

A STUDY OF POLARIZATION CAPACITY AND RESISTANCE AT RADIO FREQUENCIES

BY C. B. JOLLIFFE

ABSTRACT

Polarization capacity and resistance of electrolytic cells having Au and Pt electrodes in H₂SO₄ solution, for frequencies of 11×10⁴ to 2×10⁶ cycles per second.—The cell was placed in a tuned circuit coupled to a generating circuit, and the polarization capacity C was computed from the change of capacity required to restore resonance as indicated by means of a second loosely coupled circuit containing a detector and galvanometer. The polarization resistance ΔR was obtained by substituting for the cell a variable non-inductive resistance. Both C and ΔR were found to be linear functions of $1/\sqrt{f}$ where f is the frequency. For Au electrodes, the curves all go through the origin but for Pt the limits for infinite frequency are positive for capacity and negative for resistance and vary with the concentration. For both Au and Pt the slopes of the capacity curves increase with concentration while the slopes of the resistance curves decrease. In the case of Au, $2\pi f C \Delta R = \tan \psi = \text{const.}$ (nearly), whereas for Pt, $\tan \psi$ varies. These results may be associated with the fact that the *residual current* is only 1/20 as much for Au as for Pt. *The effect of previous polarization* with H₂ is a temporary increase of capacity, while O₂ gives a permanent increase which cannot be removed by polarization with H₂. The roughness of the surface as well as the previous history affect the values of C and R obtained. Qualitatively the results for C and ψ are in agreement with the theory of Warburg, provided some assumptions are made, but not the results for ΔR . Possible reasons for the discrepancies are suggested.

INTRODUCTION

IN 1860 Varley¹ noticed that two platinum electrodes immersed in a solution of sulphuric acid acted like a large condenser, and in 1871 he measured the capacity of such a cell by means of a ballistic galvanometer. A little later the behavior of such cells in an alternating current circuit was studied by Kohlrausch² who looked upon the capacity effect observed by Varley as due to polarization. He assumed that the e.m.f. of polarization was at any instant proportional to the total quantity of electricity that had passed through the cell, so that if E represents the e.m.f. then

$$E = \frac{1}{C} \int idt. \quad (1)$$

¹ Varley, Phil. Trans. **161**, p. 129, 1871.

² Kohlrausch, Pogg. Ann. **148**, p. 143, 1873.

C has the dimensions of a capacity and has been called the "polarization capacity" or "electrolytic capacity" of the cell. The value of this factor has been measured by several experimentors by both direct and alternating current methods. A summary of the work done up to 1881 is given by Blondlot,³ and up to 1897 by Gordon.⁴

It was found by Varley, Kohlrausch, Blondlot and others that the value of the polarization capacity was not constant for all voltages but increased as the voltage increased. Below a certain value depending on the solution, the capacity was however only slightly dependent on the voltage. Blondlot called the limiting value of the capacity as the voltage approached zero the "initial capacity." Bouty⁵ and Vaillant⁶ found that this initial capacity was proportional to the area of the electrodes.

M. Wien⁷ studied the action of several kinds of electrolytic cells under the action of an alternating current supplied from an induction coil and measured both the initial capacity and the resistance. Assuming the relation of Kohlrausch and also as he did that the e.m.f. of polarization is 90° behind the current producing it, if an alternating e.m.f. $E_0 \sin \omega t$ is applied at the terminals of the cell,⁸ then,

$$E_0 \sin \omega t = I_0 [R \sin \omega t + (1/C\omega) \sin(\omega t - \pi/2)] \quad (2)$$

where I_0 is the amplitude of the current produced, R the resistance, and $\omega = 2\pi$ times the frequency. Wien found that the measured resistance was always larger than the value computed from the constants of the cell. To account for this he assumed that there was a spontaneous depolarization at the electrodes which caused the polarization to reach its maximum earlier than it otherwise would. In Eq. (2) instead of $(1/C\omega) \sin(\omega t - \pi/2)$ he put $(1/C'\omega) \sin [\omega t - (\pi/2 - \psi)]$; then it becomes

$$E_0 \sin \omega t = I_0 \{ R \sin \omega t + (1/C'\omega) \sin [\omega t - (\pi/2 - \psi)] \} \quad (3)$$

or

$$E_0 \sin \omega t = I_0 [R + (1/C'\omega) \sin \psi] \sin \omega t + (I_0/C'\omega) \cos \psi \sin(\omega t - \pi/2). \quad (4)$$

That is the resistance is increased by

$$\Delta R = (1/C'\omega) \sin \psi; \text{ and } C = C'/\cos \psi, \tan \psi = \Delta R C \omega. \quad (5)$$

Wien studied the effects of frequency on the capacity and resistance between 64 and 535 cycles per second and found that C and ΔR decreased with frequency and that the product $\Delta R C \omega$ was nearly a constant.

³ Blondlot, Jour. de Phys. p. 277, 1881.

⁴ Gordon, Diss. Gött. 72, 2nd paper.

⁵ Bouty, Jour. de Phys. (3) 3, p. 498, 1894; Comptes Rendus, 116, p. 629.

⁶ Vaillant, Comptes Rendus, 157, p. 1141.

⁷ Wien, Ann. der Phys. 294, p. 37, 1896.

⁸ Wien derived the equations with an applied e.m.f. of $E_0 \cos \omega t$. It has been changed in this paper to make the results consistent with later equations.

E. Warburg⁹ proposed a theory to account for and determine the magnitude of the capacity from chemical data on the basis of diffusion of the products of electrolysis. He developed the relation that the e.m.f. to overcome polarization is

$$p = \frac{I_0}{sK\omega} \sin \phi \sin [\omega t - (\pi/2 - \phi)], \quad K = \frac{107.9}{AA'(\partial e/\partial \gamma)_0}, \quad s = \sqrt{\frac{k_1}{2\omega}}, \quad (6)$$

$$\tan \phi = 1/(1 + \mu/s), \quad (7)$$

where $k_1 = k \left(1 + \frac{\gamma}{\gamma'} \sqrt{\frac{k'}{k}} \right)^2$, $\frac{\partial e}{\partial \gamma} = \frac{e - e_0}{\gamma - \gamma_0}$, $\mu = \frac{\partial \Gamma}{\partial \gamma}$,

k and k' = diffusion coefficients of hydrogen into the solution and electrode; e and e_0 = e.m.f. at the surface of the electrode with and without current flowing; γ and γ_0 = density of hydrogen in solution with and without current flowing; A and A' = electrochemical equivalent of silver and of hydrogen; Γ = surface density of the hydrogen layer on the surface of the electrode.

From Eq. (3) it may be seen that the e.m.f. necessary to overcome that due to polarization is

$$p = (I_0/C'\omega) \sin[\omega t - (\pi/2 - \psi)]. \quad (8)$$

Comparison of Eqs. (6) and (8) shows that

$$C' = sK/\sin \phi \quad (9)$$

where

$$C' = C \cos \psi, \quad \tan \phi = \tan \psi. \quad (10)$$

Wien¹⁰ tested the validity of these equations for palladium electrodes in sulphuric acid. He concluded that C and ψ are only slightly dependent on frequency.

The studies of polarization capacity that have been made heretofore have with one exception been made at frequencies in the audible range and with an induction coil as a source of alternating current. Merritt¹¹ using an electron tube generating set, measured the polarization capacity at frequencies in the audible range and also over a narrow band of radio frequencies. The object of the present work was to extend the range of radio frequencies and to measure the apparent resistance of the cell.

METHOD

The method used in this work was the same as that used by Merritt. The schematic diagram of connections is shown in Fig. 1. The coupling between the generating set and circuit A and also between A and B was

⁹ Warburg, Non-polarizable electrodes: *Ann. der Phys.* **303**, p. 493, 1899; *Verh. d. Phys. Ges.* p. 120, 1896. Polarizable electrodes: *Ann. der Phys.* **311**, p. 125, 1901.

¹⁰ Wien, *Ann. der Phys.* (4) **8**, p. 372, 1902.

¹¹ Merritt, *Phys. Rev.* **17**, p. 524, 1921.

always very loose in order to reduce as much as possible the reaction of one circuit on the other. The frequency was measured by means of a calibrated Signal Corps wave-meter (*SCR 61*) and was varied from 11×10^4 to 210×10^4 cycles per second. The detector used was a very sensitive molybdenite crystal which remained constant over a long period.

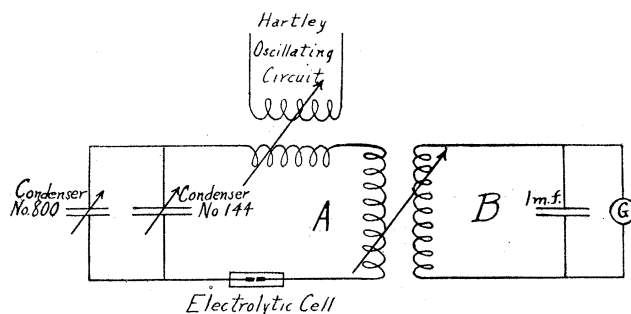


Fig. 1. Schematic diagram of circuits used.

The type of electrolytic cell used is shown diagrammatically in Fig. 2. The electrodes were made by sealing into glass tubing with DeKotinsky cement, rods of the metal used, 2 mm in diameter and 1 cm long, electrical connection being made by means of wires soldered to the rods and running through the tubing to the outside. The ends of the tubes were ground with emery so as to make the surface of the metal as nearly plane as possible. These tubes were then mounted by means of sealing

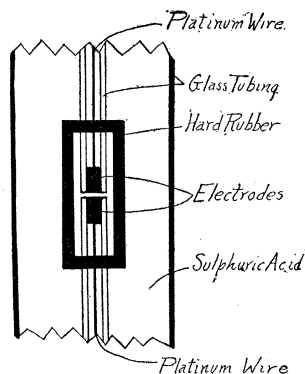


Fig. 2. Arrangement of the electrolytic cell.

wax in a hard rubber frame forming two parallel plates 2 mm in diameter and about 0.5 mm apart. This was mounted in a glass tube which contained the acid. The distance between electrodes was measured by means of a micrometer microscope. The cell so formed was linear, and a straight wire could be substituted for it without materially changing the

inductance of the circuit. Two of these cells were made, one having platinum electrodes and the other gold electrodes.

In order to measure the capacity of a cell the generating circuit was set for the frequency desired, the electrolytic cell being in circuit *A*. This circuit was then brought near the resonant frequency by adjustment of the inductance and the capacities to give maximum reading of the galvanometer *G* in the circuit *C*. To make the final adjustment for resonance, condenser No. 800 was fixed at a certain value and condenser No. 144, which had a small capacity, was varied until the circuit had passed through the resonance frequency. After this value for resonance was obtained accurately, the electrolytic cell was removed and in its place was put a piece of No. 40 B. and S. gauge Advance wire, the length of which was adjusted until the same current flowed at resonance as flowed with the cell in the circuit. This was indicated by the reading of the

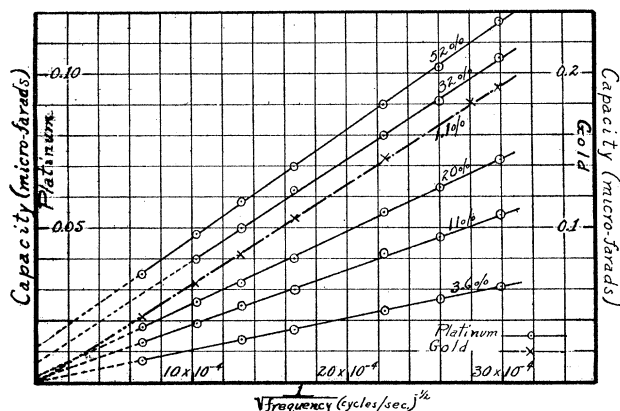


Fig. 3. Relation between capacity and frequency for different concentrations of H_2SO_4 . galvanometer being the same at resonance in both cases. The new value of the capacity required for resonance was obtained as before.

In order to be certain that the potential at the terminals of the cell was small enough so that the capacity could be considered as the initial capacity, the coupling between *A* and the generating circuit was changed so as to reduce the current in *A*. The capacities required for resonance were again determined with the cell and the resistance. The capacity reached a value which remained constant with further reduction in the current in circuit *A*. This was called the capacity of the cell and is the value plotted on the curves. The capacity of the electrolytic cell may be computed from the observed values of the capacity for the two resonance points. Since the current and phase relations of the circuit remained unaltered the resistance of the wire substituted is equal to the resistance of the cell.

The capacity measured was that corresponding to an equivalent air condenser so that this gave directly the angle ψ used by Warburg,

$$\tan \psi = \omega C(R - R_0) \quad (11)$$

where R_0 is the resistance of the cell as calculated from the dimensions and the conductivity of the acid.

RESULTS

The results obtained are shown graphically in Figs. 3 to 6 inclusive. The observed values of capacity and $\Delta R = R - R_0$ are plotted as coordinates with $1/\sqrt{f}$ as abscissas where f is the frequency of the oscillations in cycles per second. The concentration of the sulphuric acid was varied over wide limits, the per cent of acid used in the solution in the cell being indicated on each of the curves. Within the limits of accuracy of the measurements all the curves are straight lines.

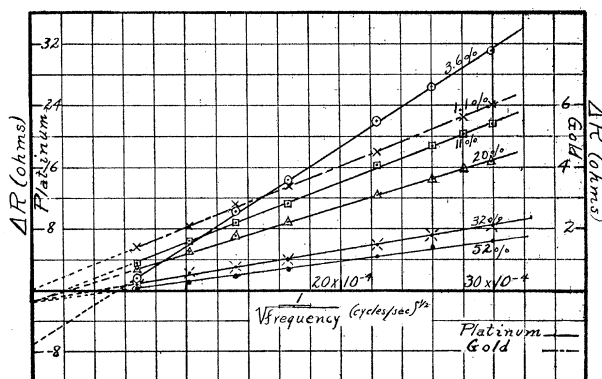


Fig. 4. Relation between ΔR and frequency for different concentrations of H_2SO_4 .

For the curves of capacity and ΔR against $1/\sqrt{f}$ the straight lines when extended back pass through the origin when the gold electrodes were used but have intercepts on the capacity and resistance axes when the platinum electrodes were used. These intercepts are too large to be due to experimental errors and could be reproduced in every case.

When the curves shown in Figs. 3 and 4 were taken the electrodes had been exposed to the air for several weeks and at times this air was laden with fumes from a chemical laboratory. In order to bring the electrodes to a more standard condition the platinum was heated to about $1000^\circ C$ and the gold to about $800^\circ C$ in air in an electric furnace, and then a new cell made. This required that the surface be reground, and this time a glass plate with emery was used instead of a steel plate with emery as was used before. This gave entirely new surfaces, which were kept

immersed in the solution and only exposed to the air for a short time when the solution was changed.

Figs. 5 and 6 show the results after this treatment. The capacity and resistance show the same variations with frequency as before but the values are different as a result of the change in the character of the surface. It was found that these values could be decreased to one half by

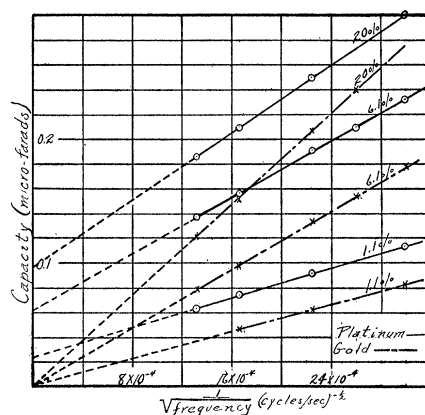


Fig. 5. Relation between capacity and frequency after new surfaces had been obtained.

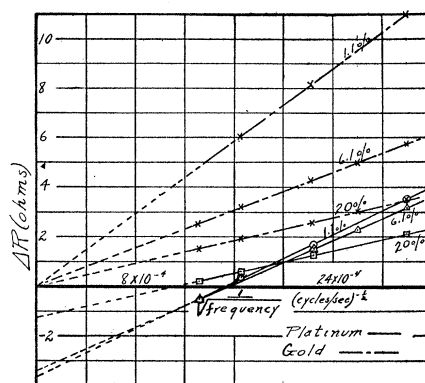


Fig. 6. Relation between resistance and frequency after new surfaces had been obtained.

polishing the surface somewhat instead of leaving it as it was after grinding it with the finest emery available (finishing emery).

For the platinum cell, $\tan \psi = \Delta RC\omega$ is a variable having both positive and negative values. For gold, $\tan \psi$ is a constant for each concentration and nearly constant for all concentrations both before and after heating. The value for ψ for all cases is between 30° and 40° .

It should be noted that the results obtained for capacity using platinum electrodes are different from the results of Merritt in that he found at radio frequencies that the polarization capacity varied inversely with f instead of inversely with \sqrt{f} . He found, however, that the square root relation was followed in the audible range of frequencies.

It was found by Scott¹² that when an electrolytic cell with platinum or gold electrodes was polarized, the capacity increased. In the method here used it was not practicable to keep the polarizing e.m.f. connected while measurements were being made. In order to polarize a cell both electrodes were connected together and to one pole of a dry cell. The other pole of the dry cell was connected to a platinum wire immersed in the solution. It was allowed to stand so connected for 24 hours and then was removed and measured as soon as possible. No bubbles of gas were visible.

Both the platinum and gold cells acted alike under this treatment. When the electrodes had been connected to the negative pole of the battery the capacity was initially doubled but decreased so rapidly that it was impossible to make accurate measurements. Within an hour it had decreased to the original value. The electrodes were then connected so that they were attached to the positive pole of the dry cell. When they were removed after 24 hours and measured the capacity was three times as great and this value was constant. It was measured three days later and had the same value. It was then connected again so that the electrodes were attached to the negative pole and allowed to stand. This caused the same temporary effect as before but the value to which it returned was the large value obtained after being connected to the positive pole. When the cell was taken apart and the electrodes examined it was found that they were considerably dulled. They were reground and when the surface was brought back as nearly as possible to the original condition the value of the capacity was found to have approximately its original value. From these results it appears that when the electrodes were polarized with hydrogen the increase was due to a temporary change in the solution or electrodes, possibly a change in the density of hydrogen, which soon returned to the original condition when the e.m.f. was removed. When the electrodes were polarized with oxygen, however, a permanent change was effected on the surface of the electrodes.

COMPARISON WITH THEORY

In order to compare the results obtained with the theory of Warburg, Eqs. (7) and (9) may be solved for C and ΔR .

¹² Scott, *Ann. der Phys.* **303**, p. 388, 1899.

$$C = Ks[1 + s/(s + \mu)] + K\mu; \quad (12)$$

$$\Delta R = \frac{2s}{k_1 K} \cdot \frac{1}{(1 + \mu/s)^2 + 1}; \quad \cot \psi = 1 + \mu/s. \quad (13)$$

For the case of non-polarizable electrodes $\mu = 0$ and these equations reduce to

$$C = 2Ks; \quad \Delta R = s/k_1 K; \quad \tan \psi = 1. \quad (14)$$

The case of gold electrodes would seem to fall under the class of non-polarizable electrodes for the range of frequencies used except that $\tan \psi$ is not equal to unity. However the value of $\tan \psi$ is almost constant and does not differ much from unity. In the usual classification gold electrodes in sulphuric acid would not be classed as non-polarizable electrodes. It may be, however, that the value of μ is so small that it becomes of consequence only at higher frequencies than those used in this work.

For platinum electrodes the results for capacity would seem to agree with Eq. (12) for polarizable electrodes if it is assumed that μ is small in comparison with s . The results for ΔR do not agree with Eq. (13) for this equation does not allow a negative intercept on the resistance axis. The value of $\cot \psi$ for the platinum electrodes increases with decrease of s but becomes negative, which would not be allowed by Eq. (13).

In the light of these facts it may be concluded that through the frequency range used in this work, the theory of Warburg can only roughly explain the phenomenon both in the case of gold and platinum electrodes. However, further work is necessary before an entirely satisfactory quantitative test can be made. Further information might be obtained by extending the investigation to higher frequencies. The quantity μ should be investigated since even qualitative comparison of the results and the theory depends on the magnitude of this quantity. Warburg assumes that this quantity is a constant and that Γ is always in equilibrium with γ . At frequencies of the order used it is probable that this assumption is not justified and μ may be a function of frequency.

It has been assumed in this work as well as in the work of others that the electrolytic cell is equivalent to a capacity and a resistance in series and that $\Delta R = R - R_0$, where R_0 is calculated from the dimensions of the cell and the conductivity of the electrolyte. The fact that there is a "residual current" when the cell is charged with direct current would suggest that this is not a true representation. Possibly a truer assumption would be that the cell is a combination of two capacities in series with a resistance and this combination in parallel with a high resistance. Then $R - R_0$ would not give the ΔR required by Warburg's theory but

something smaller, and consequently a negative intercept might be expected when ΔR is plotted against $1/\sqrt{f}$.

To compare the residual current for the two kinds of cells, each cell was connected in series with a sensitive galvanometer and a variable direct e.m.f. The residual current is the value when the steady state has been reached. The following data were obtained for the residual current in scale divisions.

<i>Voltage</i>	<i>Residual current</i>	
	<i>Platinum</i>	<i>Gold</i>
0.1	4.7	0.0
0.2	7.0	0.2
0.3	9.4	0.3
0.4	13.5	0.4
0.5	15.0	0.7
0.6	17.0	1.0
0.7	25.0	1.3

This can be interpreted as indicating that the parallel resistance in the case of the cell formed by platinum electrodes is much smaller than in the case of the cell with gold electrodes. This may explain the lack of agreement of theory and experimental results in the case of the platinum electrodes.

In conclusion the writer wishes to express his thanks to Professor Ernest Merritt for his interest and suggestions concerning the work, and to Professor C. C. Murdock for the use of his bibliography on Electrolytic Capacity and for suggestions concerning the interpretation of the results.

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