigation seem to indicate that after a rather definite time of closed circuit the opposition to the flow of current when the aluminum is the anode is due primarily to the ohmic resistance of the solid layer, which increases in value with time of closed circuit. The current does not attain a steady minimum value but constantly drops at a diminishing rate with time of closed circuit. Tests carried over a period of several days showed this to be true. It has been shown that nearly all of the gas liberated at the anode combines with aluminum to form the solid layer. Consequently if the substance formed is aluminum oxide, the computed value of the specific resistance and the thickness of the solid layer are reasonably correct. The results are in agreement with the theory of Guthe as modified by Fitch.

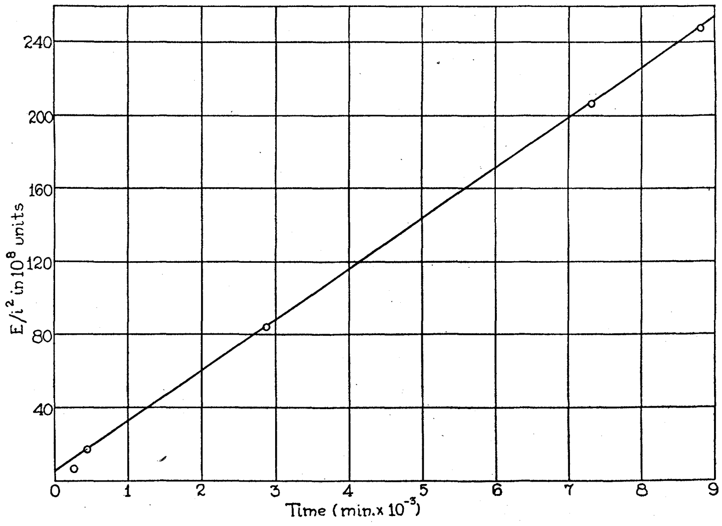


Fig. 6. E/i^2 plotted against time of closed circuit for a tantalum anode having an area of 12.5 sq cm in a 5% N solution of potassium nitrate with impressed voltage of 100. Temperature, 20°C.

In conclusion the writer wishes to express his thanks to Professor A. L. Fitch, at whose suggestion the problem was undertaken, for his kindly interest and helpful counsel during the progress of the work; and to Professor Ernest Merritt of Cornell University for aid in the arrangement of the material for publication.

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