

MINOR CONTRIBUTIONS.

ON THE FORMATION OF LEAD SULPHATE IN ALTERNATING CURRENT ELECTROLYSIS WITH LEAD ELECTRODES.

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IN a paper on the Capacity of Electrolytic Condensers¹ it was shown that condensers formed by submerging the ends of platinum wires in dilute sulphuric acid were of very large capacity. These were, however, not adapted to commercial ends, because the capacity was not constant with varying voltages, and especially because the efficiency was very low. Efforts to determine whether electrolytic condensers, formed with lead electrodes, might not have a much higher efficiency, acting much in the same manner as the lead plates of a storage battery, yielded the results imparted in this paper.

Condensers were made with electrodes of lead wire, 0.5 mm. in diameter, passing through glass tubes and imbedded, at the ends, in a cement formed of venice turpentine and shellac. Only the polished ends of the wires were in contact with the electrolyte (dilute H_2SO_4). Endeavors to determine the capacity of these condensers, by the method of reversals outlined in the above-mentioned paper, yielded nothing but non-concordant results. The cause of these discrepancies was suggested upon introducing the condensers into an alternating current circuit in a vain endeavor to determine whether the phase was shifted by their introduction. The immediate result, upon passing the current, was the dissolution of the electrodes and the formation of insoluble lead sulphate. The latter, after a long time, settling to the bottom of the electrolytic cell.

The results of an investigation concerning the causes which influence the dissolution of lead electrodes in H_2SO_4 , when traversed by alternating currents, are given in the tables which follow.

There are three main causes which affect the quantity of lead dissolved per coulomb of electricity passing through the circuit. They are the current density at the electrodes, the frequency of the alternations of the current, and the temperature of the electrolyte.

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The Influence of Current Density.

Three pairs of electrodes, made of hollow cylinders of polished lead of about 0.8 cm. diameter, were submerged in a 5 per cent solution of H_2SO_4 to such a depth that the individual electrodes of the pairs exposed areas of 4, 8, and 12 square centimeters respectively to the action of the electrolyte. The interiors of the cylinders were filled with a cement not affected by the acid. Current from a small Westinghouse alternator was sent through these cells connected in series, and its magnitude was measured by an electro-dynamometer. The time during which the circuit was closed was determined by means of a stop watch. Each pair of electrodes was weighed before and after each run. It was desirable that the run should be moderately long in order that the loss in weight of the electrodes might be determined with sufficient accuracy. On the other hand, it was difficult to maintain the temperature of the electrodes constant during a long run, owing to the heat generated by the current. The durations of the runs in each case were so chosen as to yield the best results. In calculating the number of coulombs which had passed through the cell in a given time, the assumption has been made that the shape of the current curve given by the alternator was sinusoidal. This assumption does not involve a very large error, as was proved by comparison of the curve, yielded by the alternator and obtained by the wiping contact method, with a sine curve of equal maximum value. The machine gave four complete alternations per revolution. The maximum positive and negative values of the current were, in arbitrary units, +93, -86.5, +86, -91, +91.5, -93, +93, -93. Plotting a curve of current i as a function of the time t , the area $\int i dt$, inclosed between this curve and the time axis, represents the quantity of electricity passed through the circuit. During one revolution these areas, as determined by a planimeter and expressed in arbitrary units, were +211, -205, +202, -214, +214, -217, +220, -210. The area contained between a sine curve and the same portion of the time axis intercepted by the current curve, the maximum ordinate of the sine curve being 90.9, *i.e.* an average of the maximum current values, was 213. This is practically the same as the average of the current areas. It thus appears that no very great error is introduced, if the coulombs passing through the circuit in t seconds be taken as the product of the $\sqrt{\text{mean}^2}$ current, as obtained from the electro-dynamometer, and $\frac{2t}{0.707\pi}$. The results given in Table I. are graphically represented by Fig. 1.

TABLE I.

Temper- ature.	Weight of lead dis- solved. Milligrams.	Duration of run. Seconds.	Surface of electrode. Sq. centi- meters.	$\sqrt{\text{mean}^2 \text{ cur-}}\br/>rent.$ Amperes.	$\int idt.$ Coulombs.	At 18° milligrams of lead dis- solved per coulomb.	Current density. Amp. per cm. ²
16.98	33.3	600	12.0	0.452	271.0	0.124	0.0380
18.00	15.6	180	12.0	0.543	97.6	0.160	0.0452
21.30	26.8	180	12.0	0.723	130.0	0.214	0.0600
18.00	27.2	180	6.5	0.543	97.6	0.279	0.0835
21.37	37.7	180	8.0	0.723	130.0	0.302	0.0900
17.00	47.6	120	12.0	1.127	135.2	0.348	0.0940
17.17	104.6	600	4.0	0.452	271.0	0.382	0.1130
22.37	96.3	118	12.0	1.710	202.0	0.503	0.1420
17.30	75.5	120	6.5	1.127	135.2	0.553	0.1730
20.84	94.9	120	8.0	1.422	171.0	0.575	0.1780
20.97	126.1	300	4.0	0.755	226.0	0.579	0.1890
22.50	123.7	118	8.0	1.710	202.0	0.646	0.2140
20.65	122.2	180	4.0	1.020	183.7	0.690	0.2550
20.17	133.0	120	4.0	1.422	171.0	0.799	0.3560
23.49	157.8	118	4.0	1.710	202.0	0.834	0.4280
17.24	206.4	60	4.0	3.810	228.6	0.895	0.9520
16.77	220.0	60	4.0	4.037	242.2	0.895	1.0100

The Influence of Frequency.

In investigating the influence of the frequency of alternations upon the quantity of lead dissolved per coulomb, two methods of altering the frequency were employed. By the first, the speed of the motor which drove the alternator was varied so as to give from 13 to 145 complete alternations per second. At the lower speeds the electromotive force of the generator was small. Accordingly, to obtain a uniform current density throughout the range of frequencies, a small current was employed. For alternations between 0 and 20 per second a direct current was employed, and its direction was commutated by a slow speed revolving commutator of two sections, which was driven by a small motor. The current was measured by a Weston ammeter. At these low frequencies the rate of formation of the lead sulphate is very sensitive to small changes in the frequency, and there seems to be an unstable chemical condition. For instance, during one run with three alternations per second, after about thirty seconds the electrodes took on the dark brown color of a storage battery positive, and after that no sulphate appeared to be formed. With

two alternations per second the attack on the electrodes ceased after twenty seconds. At these low frequencies, therefore, the runs were of necessity of very short duration, and the loss in weight of the electrodes was very small. No great amount of accuracy can be claimed for the results. They are, however, interesting as indicating, in a general way, the relation which exists between the rate of loss and the frequency. As it was impossible

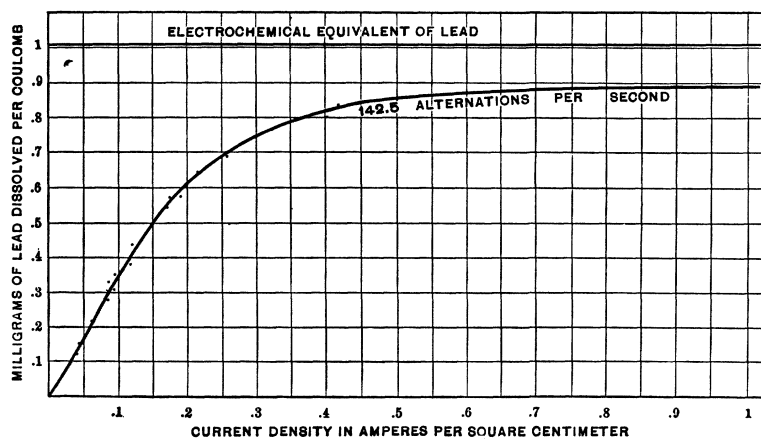


Fig. 1.

to obtain exactly the same current density in the various observations, the differences must be allowed for, if the different observations are to be connected. No great error will be introduced by assuming that the milligrams of lead dissolved per coulomb are directly proportioned to the current densities.

The results obtained are given in Table II., and are graphically represented in Fig. 2.

TABLE II.

Milligrams of lead dissolved per coulomb at 18°.	Number of alternations per second.	Current density in amperes per cm. ²	Milligrams of lead dissolved per coulomb at current density = 0.22.
0.202	2.0	0.209	0.212
0.334	3.0	0.221	0.333
0.523	4.0	0.222	0.520
0.618	5.0	0.220	0.618
0.714	5.5	0.223	0.705
0.756	10.1	0.226	0.735
0.800	20.1	0.226	0.779
0.785	84.2	0.246	0.703
0.646	142.5	0.224	0.635

The Influence of Temperature.

In determining the effect of temperature upon the amount of lead dissolved per coulomb of electricity, the commutated direct current was employed. The speed of the commutator was regulated to give such a number of alternations per second that small variations in frequency would have but little influence on the weight of lead dissolved per coulomb. A pair of electrodes, each exposing four square centimeters of surface to the action of the electrolyte, was placed in a beaker of 5 per cent H_2SO_4 at any desired temperature. Current at an electrode density of 0.215 amperes per square centimeter was passed through the cell for thirty seconds. The temperature during this interval remained practically constant. Maintaining, in this manner, the current density constant, the milligrams of lead dissolved per coulomb of electricity passed through the circuit was found to be 0.794, 0.744, and 0.683 for temperatures 17.134, 22.330, and 28.125° C., respectively. These results yield a temperature coefficient of

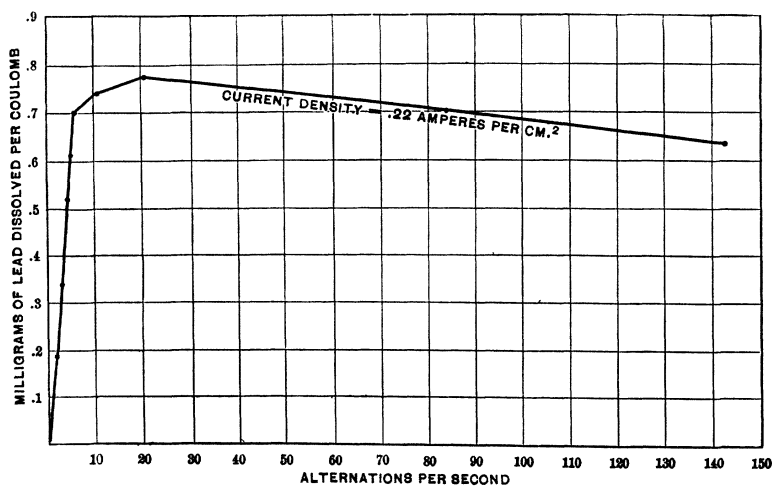


Fig. 2.

—0.0125, *i.e.* the current density remaining constant, the milligrams of lead dissolved per coulomb of electricity passed decreases 1.25 per cent of the amount dissolved at 18° C. for each degree rise of temperature above 18°.

Conclusion.

The authors have no theory to offer as explanatory of their results. The facts brought out are unquestionably associated, in some manner, with the

velocities or rates at which the involved chemical processes take place. The experiments on very low frequencies have developed the fact that PbO_2 is not soluble in H_2SO_4 , or acted upon by the products of the electrolytic decomposition of H_2SO_4 . The fact that PbSO_4 is formed with the alternating currents would seem to indicate that a lower oxide than the peroxide was first formed in quantity, and that this was afterwards acted upon by the electrolyte to form PbSO_4 . If this be so, the velocity of formation of the lower oxide must be greater than the velocity of oxidation to PbO_2 .

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POLARIZATION AND INTERNAL RESISTANCE OF A GALVANIC CELL.

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THE electromotive force of many cells decreases very rapidly upon closed circuit, and after a period of rest it nearly recovers its original value. In some cells this is so marked that they are called "open circuit" cells. This is rather a conventional use. It means only that the cells cannot be used on closed circuit any considerable length of time. Carhart, in his *Primary Batteries*, gives curves for change in electromotive force, current, and internal resistance of a great many such cells. The cells are run for a certain period, and then allowed to recover for the same length of time. The total electromotive force, E , and fall of potential, E' , over a known external resistance, R , are measured. The current can be calculated from the equation $C = \frac{E'}{R}$, and the internal resistance, r , is determined from the equation $r = \frac{E - E'}{E'} \cdot R$.

While this method reveals the fact and magnitude of polarization, it by no means localizes it. That is, it does not tell us how much polarization occurs at each electrode. In cells of the Leclancé type it has generally been assumed that the polarization occurs at the carbon electrode, and that the potential difference between zinc and solution is constant. The fall in electromotive force on closed circuit, at first rapid, has generally been attributed to the formation of gas liberated from the positive ion at the carbon electrode. The later decrease would therefore be slower, owing to the slow absorption of gas at the carbon. Depolarizers are therefore frequently added to minimize the formation of gaseous products. On the other hand, when the cell is thrown on open circuit, it was reasoned that the gas actually in contact with the electrode would be rapidly given off,