A DIRECT MEASUREMENT OF POLARIZATION CAPACITY AND PHASE ANGLE

By Carl W. Miller

Abstract

Polarization capacity and phase angle of electrolytic cell having gold electrodes and potassium bromide as electrolyte.—Using symmetrical condensers in which the separation of the plates could be varied from .002 cm to .3 cm, the series resistance and the capacity for small current density were measured by means of an alternating current bridge. Within the errors of the experiment, the "initial" capacity was independent of the separation of the plates, and the resistance was a linear function of the separation, approaching, however, a definite surface resistance as the distance between the plates was reduced. For concentrations greater than hundredth normal it was possible to work with such small separations that the resistance of the electrolyte could be neglected in comparison with the surface resistance. Direct measurements were, therefore, possible of capacity, resistance, and phase angle ($\tan^{-1}\omega CR$). Using clean gold electrodes as soon as possible after immersion in the electrolyte, a study was made of the variation of these constants with concentration, and for a few frequencies from 570 to 3500 cycles. The capacity varied very nearly directly and the resistance inversely as the one-fourth power of the concentration, the product CR being nearly constant. The phase angle was very nearly constant for variations both of concentration and of frequency, showing only a slight decrease with increasing concentration, and a slight increase with increasing frequency. It was about 65°.

Introduction

It has long been known that the polarization capacity of an electrolytic condenser decreases as the current passing through decreases, but approaches a limiting so-called "initial" capacity. Measurements of this initial capacity have been made by Wien, Krueger, Warburg, and others, while a number of theories have been proposed to explain the observed phenomena.

Related to the polarization capacity is the dissipation of energy at the surface of the condenser plate which is evidenced by the apparent increase in the resistance of the condenser over and above the calculated resistance of the electrolyte. Hitherto, estimates of this surface resistance have been made by comparing the observed series resistance of the condenser with that to be expected from the nature and dimensions of the electrolyte. In case the condenser used was unsymmetrical and this could not be done, a less certain estimate was still possible from the variation of capacity and resistance with frequency.

EXPERIMENTAL PROCEDURE

In the measurements here described symmetrical condensers have been used, but the surface resistance has been determined by a study of the variation of capacity and resistance as the separation of the plates was progressively decreased. By this method I have been able with all but the most dilute solutions to bring the plates so close together as to render the resistance of the electrolyte itself negligible. The disadvantage of this procedure is that it unavoidably confuses the quite different processes which are probably going on at a given instant at the two plates. We may think of the cell as made up of two identically equal leaky condensers in series with one another and with the electrolyte. We must, however, not lose sight of the fact that this conception may be very far from representing the processes which are actually taking place.

Practically all previous measurements have been made on cells which have been assembled for at least twenty-four hours. This has been rendered necessary by the constant changes which take place at the surface of the plate after it is immersed in the electrolyte. These changes are quite rapid at first, and persist for many hours, thus rendering consistent measurements difficult. We are, of course, somewhat in doubt as to the exact nature of the metallic surface after such a prolonged immersion.

The measurements described in this paper were, on the other hand, made as soon as possible after the electrodes were brought into contact with the electrolyte. Considerable care has been exercised in cleaning the metal surfaces used, and the results show, at least approximately, what is to be expected from a clean metal surface in contact with a clean electrolyte. Since the cell was changing relatively rapidly, it has, of course been impossible to make series of measurements with the precision attainable after long immersion.

An alternating current bridge was used. The two balancing arms were 1000 ohm non-inductively wound resistances, the third arm contained a variable capacity and resistance which could be used either in parallel or in series, while the fourth arm contained the electrolytic condenser to be studied. Provision was made for substituting in place of the electrolyte a second variable capacity and resistance for the purpose of direct comparison, so as to eliminate any possible error which might arise from inequality of balancing arms or leakage of current from capacitance to ground. The disadvantage of this method was its cumbersomeness, and during a part of this work the same purpose was served, though less satisfactorily, by a device, due to Wagner,[1] through which the midpoint of the bridge was maintained at ground potential without any actual ground connection. A two stage tuned amplifier was used in the telephone circuit to increase the sensitiveness of the apparatus.

Two types of symmetrical condenser were devised which proved particularly useful in these measurements. The first and simplest consisted of a micrometer caliper to the anvil of which had been cemented an insulated brass cylinder 1 mm thick and, like the anvil, one-quarter inch in diameter. This disk and the opposing face of the movable spindle were gold plated, and together constituted the condenser. All except the opposing faces were covered with an insulating coat of shellac, and a single drop of electrolyte was held between the plates by capillarity. One lead was brought to the brass cylinder and the other to the frame of the caliper. It was possible to bring the plates of this condenser to within .002 mm of one another without shortcircuiting. The plates could be readily cleaned and polished, and one drop of electrolyte could be conveniently replaced by another. It was, of course, not suited to long series of observations owing to gradual changes in concentration consequent on evaporation.

The other type of condenser consisted of two circular opposing disks, the separation of which could be controlled by a micrometer screw. All except the front faces of the disks and the leads were carefully insulated so that they could be immersed in a beaker of electrolyte without permitting any conduction except between the opposing faces. The difficulties resulting from evaporation were eliminated by this arrangement, but the simplicity and convenience of the caliper condenser were to a certain extent sacrificed.

EFFECT OF CHANGING THE SEPARATION OF THE PLATES

The following table shows a series of measurements made with the immersion condenser. The plates were gold plates, and a 1/500 normal solution of KBr was the electrolyte. An alternating current of 3400 cycles was furnished by a vacuum tube oscillator.

t:	.10	.15	.20	.25	.30	.10 mm
R:	9.662	12.91	16.22	19.73	23.16	9.86 ohms
C:	6.57	6.52	6.56	6.55	6.68	6.65μ-farads

t is the separation of the plates in millimeters, R is the series resistance of the condenser in ohms, and C is the series capacity in microfarads. C remains satisfactorily constant, indicating that its seat is at the surface of the metal and not in the electrolyte. R is plotted in the large curve of Fig. 1 against the separation. It is quite accurately linear, and clearly approaches a limiting value of about 3 ohms as the separation approaches zero. The slope of this line is 675 ohms per cm separation. The plates were one inch in diameter, and the molecular conductivity would then be

$$\Lambda = \sigma/\eta = [.02/13.5 \times \pi(1.27)^2 \, 2(10)^{-6}] = 146$$

Calculating Λ from the sum of the mobilities of the bromine and potassium ions, and from the degree of dissociation for a five-hundredth normal solution, we get $\Lambda = 128$. The check would seem to be as good as could be expected.

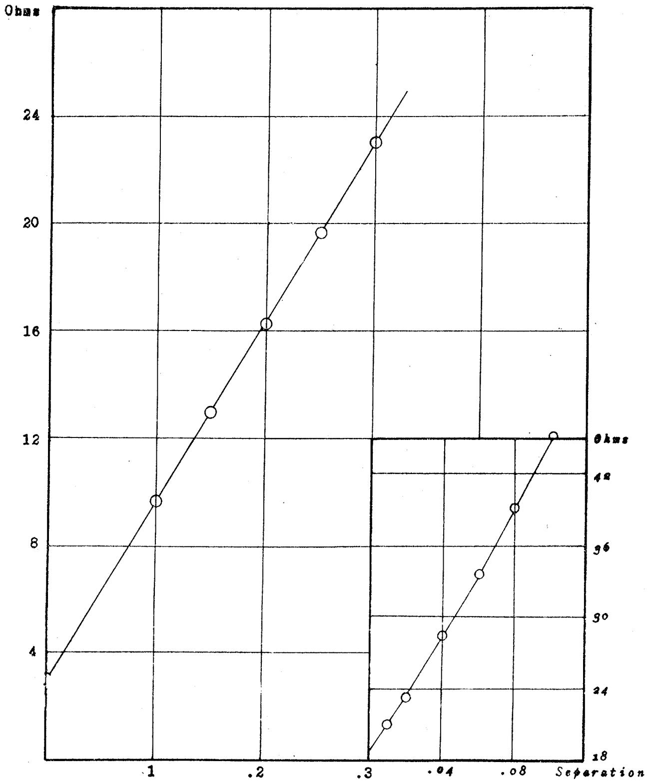

Fig. 1. Series resistance as a function of separation of the plates.

The following data are for a similar series of measurements made with the caliper condenser. A .001 normal solution of KBr was used, and a 3500 cycle current. The lack of constancy of C and the lack of exact linearity in the variation of R is to be attributed to the gradual evaporation of the electrolyte.

t:	.10	.08	.06	.04	.02	.01	.10 mm
R:	45.3	39.3	33.4	28.4	23.3	20.9	39.2 ohms
C:	.668	.698	.723	.746	.768	.793	.735 μ-farads

These values of R are plotted against t in the insert of Fig. 1. The limiting resistance as t approaches zero is here seen to be about 18.7

ohms. It is clear that for this .001 normal solution, the resistance of the electrolyte alone at .003 mm separation is very nearly negligible compared to the surface resistance; for higher concentrations it is of still less importance.

EFFECT OF CHANGING THE CONCENTRATION OF THE SOLUTION

Using the caliper condenser and a separation of between .002 and .003 mm, a large number of measurements were made with several different electrolytes, KBr, Na_2CO_3, $AgNO_3$. The following results with KBr are typical of all these measurements.

The instant a drop of solution was placed between the jaws of the caliper a stop clock was set into operation. A balance was obtained as quickly as possible on the bridge, and readings made of capacity, resistance, and time. These measurements were repeated at intervals over a period of ten to fifteen minutes, after which the plates were again cleaned and a new set of readings begun.

The results are indicated in Table I for three different concentrations and a 2500 cycle current. The current density was in all cases between one and two milliamperes per cm, and we are accordingly dealing with the "initial" capacity.

TABLE I

Concentration	Time (min.)	Resistance (ohms)	Capacity (μ-farads)	$\tan\varphi$
.01 N	1:00	143	.983	2.21
	3:00	140	1.039	2.24
	5:30	136.2	1.076	2.30
	8:00	133.2	1.096	2.30
	10:30	130.5	1.120	2.30
	——	127.5	1.135	2.28
.1 N	:50	82.7	1.659	2.16
	3:00	75.6	1.819	2.16
	5:00	72.5	1.884	2.15
	6:50	71.0	1.914	2.14
	9:30	70.2	1.934	2.14
	12:00	70.4	1.934	2.14
1.0 N	1:05	35.9	3.564	2.02
	2:35	36.2	3.582	2.04
	4:15	36.7	3.555	2.05
	6:30	37.7	3.481	2.06
	8:50	38.6	3.423	2.08
	11:00	39.1	3.389	2.08

It will be noted that at the two lower concentrations the resistance decreases with the time, while the capacity increases. At the highest concentration, however, the resistance increases and the capacity decreases. In all three cases RC and hence the phase angle stays nearly constant. Furthermore, despite the great range of concentrations, this phase angle does not differ much in the three cases.

The variation of C and R individually with concentration is not so easy to estimate, owing to the rapid changes which take place with the time. If, however, we compare the values of C and R which correspond to the same length of time after immersion, it is readily seen that C varies very nearly directly and R inversely as the one-fourth power of the concentration.

It is interesting to compare this one-fourth power law with the observations of previous investigators. Warburg's theory for reversible electrodes requires that C shall increase in direct proportion to the first power of the concentration, and this law was verified by Neumann. Wien, on the other hand, found a very slow rate of variation of C with the concentration in the case of nickel, much slower, in fact, than we have observed with gold. It is worthy of note, however, that the phase angle we have found for gold, 65°, lies well between the 45° characteristic of reversible electrodes and the 82° found by Wien for nickel. There would seem, therefore, to be a very intimate connection between the phase angle and the rate of variation of the capacity with the concentration.

Effect of Changing the Frequency of the Applied Current

A range of frequencies from 570 to 3500 cycles was available for these measurements, and the following table gives four different pairs of observations obtained at different times over a period of several months. The differences observable must be attributed to differences in the condition of the condenser plates. In each case, however, the plates had been subjected as nearly as possible to the same process of cleaning and polishing, and the disturbing causes are not understood.

Concentration:	.1 *N*	.1 *N*	.1 *N*	.1 *N*	.01 *N*	.01 *N*	.01 *N*	.01 *N*
Frequency :	3500	2000	3500	2270	3500	2700	1040	570
Resistance :	8.18	10.4	9.5	12.0	20.4	21.7	50.3	91.1
Capacity :	2.458	3.554	2.040	2.532	.894	1.071	1.457	1.66
$\tan \varphi$:	2.27	2.16	2.35	2.31	2.49	2.47	2.09	2.06

It is to be noted that in all cases both R and C decrease as the frequency increases, but in such a fashion that the phase angle remains very nearly constant. There would appear, however, even with the small range of frequencies available, to be a slight increase in the phase angle with increasing frequency. These variations are, however, of an entirely different order of magnitude from the variations of C and R.

The recurrence of this curious constancy of the phase angle both as regards variations of concentration and frequency would seem to be highly significant. Any thoroughgoing theory must give an adequate explanation of this phenomenon.

These measurements were carried out during the spring and summer of 1922 in the Cruft Laboratory of Harvard University.

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