THE CAPACITY AND RESISTANCE OF ALUMINIUM ANODE FILMS.[1]

By C. McCheyne Gordon.

THERE is formed on aluminium when used as an anode in most solutions, a film which is highly insulating in character so long as the voltage applied is not too high, or the direction of the current is not reversed. These films have been the subject of a large number of investigations; interest in them having been especially lively during recent years since the possibility of taking advantage of the asymmetric resistance for rectifying alternating currents has been realized. These investigations have proven that the resistance of the films and the voltage at which the resistance begins to decrease rapidly, generally called the critical voltage, vary with the electrolyte used as well as with the temperature. They have shown however considerable conflict of evidence and opinion as to the chemical constitution and reasons for the asymmetry of resistance and its breaking down at higher voltages.

No extensive study of the electric capacity of these films has heretofore been made. Scott[2] made a few measurements on the polarization capacity of aluminium in connection with a number of other metals, while the electrodes were subjected to a definite polarization, but his measurements on aluminium are all taken at low voltages — not greater than 1.75 volts; and only in one solution — sulphuric acid. A number of others have given capacity values, but without explicit statements as to conditions or method of measurement.

Method of Measurement.

The method used to measure the capacity is that developed by the writer[3] at the suggestion of Nernst for the measurement of the

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[1] A summary of this paper was given at the Ithaca meeting of the A.A.A.S., July, 1906.

[2] Scott, Wied. Ann., 67, p. 388, 1889.

[3] Gordon, Wied. Ann., 61, p. 1, 1897.

capacity of polarization. It is the well known wheatstone bridge arrangement for comparing capacities with slight modifications. The connections are shown in the figure. E_1 and E_2 are the aluminium electrodes dipping into the solution S; E_1 is made so large in comparison with E_2 that the capacity measured is practically that of the small electrode alone; K is a three-point switch by means of which the cell is connected first to the battery P, in order to form the film on E_2, and then switched into the bridge for measurement.

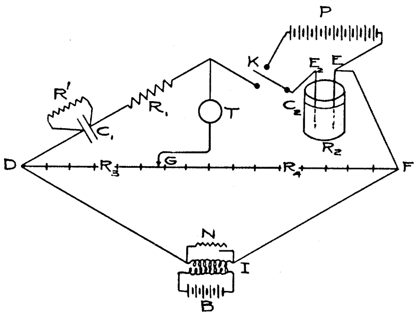

Fig. 1.

The capacity C_1 was a mica condenser of 0.5 Mf., or a paper condenser of 6.8 Mf. This paper condenser was marked by the maker 10 Mf., which was evidently its value by direct current measurement. Such condensers always give much lower values when measured by alternating currents; but their values are always consistent with one another, if a number of such condensers are compared with one another or with mica condensers.

R_1 is a variable non-inductive resistance in series with the condenser C_1, which is necessary to balance the conductivity of the solution. DGF is the bridge wire and T the telephone receiver. I is a small induction coil with automatic breaker, operated by the battery B; N is a shunt by means of which the current is kept small. Large currents give polarization effects which interfere with the accuracy of the bridge setting.

R' is a variable resistance which serves to balance the conductivity of the film itself. This resistance was found however to be unnecessary in most of the measurements of the capacity and was generally omitted.

With this arrangement of the bridge three conditions must be satisfied simultaneously in order that there shall be no current in the telephone, namely;

$$C_2 = C_1 \frac{R_3}{R_4}, \quad R_2 = R_1 \frac{R_4}{R_3}, \quad \text{and Film } R = R' \frac{R_4}{R_3}.$$

Using electrodes of a few square centimeters area, the position of the minimum is practically determined by the capacities. If the resistances are too far off from the proper ratios, the minimum is not sharp but with an approximate adjustment of the resistances it is possible to obtain a setting on the bridge certain to one millimeter.

These experiments were planned with the expectation that we could thus readily obtain an accurate measurement of the capacity and the resistance of the films at the same time. It was found however that the films most suitable for capacity measurements had a resistance so large as to have little effect on the sharpness of the telephone minimum, and it was accordingly decided to leave the resistance of the films for a later investigation, which is still in progress. Some interesting preliminary results on the resistance obtained are given further along in this paper.

The electrode E_2 on which the films were formed was a strip of sheet aluminium about 1 cm. wide and dipping into the solution from 1 to 4 cm. The other electrode was a sheet of aluminium about twenty times as large. In preliminary measurements a small electrode was also tried in place of the large one ; a large sheet of lead was also substituted for the large aluminium electrode. The capacity calculated per $cm.^2$ of one side of the electrode was the same for all three cases.

The Polish of the Surface.

The degree of the polish of the surface makes a considerable difference in the size of the capacity. Surfaces formed by cutting the aluminium under turpentine with a sharp instrument gave the smallest capacities. Sheets polished with emery cloth and sand paper gave larger values. At higher voltages the difference in the polish does not make so much difference. The variations in capacity with the polish of the surface are probably due to the actual differences in surface area. With the higher formation voltages the films are thicker, the uneven places are probably to some extent filled up and the capacity values consequently not so far apart. As the capacity values for surfaces cut under turpentine were practically the same as those of smoothly polished aluminium as obtained from the manufacturers, the latter was used for the rest of the experiments. A series of measurements showing the amount of the variation with the differently polished surfaces is given in Table I.

Table I.

$(NH_4)_2CO_3$ Solution.

Preparation.	Capacity in Mf. per cm.^{2}	
	20 Volts.	100 Volts.
Cut under turpentine	0.33	0.0686
Emery cloth under turpentine	0.57	0.111
Emery cloth in air	0.70	0.129
Sand paper in air	0.65	0.129

Tubular Electrodes.

A number of observers have found that tubular electrodes, especially when water-cooled, are better for rectifying the current than the ordinary sheet electrodes. Fischer[1] found that water-cooled tubular electrodes, in sulphuric acid, insulated well at 100 volts and gave films several tenths of a millimeter in thickness. The tubular electrodes, however, even when cooled with water near 0°, give the same capacity values as the sheet electrodes. The thicker films found for sulphuric acid and sodium sulphate seem to be composed of two layers, the thicker part being a film of good conductivity, concerning which more will be said further on, under the discussion of the thickness of the films. The most noticeable difference between the water-cooled tube electrodes and those without water was in the rapidity with which the capacity increased after the formation current was turned off. In the first five minutes after turning off the current from the water-cooled electrode the capacity increased about ten per cent., while without water the increase was less than one per cent. in the same time.

Temperature.

A number of observers have found that the voltage at which the films begin to break down — the so-called critical voltage — decreases rapidly with the increase of the temperature. No corresponding variation in the capacity was found. The capacity re-

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[1] Fischer, Zeit. für Eleck. Chem., 10, p. 869, 1904.

mained the same from 10° to 25° C., at least within the limits of experimental error, two to three per cent. After this had been established for three or four solutions, the remaining measurements were taken at room temperatures, probably varying between 15° and 25° C.

TIME FOR THE FORMATION OF THE FILMS.

The formation of the film is not by any means instantaneous. The current is at first large, but decreases rapidly, coming to practically constant values after some time. The decrease in the capacity as the current continues to run is likewise at first rapid and then slower, approaching a minimum value. This decrease in the capacity is not proportional with that of the residual current. For example in one case where the residual current was measured, the capacity decreased but six per cent. while the residual current changed in the ratio of six to one. Generally after five seconds application of the direct current the capacity was within a few per cent. of its minimum value. The time required to bring it within one per cent. of its minimum value varied largely with the voltage and somewhat with the solution. For 20 volts it was generally about five minutes and for 100 volts sometimes as much as twenty minutes. The values for the capacity given in this paper are minimum values, assuming that the minimum is attained when a further application of the formation current for five minutes gives a decrease of capacity of less than one per cent.

CAPACITY MEASUREMENTS WHILE THE POLARIZING E.M.F. IS STILL APPLIED.

Scott inserted the polarizing battery in the telephone arm of the bridge, and thus was able to take the capacity measurements while the polarizing current was acting. I made a comparison of this method with that as given above and found that the capacity measured with the current on, was the same as after it was off. The method as given above was accordingly used on account of its greater simplicity. The two methods give very different values for the film resistance, but more will be said about this in another paragraph.

FORMATION VOLTAGE AND CAPACITY.

After the above preliminary experiments, the first question considered was as to how the capacity changes with the voltage applied to form the film — which we shall speak of hereafter as the "formation voltage." Scott found that the capacity of aluminium in sulphuric acid decreased rapidly as the formation voltage increased, but as he did not use voltages higher than 1.75, he did not discover any simple relation between capacity and voltage. My first measurements were with a potassium alum solution and it was seen at once that for higher voltage the *capacity varies inversely as the formation voltage.* Measurements for two solutions are given in Table II. Similar results were obtained for a number of other solutions. The areas of the films whose capacities are given in this table were not measured.

TABLE II.

$HNaNH_4PO_4$ Solution.			$K_2Cr_2O_7$ Solution.		
Formation Voltage. I.	Capacity. II.	Product. I. × II.	Formation Voltage. I.	Capacity. II.	Product. I. × II.
20	1.60	32.0	10	3.8	38.0
30	1.11	33.3	20	1.95	39.0
40	0.83	33.2	40	0.95	38.0
50	0.64	32.0	81	0.48	38.9
60	0.54	32.4	90	0.42	37.8
71	0.46	32.7	100	0.38	38.0
80	0.40	32.0			
91	0.35	31.8			
100	0.32	32.0			

The variations of the product from a constant value are well within the experimental error. The natural explanation of this relation between the capacity and the formation voltage is that the thickness of the films is proportional to the formation voltage. During the progress of this investigation an article has been published by Fischer[1] in which he comes to the same conclusion in regard to the films formed in sulphuric acid; but the sulphuric acid films are quite different in character from those of most solutions as will be set forth below.

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[1] Fischer, Zeit. für Elek. Chem., 10, p. 869, 1904.

The Capacity in Different Solutions.

Experiments were next made to determine how the capacity might vary as the electrolyte was changed. The literature of the subject shows that with a change of the electrolyte there are large variations in the insulating power of the films and in the critical voltages. With sulphuric acid for instance, at room temperatures, the films break down between twenty and thirty volts, while for sodium potassium tartrate the critical voltage has been found to be at least as high as one hundred volts and for citric acid five hundred volts. Where chemical analyses of the films have been made they have been found to contain a considerable portion of the acid radical of the electrolyte. In view of these facts it was expected that each electrolyte would have, for any given formation voltage, its own individual capacity value, differing from that for other electrolytes, because of the difference in thickness and dielectric constant, which a difference in the chemical nature of film would probably cause. This expectation, however, was not realized, as will be seen from the figures given in Table III.

Table III.

Electrolyte.	Capacity in Mf. per cm.^{2}	
	Formation Voltage 20.	Formation Voltage 100.
$(NH_4)_2CO_3$	0.34	0.069
$K_2Cr_2O_7$	0.35	0.069
$(CHOH)_2\ (CO_2)_2\ KNa$	0.35	0.069
$NaNH_4HPO_4$	0.34	0.072
$(CH_2)_2\ (COH)\ (CO_2H)_3$	0.33	0.070
Na_2SO_4	0.39	
H_2SO_4	0.50	

The above series of measurements was repeated several times. The variations seldom amounted to as much as three per cent. These small variations are easily accounted for when we take into consideration that with the voltmeter used errors in reading as large as two per cent., at twenty volts, might readily be made. The exact length of the film, determined simply from the depth immersed, could likewise not be measured with any great accuracy on account of capillary irregularities. The above figures show, therefore, that within the experimental error at least, the capacity of the first five solutions, both at twenty and one hundred volts, is the same; and at the same time confirm the relation found before, *i. e.*, that the capacity is inversely proportional to the formation voltage.

The larger values found for sodium sulphate and sulphuric acid may be due to the fact that in these solutions the film dissolves more rapidly than in the others. While for the other solutions there was no decrease of the capacity with the film standing in the solution for five minutes after the formation current was turned off with sodium sulphate there was a small, and with sulphuric acid a large decrease in this time. Two sets of measurements showing the rapidity of this increase are given in Table IV.

Table IV.

H_2SO_4 Solution, Dilute.

Seconds after Disconnecting the Formation Current.	Capacity (Size of Electrode not Measured).	
	Series I.	Series II.
20	0.400	0.393
80	0.452	0.427
170	0.65	0.62
230	0.93	0.89
290	1.09	1.07
350	1.20	1.16

Films in Fused Salts.

Insulating films are also formed with fused salts as the electrolyte. In a mixture of fused sodium and potassium nitrates, the capacity was found to be smaller than in the water solutions. The capacity increased, however, so rapidly after the formation current was switched off, that no accurate determinations of the minimum value could be made. A series of measurements showing this rapid increase in capacity is given in Table V.

It is evident that the value obtained five seconds after the formation current is switched off is not the minimum value, but even this is only about one-sixth as large as water solutions give at the same voltage. The film evidently dissolves rapidly, making the film thinner and the capacity consequently larger.

TABLE V.

Fused KNO_3 and $NaNO_3$. Temperature 265° C. Form. Volts 20.

Seconds after Formation Current was Disconnected.	Capacity in Mf. per $cm.^2$
5	0.06
60	0.16
120	1.05

The resistance of these fused salt films is much less than those of water solutions. While the resistance of the latter was so large that a resistance in parallel with the condenser had little effect upon the minimum, in case of the fused salts this parallel resistance must be adjusted somewhat carefully. On account of the rapid shifting of the position of the minimum no very accurate measurement of this resistance could be made but the largest value obtained was about 400 ohms for a surface of 15 $cm.^2$ or 6000 ohms per $cm.^2$

THE RESISTANCE OF THE FILMS.

As was stated in a previous paragraph the resistance of the films formed at these voltages is so large as to have little effect on the bridge minimum. As these voltages seemed to be the most suitable for obtaining the comparative values of the compacity, it was decided to carry through the above measurements without attempting to obtain accurate values for the resistance at the same time, and to make an investigation of the resistance of the films later. The latter investigation is not yet completed but a few of the more striking results as determined from the preliminary experiments are included here.

1. The apparent resistance, as calculated from the residual direct current, does not increase at all in proportion with the decrease in capacity. If, as it seems reasonable to suppose, the decrease in the capacity during the formation of the film is proportional to the increased thickness of the film, the increase in apparent resistance is due to something else than mere increase of thickness.

2. The resistance as measured with the small alternating current in the bridge is much smaller than the apparent resistance as calculated from the size of residual current.

3. The resistance as measured in the bridge while the formation

current is still active (the arrangement of Scott) is only about one third as large as when measured after the direct current is taken off (the arrangement of the figure above). A discussion of the probable cause of this striking difference is deferred until some measurements of the resistance under other conditions are completed.

The Thickness of the Films.

If we knew the dielectric constant for these films we could of course calculate their thickness from their capacity. But even without such knowledge we can draw some conclusions as to the maximum and minimum values of the thickness from what we know as to the possible range of the dielectric constants, as well as to the relative thickness of the films under various conditions of formation.

In the first place it is to be noted that the films formed in sulphuric acid and sodium sulphate are very different in character from the other films. In the sulphates the whole film is evidently not insulating in charater; *but it seems as if we have an insulating film covered with a much thicker conducting one.* The reasons for this conclusion are as follows. Mott[1] and others had found that the films in sulphuric acid were much thicker than in other solutions. Mott says in one place that he found the thickness in sulphuric acid at twenty volts greater than that in a phosphate solution at 100 volts. In *apparent* contradiction to this I found the capacity of the sulphuric films to be somewhat larger than in any other solutions at corresponding voltages. If we use water cooled tubular electrodes it is easy to form films in sulphuric acid at formation voltages as high as 100, whose thickness is readily measured as it amounts to several tenths of a millimeter. Fischer[2] found the thickness of such films at 72 volts to be 0.03 cm. and I have found films formed at 100 volts to be between 0.03 and 0.04 cm. thick. The lowest values found for the capacity of such a film was 0.15 Mf. cm.^{2} (Sheet aluminium with same surface polish gave 0.129 Mf.)[3] As the film stood in the solution the capacity increased very rapidly, becoming about ten times as large within a half hour, but there was no corresponding change in the thickness during that time.

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[1] Mott, Elect. Chem. Ind., 2, p. 268, 1904.

[2] Fischer, l. c.

[3] This was in sodium carbonate solution, as given in Table I.

This alone would be enough to cause us to conclude that the visible film is not the same as the insulating film whose capacity is measured. The calculation of the dielectric constant which would be necessary in order that the whole film should have such a large capacity makes this conclusion doubly sure. Using the formula

$$C=\frac{KA}{4\pi d},$$

where C is the capacity, K the dielectric constant, A the area, and d the thickness, all expressed in c.g.s. units, for a capacity of 0.15 Mf. per cm. and a thickness of 0.03 cm., the dielectric constant would be over 50,000, which is of course out of the question.

In all the other solutions the films are not thick enough to be noticeable to the eye, and I know of no reason for supposing them to consist of anything else than a single insulating layer. It is safe to assume that the dielectric constant for this layer is somewhere between 1 and 80. Mott[1] and Zimmerman[2] conclude from their experiments that it is probably about 14. Table VI. gives the thickness of the films calculated from the capacity per cm.^{2} found above, assuming the dielectric constant to be 1, 10 and 100.

Table VI.

Calculated Thickness.

	$K=1$.	$K=10$.	$K=100$.
20 volts	2.5×10^{-7}	2.5×10^{-6}	2.5×10^{-5}
100 volts	12.5×10^{-7}	12.5×10^{-6}	12.5×10^{-5}

Zimmerman and Mott have estimated the thickness of such films from their interference colors. Mott estimates the thickness for 100 volts to be 10×10^{-5}. Zimmerman gives the thickness of a 100 volt film as 7.5×10^{-5}, but in another place speaks of a 100 volt film with a thickness of 2×10^{-5}.

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[1] Mott, Elect. Chem. Ind., 2, p. 352, 1904.

[2] Zimmerman, Trans. A. E. S., 5, p. 147, 1904; 7, p. 309, 1905.

The Nature of the Films.

Mott[1] has advanced the hypothesis that the chemical nature and consequent thickness of the films are largely dependent upon the nature of acid radical of the electrolyte. Since, however, the capacity is independent of the electrolyte, this view, at least in so far as it has to do with the insulating film, is no longer tenable. The capacity being the same, we must conclude that the thickness and the dielectric constant are both independent of the electrolyte, or that in all the different solutions tried, the one varies exactly as the other. The latter might accidentally happen for two solutions but that it should be so for so many solutions is too improbable to be considered. If, however, we have the thickness and the dielectric constant both unchanged, it follows that we have practically the same chemical constitution for all these solutions. Of course there must be some chemical or physical differences in the films to account for the differences in conductivity and critical voltages. The results of this paper seem to fit in best with the theory that the films in all the water solutions are made up of aluminium hydroxide full of pores, and that the variations in the behavior of the films as we go from one electrolyte to another are due to the variation in the size or number of such pores.

Central University,
Danville, Ky., July, 1906.

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[1] Mott, Elect. Chem. Ind., 2, p. 444, 1904.