

ON THE THEORY OF THE ELECTROLYTIC RECTIFIER.

By S. R. COOK.

WHEN aluminum, with a free metallic surface, is the anode of an electrolytic cell which has dilute sulphuric acid, aluminum sulphate, potassium aluminum sulphate (alum), ammonium aluminum sulphate, potassium cyanide, or potassium ferrocyanide for the electrolyte, there is quickly introduced into the electrolytic cell a condition which produces a very high apparent resistance, so long as the voltage is not above a certain critical value. If, however, the aluminum is made the kathode, in any of the above solutions, and carbon or platinum the anode, the cell becomes a very good electrolytic conductor. This anomalous action of the aluminum anode in an electrolytic cell, in which oxygen is one of the products of electrolysis, was observed in 1857 by Buff,¹ while making more detailed observation on Wheatstone's² experiments for determining the position of aluminum in the voltaic series. Buff found that when dilute sulphuric acid was the electrolyte, a dark skin appeared on the surface of the aluminum anode and that the resistance was very much greater than when the aluminum was the kathode and either carbon or platinum was the anode.

In 1869, Thomson's electrometer being accessible for the measurement of potential, independent of resistance; Tait³ while measuring the polarization of several cells determined the polarization of aluminum in dilute sulphuric acid. He applied an electromotive force of six Grove cells (10.44 Daniels) and with the Thomson electrometer found a counter electromotive force of 5.20 Daniels. No explanation was given for this very high counter E.M.F. and until very recently no explanation has been offered for the very high apparent resistance of the aluminum anode.

¹ Buff, Liebig's Annalen, CII., p. 169, 1857.

² Phil. Mag. (4), X., p. 143, 1854.

³ Phil. Mag. (4), XXV!!!., p. 243, 1869.

In 1877 Beetz¹ investigated the dark skin observed by Buff and concluded that it was the normal oxide or hydroxide. While Lawrie,² from the effect of amalgamation on the electrochemical behavior of aluminum, came to the conclusion that the action of the aluminum anode was due to an oxide or suboxide. Oberbeck³ and Streintz⁴ considered the film formed on the aluminum anode a non-conductor and suggested that the aluminum, non-conducting film, and solution formed a condenser. They found that this cell had a measurable capacity, and a condenser consisting of two aluminum plates in dilute sulphuric acid has been described by Haagn.⁵ In 1897 it was shown by Pollak⁶ and independently by Gratz⁷ that a cell composed of aluminum and carbon or aluminum and platinum with dilute sulphuric acid as the electrolyte could be employed to rectify an alternating current. This discovery brought the cell into practical importance and in 1898 the efficiency of this electrolytic rectifier was investigated by Wilson.⁸

Norden⁹ investigating the chemical composition of the film on the aluminum anode, came to the conclusion that with dilute sulphuric acid as the electrolyte the film was composed of the normal aluminum hydroxide $Al_2(OH)_6$ with some aluminum sulphate. Wilson has shown that this film of oxide or hydroxide formed on the aluminum anode has a very high resistance; having observed values up to 10,000 ohms. Norden¹⁰ attempted an explanation of the cause of the high anodic resistance of aluminum. From observations he found that the resistance of the resting cell was much less than the active cell and also that the film (supposed aluminum hydroxide) was acted upon by the solution and he concluded that if the film was weakened by the dissolution action of

¹ Pogg. Annalen, Vol. CXXVII., p. 45; Vol. CLVI., p. 464.

² Phil. Mag. (5), XXII., p. 213, 1886.

³ Wied. Annalen, XIX., p. 625, 1883.

⁴ Wied. Annalen, XXXII., p. 116, 1887; XXXIV., p. 751, 1888.

⁵ Zeit. für Electrochemie, III., p. 470, 1896-1897.

⁶ Compt. Rend., CXXIV., p. 1443, 1897.

⁷ Weid. Annalen, LXII., p. 323, 1879.

⁸ Electrical Review (London), p. 371, 1898; Pro. Royal Society, Vol. LXIII., p. 329, 1898.

⁹ Zeit. für Electrochemie VI., pp. 159, 188, 1899-1900.

¹⁰ Elec. World and Eng., Vol. 38, p. 681, Oct. 26, 1901.

the liquid bathing it while resting, the same action would take place in the active cell and the current would break through these weakened parts. Burgess and Hambuecher,¹ following the same general theory, tried to establish the existence of these small areas of disruption by removing the aluminum anode and depositing copper from a solution of copper sulphate in the openings made by the dissolution of the film. This theory, namely, that the high apparent resistance of the cell, when aluminum is the anode and low resistance when aluminum is the kathode, is due to the high ohmic resistance of the film which by disruption or dissolution action allows the current to flow through uninterrupted in one direction and closes up and almost completely prevents the passage of the current in the other direction, will be discussed later in connection with the data here presented.

Dr. Guthe² in a paper read before the American Association for the Advancement of Science, at its Pittsburg meeting, advanced another theory for the explanation of the resistance of the aluminum anode. From experiments performed he concluded that the resistance was due to a film of gas, probably oxygen, at the anode, which, when the current was reversed, united with hydrogen or was dissolved in the solution. This theory will be reverted to again after the presentation of the data.

Taylor and Inglis in the *Philosophical Magazine* of March, 1903, have also suggested a theory of the aluminum anode. They have shown that by adding salts, containing negative ions, which would normally dissolve the anode, to the dilute sulphuric acid solution, the high resistance at the aluminum anode was prevented or destroyed. The theory advanced is that the high resistance is due to the property of the film of hydroxide to allow all ions except the SO_4 ions to pass through.

In view of the fact that Tait had, by a method independent of the resistance, obtained a counter electromotive force greater than is usual in electrolytic cells, and in view of the fact that the theories heretofore advanced to explain the apparent high resistance of the aluminum anode are not without objection, it seemed possible that,

¹Trans. Amer. Elec. Chemical Soc., Vol. I., p. 147, 1902.

²PHYSICAL REVIEW, Vol. XV., p. 327, 1903.

by a closer investigation of the value of the counter electromotive force, some further explanation of the high anodic resistance of the aluminum cell might reveal itself.

2. *Apparatus.*—The apparatus for the investigation of the counter electromotive force of the electrolytic rectifier consisted of an accumulator of twenty-eight cells, the electrolytic rectifier, which consisted of a cell with an aluminum plate, 7.5×10.2 cm., and a carbon plate of the same cross-sectional area, in a solution of potassium aluminum sulphate, a Weston ammeter, milliammeter and voltmeter, a relay and several keys and pole-changers arranged as in Fig. 1.

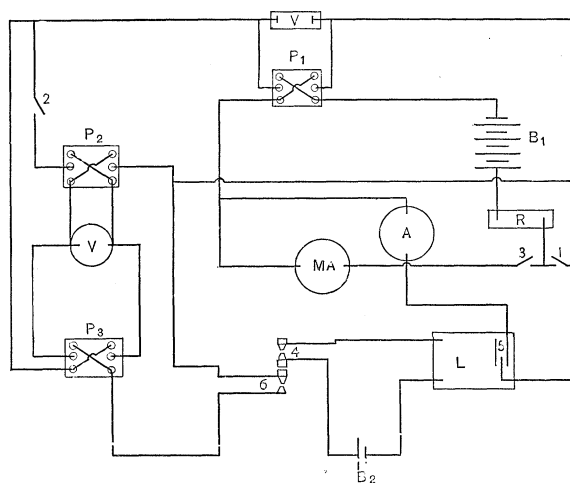


Fig. 1. Apparatus Diagram.

In the diagram V is the electrolytic rectifier, B_1 the accumulator, R a rheostat, L the relay, A and MA are the ammeter and milliammeter respectively, and V is the voltmeter. The pole-changers are designated by p_1, p_2 , etc., and the keys by the numbers 1, 2, 3, etc., No. 5 being the break key on the relay, which was operated by the auxiliary battery B_2 .

3. *The Method of Making the Observations.*—All connections having been made the plates were set at a distance of about 2 cm. and the electrolyzing current made by closing keys 1 and 5. The electrolyzing current now flows through the relay, the ammeter and the

electrolytic cell. The applied electromotive force is measured by closing key 2, thus putting the voltmeter across the terminals of the cell. The current flowing through the cell, when small, was measured by opening key 1 and closing key 3, thus putting the milliammeter in the circuit. When key 3 was opened key 1 was closed and remained closed throughout the remaining time for each observation. In order to measure the counter electromotive force, key 2 being open, key 4 was closed. The action of the relay opened key 5 and broke the electrolyzing current and the next moment the closing of key 6 put the voltmeter across the poles of the cell.

4. *Errors of the Observations.*—When the voltmeter was thus placed across the terminals of the electrolytic rectifier, after the electrolyzing current had been broken, the indicator of the voltmeter would quickly swing up to a position depending on the applied electromotive force and the temperature of the cell, and would fall back more slowly to a comparatively small value.

It will be evident that the method was not one of great precision, there being at least two errors which could not be accurately determined. First the momentum of the moving system of the voltmeter would tend to carry the pointer beyond the true reading, by an amount depending upon the voltage to be measured. It was found by repeated observation, by quickly applying a constant voltage for a short time to the voltmeter that if the voltage applied was 14 volts, the pointer would swing to a position indicating 15 volts and that if the applied voltage was 30 volts the pointer would be carried to a position indicating 32 volts, showing that the momentum of the system caused an error of about six and two thirds per cent. This, however, depended on the time during which the electromotive force was applied. The percentage here given is that for infinite time. Secondly there exists an error due to the decrease of the counter electromotive force, during the interval between breaking the electrolyzing current and making the voltmeter circuit. This interval was short, but as the polarization diminished very rapidly at first, the error may have been several per cent. We may also include in this error the error due to the time required for the pointer of the voltmeter to swing up to its maximum reading. The value of this second error could not be determined with the ap-

paratus used, and no correction has been made for it. The data in the tables are corrected for the error due to momentum. It will be observed that the second error, not corrected for, decreases the true value of the counter E.M.F.; accordingly the values recorded are not so great as the true values.

5. *Measurements of the Counter E.M.F.* — In the following tables are given a series of sets of measurements of the counter electromotive force of the electrolytic rectifier, at various temperatures and conditions of the cell. Four representative sets at temperatures 1° , 23° , 48° and 58° , respectively with aluminum as anode and one at 1° with aluminum as kathode are recorded. These determinations were several times repeated with results agreeing substantially with those recorded.

Measurements of applied E.M.F. current and counter E.M.F. at 1° with a well-formed aluminum anode and a carbon kathode are given in Table I.

TABLE I.

Temperature 1°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.1	.0002	1.9	28.0	.0040	24.5
4.5	.0003	3.3	30.0	.0045	26.2
6.7	.0005	6.0	32.0	.0075	26.8
9.0	.0007	7.6	34.0	.0160 ?	27.6
11.2	.0010	9.8	36.4	.0165	28.8
13.5	.0015	11.6	38.7	.0220	30.0
15.5	.0020	13.5	41.0	.0250	31.0
17.4	.0025	15.0	43.2	.0275	31.2
19.5	.0025	17.0	45.0	.0460	31.0
21.3	.0027	18.8	47.2	.1100	29.0
23.4	.0031	20.7	49.3	.1800	27.0
25.7	.0036	22.6	51.0	.5000	19.0

The data from this table are exhibited in the curve in Fig. 2 so far as 30 volts. Curve *I* exhibits the applied E.M.F. and current. Curve *II* exhibits the counter E.M.F. and current. Curve *III* exhibits the electromotive force from Ohm's law, assuming the resistance to be constant at 2 ohms, the value obtained from a series on measurements by Kohlrausch's method.

Table II. gives the data for the same cell under the same conditions with aluminum as the kathode.

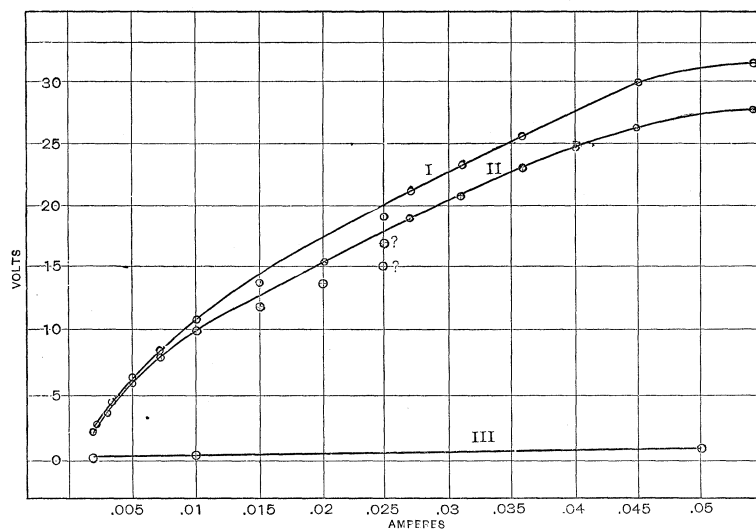


Fig. 2. Applied Counter and Reversed E.M.F.

TABLE II.
Temperature 1°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
1.07	.020	0.4	1.5	.150	0.8
1.2	.020	0.4	2.0	.300	1.25
1.3	.050	0.6	2.5	.500	1.5

Tables III., IV. and V. give applied and counter E.M.F. of the same cell for temperatures 23°, 48° and 58° respectively.

TABLE III.
Temperature 23°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.0	.0002	1.2	19.6	.0046	16.0
4.4	.0009	3.0	21.0	.0060	17.0
6.4	.0012	5.0	23.0	.0110	19.0
8.5	.0015	7.0	25.2	.0160	20.0
10.2	.0019	9.0	27.0	.0320	21.0
13.0	.0022	11.0	29.0	.0900	21.0
15.2	.0025	12.0	32.0	.2250	21.0
16.7	.0035	14.0	32.2	1.2000	19.0

TABLE IV.
Temperature 48°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.1	.0002	1.2	20.0	.0120	17.0
4.4	.0020	3.0	22.2	.0700	16.0
6.8	.0030	4.5	24.3	.1600	16.0
9.0	.0040	7.0	26.2	.2100	16.5
11.3	.0050	9.0	28.5	.2250	18.0
13.8	.0065	10.5	31.0	.2500	19.0
16.0	.0080	12.5	33.0	.3100	19.8
18.2	.0115	15.5	34.7	.6000	19.0

TABLE V.
Temperature 58°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.0	.075	0.5	19.4	.280	11.3
4.2	.120	2.0	21.2	.340	13.0
6.4	.140	3.8	23.2	.425	14.0
8.5	.160	5.0	26.2	.460	15.0
11.0	.185	6.5	28.2	.550	16.5
13.0	.200	8.0	29.8	.860	17.0
15.0	.250	9.0	31.0	1.300	16.0
17.5	.250	10.0			

The data from the respective Tables I., II., III. and V. are exhibited in Fig. 3.

Curves *I* and *I'* exhibit the relation of the applied and counter electromotive forces to the current, the temperature of the cell being 1°.

Curves *II* and *II'*, and *III* and *III'* exhibit similar data from Tables III. and V. respectively at temperature 23° and 58°, and curve *IV* exhibits the data from Table II. giving the applied E.M.F., when the aluminum is the kathode, at a temperature of 1°.

The effect of temperature upon the apparent resistance of the aluminum anode is very marked. At temperatures not much above 55° the very rapid increase in current at a certain critical electromotive force is hardly perceptible, while at temperature below 50° the position of the critical value of the electromotive force is

clearly defined. The value of the critical electromotive force decreasing as the temperature increases at the rate approximately of 1 volt per degree between 1° and 23° .

6. *Discussion of Data.*—A comparison of the applied and counter electromotive forces in Tables I., III., IV. and V. and their corresponding curves, Figs. 2 and 3, show that eighty-five to ninety-five per cent. of the apparent resistance is accounted for by the counter electromotive force and it only remains to explain the cause of this very high counter electromotive force and account for the breaking down of the high apparent resistance at a comparatively high

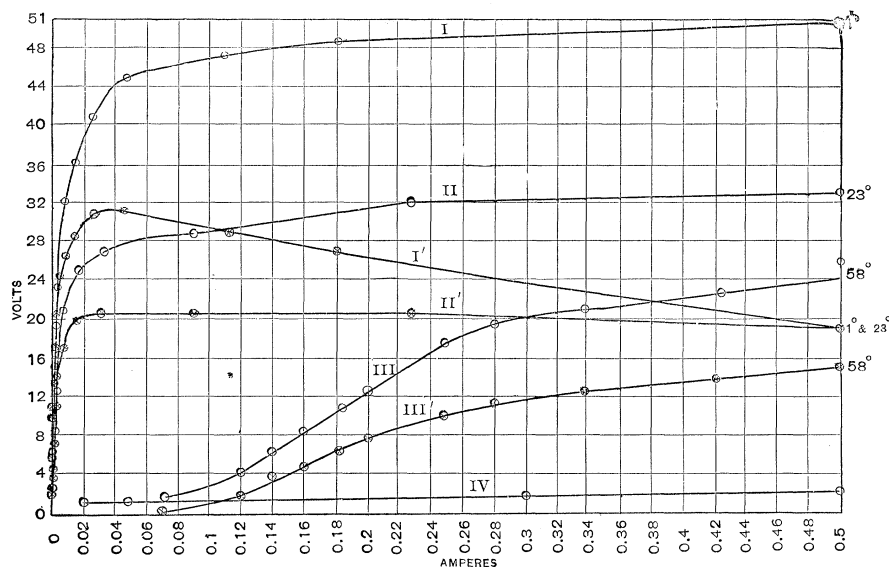


Fig. 3. Applied and Counter E.M.F. for Different Temperatures.

electrical pressure. So long as the applied electromotive force remains below a certain critical value depending on temperature, a uniform whitish film of an oxygen compound of aluminum is formed over the surface of the aluminum anode. This film can be shown to be extremely hard, compact, non-crystalline and apparently insoluble in the electrolyte. The ohmic resistance of the film has also been shown to be very high.

When, however, the applied electrical pressure is greater than a certain critical value this film of alumina changes from a white

non-crystalline substance to a dark crystalline substance. These dark crystalline formations occur in parts of the plate only and they always begin to form at those parts where the oxygen is found in the greatest quantities. This dark crystalline formation has very much the appearance of corundum or emery. If a plate is removed at this stage and carefully examined it will be found that the dark parts are elevated and rough to the touch. When examined with a microscope, of forty diameters magnifying power, the crystalline formation can be easily seen and frequently not only dark corundum-like crystals but crystals of brilliant colors could be easily detected. On a very superficial examination, these brilliantly colored crystals have the appearance of being small crystals of ruby and sapphire.

The formation of crystals exposes the metallic surface of the aluminum plate to the action of the electrolyte and allows the anions to discharge to the anode increasing very rapidly the current, while the continued formation of the crystals, so long as the electrical pressure is greater than the critical value, continues to expose fresh surfaces of the metallic aluminum to the action of the anions. When the critical value of the applied electromotive force has been reached it will be observed that the counter electromotive force decreases and the current greatly increases as the applied electromotive force is increased. That is, as soon as the anions can give up their charge to the metallic aluminum the counter electromotive force decreases. The very high counter electromotive force then is due to the presence of a large number of charged ions around the aluminum plate. These anions (possibly SO_4) are prevented from reaching the metallic conductor by the whitish film of alumina that has been formed on the anode. A further evidence of the presence of this wall of charged ions is given, if a conductor is brought near the anode, when there is a high counter electromotive force, a spark discharge will occur in the solution between the conductor and the layer of charged ions and at the time of the discharge the current greatly increases. It is not believed that this momentary increase of current is due to any rupture of the film but simply to the renewing of the layer of anions which had lost their ionic condition by discharging to the conductor.

Still another experiment shows the existence of this layer of charged ions. The electrolytic cell was under an electrical pressure of 26 volts with a counter electromotive force of 17.5 volts, giving .07 ampere of current. Air bubbles were forced into the solution and caused to pass over the surface of the aluminum anode. The current rapidly increased to 0.35 ampere and fell again to .07 ampere, when the bubbles ceased. The pointer of the milliammeter responded very quickly to the passage of a large bubble over the surface of the anode but it was not possible to measure the decrease of the counter electromotive force under these conditions. The temporary increase of the current may be explained by the temporary destruction, in part, of the concentration series, by the passage of the air bubbles over the plates.

If the electrical pressure is maintained for some time above the critical pressure the film of alumina not only forms crystals but is dissolved by the solution, forming depressions in the plate where the crystallization had produced elevation. This dissolving of the dark crystalline formation was observed by Norden and was made the basis of his theory of the aluminum anode. I think, however, that it is very doubtful that the white alumina is dissolved by the solution even by long standing. The crystalline formation may however either be dissolved by the solution or it may separate from the plate and fall into the solution in the granular form. By maintaining the voltage above its critical value for several hours an aluminum anode that had been formed with the dark crystalline formation, was largely dissolved by the electrolyte. This dissolution of the crystalline formation does not however offer an explanation of the anodic phenomenon.

The explanation given by Burgess and Hambuechen is also based upon the idea of a non-conducting film which changes its properties rapidly when the current is reversed. As already stated when the aluminum is the anode oxygen is the secondary product of the discharge anion. The oxygen unites with the aluminum, forming a film over the surface of the anode. When aluminum is the cathode hydrogen is the secondary product of the kation and is set free. The kation also discharges to the metallic surface of the aluminum. If the film is already formed hydrogen gas is formed between the

metallic surface and the film, breaking away small areas of the film. It was probably these small areas that Burgess and Hambuechen considered the valves through which the current passed and into which they deposited copper.

When aluminum is the anode and the potential is less than the critical value, it has been shown that there is formed a film of alumina on the surface of the aluminum, which prevents the anions from discharging to the metallic surface of the anode, thus causing the formation of a layer of charged ions around the plates which produces a high counter electromotive force. This high counter electromotive force decreases the effective potential and manifests itself as a high apparent resistance.

7. *Determination of the Rate of Increase of the anions Around the Anode.*—In accordance with the theory that the ions would discharge their electricity when the free metallic surface was exposed by the crystallization of the aluminum; it became important to know whether a free metallic aluminum surface would conduct an electrical current as freely when it was the anode as when it was the cathode. In order to determine the conductivity of a free metallic surface of aluminum, a plate was freed from all oxide film by scraping with a sharp tool after the application of turpentine, thus giving a very bright metallic surface. The plate was then made the anode of an electrolytic rectifier with carbon as cathode and the data in the following table were obtained, the applied E.M.F. being constant at 26 volts.

TABLE IV.

Time Hr. Min. Sec.	Amperes.	Counter E.M.F.	Time Hr. Min. Sec.	Amperes.	Counter E.M.F.
1 42 30	9.000	0.2	1 47 00	.130	16.0
1 42 35	1.500	0.5	1 48 00	.135	16.5
1 42 45	.300	3.0	1 50 00	.130	17.0
1 43 45	.250	7.0	1 55 00	.120	17.0
1 44 30	.190	15.0	2 00 00	.105	17.0
1 45 30	.150	15.0	2 10 00	.090	17.5
1 46 30	.145	16.0	2 50 00	.070	17.5

The curves exhibiting the relation between the time and the current, and the time and the counter E.M.F., are given in Fig. 4. Curve *I* shows the very rapid fall of the current from 9 amperes to

.07 ampere. Curve *II* shows the rapid increase of the counter electromotive force, and curve *III* exhibits the constant current

when aluminum was the kathode. Although the value of the current as first measured when aluminum was anode is not so great as its constant value when aluminum was the kathode, the very close approximation to the constant cathodic value is a strong argument in favor of the theory that the first anions (SO_4) discharge their electricity when in contact with the metallic aluminum and that it is the formation of the negative ions in a concentration series or the presence of the free oxygen, evolved from the union of SO_4 with H_2O ; in process of union with the aluminum that produces the high counter electromotive force which reduces the current to a minimum.

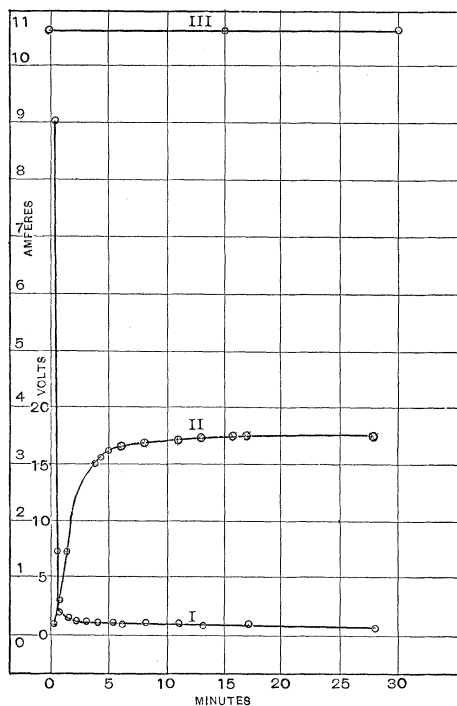


Fig. 4. The rate of Formation of an aluminum Anode and the Development of the Counter E.M.F.

8. *Is the Oxygen Added Directly to the Aluminium?* — An effort was made to answer this question by the following experiments:

A large H cell was constructed. Each leg of the cell was fitted with a carefully weighed aluminum electrode, a thermometer, and a graduated tube for receiving and measuring the gas given off. The cell was filled with a solution of potassium aluminum sulphate, placed in a constant temperature bath and a current passed through until a measured quantity of hydrogen was liberated. The electrodes were then removed, weighed and the gain or loss determined. Four independent experiments were performed and the following observations and notes were made:

First Experiment.—The aluminum electrode exposed a clean metallic surface to the electrolyte. The temperature of the cell was 15°.

Results from first experiment :

Weight of anode before the experiment,	24.3915 grams.
Weight of anode after the experiment,	24.3997 grams.
Gain in weight of anode during experiment,	.0082 grams.
Weight of kathode before the experiment,	23.9955 grams.
Weight of kathode after the experiment,	23.9949 grams.
Loss in weight of kathode,	.0006 grams.
Hydrogen liberated at kathode,	59 c.c.
Oxygen liberated at anode,	0 c.c.
Amount of oxygen that should have been liberated,	.0415 grams.

On the theory that the oxygen is added directly to the anode this experiment should have given an increase in the weight of the anode of .0415 gram, while it gave only .0082 grams of oxygen or about one fifth the amount required. However, this experiment shows that the oxygen does not remain in the gaseous form and must be accounted for either by assuming that it forms a soluble compound with the anode, and is then dissolved by the electrolyte, or that it forms an insoluble compound with the anode, part of the anode being dissolved by the electrolyte to account for the discrepancy. Norden¹ concluded that the electrolyte acts chemically on the anode at ordinary temperature, and in my own work I have been successful in dissolving a large part of an aluminum anode after it had been formed with the dark formation. In order to account for the loss by dissolution the experiment was repeated with the cell in an ice-bath.

EXPERIMENTS 2 AND 3 WITH THE H CELL.

The H cell arranged as in the former experiment was packed in ice and allowed to reach a temperature of 1°. At first an electromotive force of 33 volts was applied and the amperage during the three hours and twenty minutes fell from 0.105 ampere to .008 ampere. The electrical pressure was then increased to 52 volts and the amperage soon became constant at .07 ampere. In three hours 70 c.c. of hydrogen was liberated at the kathode. No gas was liberated at the anode.

¹ L. c.

The anode showed a gain during the experiment of .0318 grams and the kathode a loss of .0045 grams. If all the oxygen set free from the electrolyte had been added to the anode, and there had been no dissolution of the anode during the experiment there should have been an increase of .0501 grams, showing a discrepancy of .0184 grams; that is, about thirty-six per cent.

The experiment was again repeated under the same conditions and the anode showed, for 55 c.c. of hydrogen liberated, a gain of .0243 instead of .0372 grams, a discrepancy of .0149 or forty per cent.

It was here observed that some of the oxygen collected at the upper end of the anode and that most of the formation was at this place. It was also observed that the dark formation showed signs of having been dissolved by the electrolyte. To prevent this dissolution of the formed anode a band of india rubber was fitted over that portion of the anode which passed through the surface of the solution, and the experiment was again repeated at a temperature of 0°.

For the fourth experiment the following results were noted: 25 c.c. of hydrogen was liberated. The increase in weight of the anode was .0237 gram. The weight required to account for 25 c.c. of hydrogen is .01792 gram, the excess of weight at the anode being .00583 gram.

Although these experiments have by no means been conclusive in showing that the oxygen is added directly to the aluminum as Al_2O_3 , they nevertheless show that the oxygen does not remain as a gaseous film around the anode, producing an ohmic resistance, and they also show that the oxygen is added to the aluminum as a chemical compound; either, with Norden, as the normal aluminum hydroxide, $\text{Al}_2(\text{OH})_6$, or as I believe more probable as aluminum oxide, Al_2O_3 , with water of crystallization in that part of the oxide which crystallizes. It is also possible, according to Norden's analysis, that some of the sulphate is added to the solid formation of the aluminum anode. The problem of the exact composition of the formation on the aluminum anode at the different stages of its formation is one of great interest and I believe will merit the most careful investigation.

SUMMARY OF RESULTS AND CONCLUSIONS.

1. I believe the foregoing experiments have been conclusive in showing that the apparent resistance of the aluminum anode in potassium aluminum sulphate is not an ohmic resistance but a resistance of transition of the ions, primary or secondary, and that this resistance of transition manifests itself in a counter electromotive force. The formation of the film of alumina which is a very poor conductor of electricity on the surface of the aluminum anode prevents the anions from reaching a conducting surface and thus discharging. The anions, therefore, become massed around the positive plate in a layer of highly charged radicals (SO_4) or in a layer of highly charged atoms of oxygen which are in the act of entering into union with the metallic aluminum.

2. When the aluminum is the cathode hydrogen is the primary or secondary product at the aluminum surface and there is no chemical union at either the aluminum or carbon surfaces, if the aluminum surface is already covered with a film of alumina. The kation finds access to the metallic surface of the aluminum plate and hydrogen is set free between the film of alumina and the metallic aluminum, thus separating the two surfaces and exposing the metallic aluminum to further action of the kations.

3. It has been shown that when the electrical pressure is greater than its critical value the film becomes crystalline in structure and in crystallizing exposes free metallic surfaces to the action of the anions, allowing them to discharge to the metallic surface.

4. The value of the critical pressure and also the counter electromotive force depends upon the temperature. The critical electromotive force for 1° is approximately 47 volts and for 48° only 22 volts; the counter electromotive force increasing with decrease of temperature.

5. On account of the very high resistance of the film of alumina formed over the aluminum anode the anions do not give up their charge to this film, but must pass through to the metallic aluminum. When the anions have discharged the oxygen set free by secondary action of the radical SO_4 unites with the aluminum, thus increasing the film and decreasing the possibility of other anions reaching the metallic aluminum.

6. It has been shown that the high anodic resistance depends upon the temperature, and that at temperatures approaching the temperature at which aluminum decomposes water, *i. e.*, 100° , the high anodic resistance greatly decreases, thus showing that the anodic resistance depends upon the chemical conditions for the union of aluminum and oxygen.

7. The theory as here presented accounts for the following observed conditions and phenomena relative to the electrolytic rectifier. First, it explains the apparent high resistance of the aluminum anode and low resistance of the aluminum kathode. Second, it explains the critical electromotive force and the good conductivity of the anode above this critical pressure. Third, it explains the very great change of conductivity with change of temperature. Fourth, the increased weight of the anode is a direct result of the theory. Fifth, the good conductivity of the electrolyte when the aluminum has a metallic surface also follows from the theory.

In conclusion, it may be said that sufficient data have been obtained to explain many of the phenomena of the electrolytic rectifier; there are however still some interesting phenomena not explained; as, the exact composition of the film on the aluminum anode, the cause of the crystallization at and above the critical potential, the dissolution of the crystalline formation by the electrolyte, and the exact ionic condition that produces the high counter electromotive force. It is believed however that these problems are not beyond the possibility of being determined by careful investigation and it is the intention of the writer to investigate these conditions as soon as possible.

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