

# THE POTENTIAL OF THE OXYGEN ELECTRODE: A REPORT OF PROGRESS

BY E. P. SCHOCH

It is well known that the oxygen-hydrogen (Grove) cell shows great irregularity in its e. m. f.: a day or two after its preparation, it usually attains to a voltage of approximately 1.08 volts in nearly all electrolytes, but higher voltages have been observed by Wilsmore, Bose and others; and a few days later the voltage usually sinks below 1.08 volts, so that this voltage may be more or less accidental. Theory requires such a perfectly constant potential difference between the hydrogen and the oxygen poles in all electrolytes; but the maximum amount of this potential difference (1)\*, as recently ascertained by indirect methods, is 1.231 ( $\pm 0.001$ ) volts at 17° C. Hence the value 1.08 volts cannot be due to the (maximum) electromotive force of the gases—or, in other words, it cannot be the potential with which the action of the poles is reversible. If we reverse, experimentally, the action of the cell—*i. e.*, discharge oxygen and hydrogen by electrolysis—even then the reversible potential does not show itself by allowing these gases to be evolved at a potential difference slightly greater than 1.231 volts. Instead, we find that a potential difference exceeding 1.5 volts must be applied before any currents greater than mere diffusion currents will pass, and the evolution of gases will show itself.

Since we know that the hydrogen electrode is perfectly reversible in its action, that its potential is independent of the metal used in its construction (2), and that its value is accurately reproducible in all sorts of electrolytes, it follows that all the observed irregularities are due to the oxygen electrode. It is now known that the irregularities of the platinum-oxygen electrode are due to the fact that the electrode metal is oxidized, and that its potentials are due to

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\* The numbers in parentheses refer to the list of references given at the end.

the oxides and not to any oxygen gas that may be present. For this recent advance in our knowledge of the subject we are mainly indebted to Foerster (17), E. Mueller (8), Lorenz (13), Woehler (12) and Ruer (14), and on account of its general importance a brief account of this work is here given.

Since the study of the oxygen electrode involves a consideration of the discharge of the "oxygen-forming" anions, it is desirable to present here at the beginning a summary of what appears to the writer to be our present knowledge of these actions. The recent developments in our knowledge of the platinum electrode have been chiefly instrumental in clarifying our view of these actions.

The potential required for the electrolytic discharge of an ion at any particular moment is determined by the opposing potential of the electrode—irrespective of the nature of the ion. Thus, to discharge hydrogen or oxygen into an electrode absolutely devoid of any electrochemically-active material requires the application of an exceedingly small e. m. f. only, while their discharge into an electrode charged with these gases requires an e. m. f. above 1 volt. Apart from the opposing potential of the electrode *there is no such force as* "intensity of fixation," or "holding power" (3) which might have to be overcome in the discharge of ions.

With continued electrolysis the discharge potential naturally depends upon the product formed, *i. e.*, as it is commonly expressed, upon the particular process that takes place. The *process* is considered as being determined by the original substances and the final product, irrespective of the details of the transformation. Thus the discharge of the chlorine ion upon an indifferent electrode (graphite, platinum, etc.) which results in free chlorine takes place at a different potential than upon a silver electrode with which it forms silver chloride. The difference in these potentials, however, is directly due to the difference in the electromotive forces of the *products*. To illustrate again: silver, when deposited together with mercury with which it forms an amalgam

of a lower potential than pure silver, is actually deposited at this lower potential; again, oxygen gas is liberated at a lower potential on platinum than on lead with which it forms lead dioxide.

However, in actual operations, the (main) process does not necessarily determine the potential. The amount of a substance which is necessary to impart a definite potential is exceedingly small, and such a small amount of a high-potential product is frequently formed and remains, although the main product is of a nature which would impart a lower potential to the electrode; under these conditions the (main) process does not determine the potential, because its operation can be continued only by overcoming the higher potential of the portion formed in small amount. Two striking illustrations of this state of affairs are at hand. Luther and Brislee (4) found that during the electrolytic discharge of chlorine from hydrochloric acid on polished platinum electrodes, the latter are affected in such a way as to exert a greater opposing potential than that due to the chlorine, and hence the whole discharge of chlorine requires this high potential. The authors think that in this case the chlorine may be produced as a secondary product: this is not necessarily the case, since all that is required is that the reaction between the chlorine and the high potential product is so slow that enough of the latter constantly remains to impart its high potential. The second example is found in the discharge of nickel (or iron) which in its deposition always forms, wholly or partly, a hydride of a potential much above that exerted by pure nickel (5). Hence for the continued deposition of nickel this higher potential must be exceeded.

Of course, this state of affairs makes the main process an irreversible process: the extra potential to be overcome entails a loss of free energy. Since the discharge of "oxygen producing anions" always takes place at potentials above 1.23 volts, it is an irreversible process, and hence the potential of the discharge of these anions has not, in general, any relation to the process. The term "discharge potential"

even when used in its proper sense as the potential with which certain electrolytes produce certain products<sup>1</sup> should not, in general—perhaps never—be applied to irreversible changes. We are confirmed in this conclusion when we consider that an electrode discharge probably takes place simultaneously through several *series* of changes, and that these changes are, in general, differently *catalyzed* by any of the substances temporarily or permanently present in the solution or on the electrode (including the electrode material), and it is difficult, if not impossible, to ascertain which of these different processes produces the “highest potential product.” Thus it appears that all conclusions as to the process that has taken place which are based mainly on a “turn” in the “current-voltage” curve obtained in an irreversible operation are questionable, if not absolutely wrong. In this class belong the well-known explanations of the “turns” in the “current-voltage” curve obtained in the electrolysis of acids and bases, which ascribes each of the different “turns” to the setting-in of the discharge of another class of anions. It is thus seen that the cause of all abnormal pole potentials is to be found primarily in the pole itself; and specific considerations of the process should not be made until something definite is known about the pole. The following report gives the advance in our knowledge of the platinum pole itself.

We will now proceed to the main topic of this paper, and we shall present next the essential points observed in the behavior of the oxygen (platinum) electrode.

When small electromotive forces are applied to platinized platinum electrodes in dilute sulphuric acid or sodium hydroxide solution, the potential of the anode increases rapidly—though nothing but extremely small currents, of the order of “diffusion” currents pass until the potential of an anode

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<sup>1</sup> Note that the use of this term, or any other term such as “holding power,” in the sense that a certain potential is required for every kind of ion to have its electric charge separated from it, is never admissible—there is no such force.

passes 1.50 volts:\* then bubbles of oxygen gas begin to appear. From this point on the rise in anode potential is less rapid than before, yet much more rapid than that shown by a reversibly acting gas electrode. In other words, the current-voltage curve turns from its first direction, which is almost parallel to the voltage axis, to a direction which makes quite a large angle with this axis but does not turn as much as would make it almost parallel to the current axis: if it were a reversible electrode which had turned its "reversible point" at approximately 1.50 volts then its final direction would have been nearly parallel to the current axis. The polarization potential also increases steadily with the time during which the current continues uninterruptedly; but there is no indication that a definite maximum value for any particular current density exists.

This extensive polarization can not be due to a specific surface attraction exerted by the platinum upon the gas (adsorption) such as has been assumed for hydrogen and practically proven for this gas by Moeller (6), because the range of potential produced by this influence is too great (it extends to nearly three volts). Furthermore, Foerster (17) has pointed out that platinum is able to functionate definitely at either a lower or a higher potential, which would require a change in the adsorptive power without any apparent reason for such a change. Thus he observed that in an alkaline solution of sodium acetate at 75° a platinum anode showed a potential of 1.8 volts for 45 minutes, while it oxidized the action with a low efficiency—10 to 20 percent—then it seemed to undergo a transformation almost abruptly: the potential rose steadily to 2.50 volts, and the oxidizing efficiency of the current immediately increased to 80 percent and over. This fact can not be harmonized with the conception of a gas layer—neither with the conception that the potential difference might be caused by a resistance film.

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\* All potentials in this paper refer to a constant hydrogen electrode in the same electrolyte: the algebraic sign is that observed in the experimental arrangement, as recommended by Luther (see LeBlanc, Text-book, page 245).

These are the ideas that have been advanced heretofore in explanation of this phenomenon.

The continuity of the potential rise requires that the electromotively active substance formed on the anode shall be of a physical form which can change its concentration continuously: it can not be a single *solid* which is formed, because this would exhibit a constant potential irrespective of its quantity, or in other words, during its formation the potential would remain practically constant. In contra-distinction to this, the material formed should be one which is dissolved, in a sense, by the remainder of the electrode, or the substance from which it is formed, so that, corresponding to its constant increase of concentration, it would exhibit an increase of potential. We shall see that the facts indicate the actual existence of such a state of affairs.

When the oxygen electrode is left at rest after it has been polarized, it shows a *steady* decrease in electromotive force (self discharge!) until a potential of 1.08 volts is approximately attained. However, this "resting place" is not the end of the self-discharge; it is merely a point at which the potential commonly lingers for sometime, after which it drops to still lower potentials. These facts which had been more or less accurately determined by earlier investigators were carefully tested by Foerster and found as given above.

Lorenz (7), who has made a special study recently of the discharge of these anodes, and who has devised a special method for this purpose, has found that the discharge of a polished platinum electrode, in contra-distinction to the platinized electrode investigated by Foerster, exhibits a large number of distinct steps—or points at which the potential remains constant for some time during the discharge. This behavior indicates the presence of distinct oxides with different potentials. However, these steps are observable only with special manipulation, and there appears to be a distinct tendency in the action of the electrode to obliterate these steps and to exhibit a continuous drop in potential during discharge. It is on this account that these different

steps are ordinarily not observed. Their obliteration may be due to a variety of causes, but argues nothing against the interpretation of the existence of the steps.

The points at which the potentials remained constant in Lorenz's discharge of polished platinum electrodes are the following: 1.3, 1.05, 0.97 (?), 0.94, 0.74, 0.64, 0.57, 0.43, 0.27, 0.12, 0.05, 0.008 volts.

The behavior of the platinum anode can not be interpreted without considering the behavior of other metal anodes. Foerster<sup>1</sup> has shown that the behavior of the iridium anode is quite similar to that of the platinum anode, except that in its course of self-discharge it drops steadily to a much lower value than that shown by platinum—namely to 0.865 volts—and the drop is much more rapid than with platinum. Westhaver has shown that an oxygen iridium electrode shows a potential of 1.06 volts in place of 1.08 volts shown by platinum. Platinum and iridium are the only two metals that were considered heretofore as not oxidized by gaseous oxygen, and hence they were the only metals with which it was attempted to obtain the potential of this gas; as it is seen, both metals exert a specific influence in their electrochemical action with oxygen, which is difficult to explain except by the fact that it is their oxides that are active and not the free oxygen gas.

The behavior of lead as an oxygen anode is well known through the storage cell. Recently the alkaline accumulator has made the behavior of the nickel oxide anode also fairly well known. An extensive study of the behavior of copper anode in a solution of sodium hydroxide was made by E. Mueller (8): this has again clearly revealed the connection between the existence of oxides, the anode potential, and the potential at which oxygen is evolved. Lorenz (9) showed that oxygen gas electrodes constructed with such oxidizable metals as lead, silver, nickel, copper, iron, zinc, exhibit potentials which are identical with those shown by their oxides. These observations together with many others

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<sup>1</sup> Loc cit.

obtained in the study of passivity and "valve action" of metals may be summarized somewhat as follows:

(1) During the discharge of "oxygen yielding" anions all metal electrodes are oxidized.

(2) The potential of the electrode is that of the oxide irrespective of any (adsorbed) oxygen gas also present.

(3) The oxides specifically determine the potentials with which oxygen is evolved.

(4) The amount of an oxide that must be actually present to give all characteristic effects may be less than is optically perceptible.

(5) Oxygen gas does not appear to be directly electromotively active.

The proof that the platinum anode is actually oxidized and that it owes its potential to the presence of oxides was recently brought by the work of Woehler, Lorenz, and Ruer, not to mention several others who assisted in an indirect way. The essential parts of their work are here given.

Woehler (10) found that platinum black exposed to oxygen or air increased slowly in weight. It does this even at the ordinary temperature, and somewhat more rapidly at higher temperatures—up to 300°. In one case an increase of 2.3 percent was observed. Most of this oxidized portion is readily soluble in hydrochloric acid—in one case 18 percent of the platinum was dissolved. Besides this soluble oxide, which according to the determinations must be PtO, another oxide is undoubtedly present—perhaps PtO<sub>2</sub>, which is readily formed by oxidation of PtO. Woehler prepared some platinum monoxide, and showed that the general behavior of this substance towards reagents is identical with that of the oxidized platinum black. Platinum sponge and thin platinum foil showed the same behavior, although in a lesser degree, as might be expected from their relative degree of fineness. He has also studied critically the preparation and properties of the oxides of platinum, (11) and has reached the conclusion that the above-mentioned two oxides exist in the form of several hydrates. Just after preparation, these com-



pounds are readily soluble in concentrated hydrochloric acid; but only slightly soluble in sulphuric or nitric acids. They dehydrate on standing, and the dehydrated products are markedly less soluble in acids: the compound  $\text{PtO}_2$ ,  $\text{H}_2\text{O}$  is absolutely insoluble in hydrochloric acid.

Recently (12) Woehler has succeeded in preparing the oxide  $\text{PtO}_3$  by the anodic oxidation of an alkaline solution of  $\text{PtO}_2$ . Of course the first direct result was a salt of the oxide from which he obtained the oxide itself by treatment with acetic acid. This oxide is insoluble in dilute sulphuric or nitric acids and dissolves but slowly in hydrochloric acid with the evolution of chlorine. The oxide is exceedingly unstable, and decomposes into  $\text{PtO}_2$  and free oxygen. The rate of decomposition becomes markedly less as the percent of  $\text{PtO}_3$  in the mixture decreases, and this indicates that the two oxides form a solid solution in which the concentration of the higher oxide and hence its oxygen pressure becomes gradually less.

This oxide,  $\text{PtO}_3$ , is probably the oxide the formation of which on platinum anodes has been frequently observed. The slow rate of interaction with acids which characterize particularly the higher oxides of platinum probably accounts for the relatively slight loss of platinum in electrolytic operations.

Lorenz (13) undertook to determine potentials of the different oxides which Woehler had identified. He found he could not do this by the ordinary *compensation* method, on account of the ease of decomposition (dehydration, etc.), which characterizes these compounds<sup>1</sup> but his special "anode discharge" method gave him satisfactory results, and these are here given together with the corresponding "resting points" of the potential during the discharge of a platinum anode:

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<sup>1</sup> Different hydrates exhibit different potentials as Streintz has shown in connection with the oxides of lead.

Resting points	Oxide potentials	Formulae
0.94	0.93	PtO <sub>3</sub> , 4H <sub>2</sub> O
	0.86	PtO <sub>2</sub> , 3H <sub>2</sub> O
0.74	0.74	PtO <sub>2</sub> , 2H <sub>2</sub> O
0.64	0.63	PtO <sub>2</sub> , H <sub>2</sub> O
0.57	0.53	PtO <sub>2</sub>
0.43	0.45	PtO, 2H <sub>2</sub> O
	0.34	PtO, H <sub>2</sub> O
0.27	0.25	PtO.

The potential shown by the oxide PtO<sub>3</sub> has not been measured so far—possibly it is not measurable because the oxide decomposes so rapidly—but judging from the fact that it is prepared by the anodic oxidation of PtO<sub>2</sub> it should exhibit a potential above 0.93 volts, and hence it is probably the oxide to which all higher potentials are due.

Mention should be made here of the work of Ruer (14) on the dissolution of platinum during alternating current electrolysis. Ruer showed that platinum is dissolved if it is exposed first to strong oxidizing agencies, *e. g.*, extensive anodic polarization—which is followed by an exposure to reducing agencies of a sort which would produce only a partial reversal of the previous oxidation, *e. g.*, limited depolarization. Either agency or both could be exercised by ordinary chemical agents just as well as electrolytic operations. The dissolution takes place during the operation of the reducing agency. One of the ways in which he produced these conditions was by superposing a direct current electrolysis upon an alternating current electrolysis of sulphuric acid between platinum poles: under these conditions the anode was dissolved extensively. He reached the conclusion that metallic platinum is first oxidized to a high oxide which is insoluble; that the latter is then reduced to a lower oxide which is readily acted upon by the electrolyte (sulphuric acid). It is interesting to note that the properties of the oxides of platinum as recently ascertained by Woehler fully bear out this explanation.

The proofs that the behavior of the "platinum-oxygen" electrode is due to the presence of one or more oxides is prac-

tically complete. Yet, concerning the details for the potentials above one volt, two different views may be entertained. The different potentials may be due to a number of distinct oxides—including perhaps some unknown oxides, or perhaps a series of unknown hydrates of the known oxides. This is Lorenz's view. Again the potentials may be due to a solution of a higher oxide in the material of the electrode: this is Foerster's view.

Before the appearance of Woehler's discovery of  $\text{PtO}_3$ , Foerster predicted that such a high oxide should exist, that it would decompose spontaneously into its elements and that its rate of decomposition would be slower as its concentration in the solid solution which it forms with the electrode metal becomes less. We note that Woehler found the properties of  $\text{PtO}_3$  to conform to this prediction with the exception that the decomposition products are oxygen and a hydrate of  $\text{PtO}_2$  in place of oxygen and the metal, as Foerster had predicted. This property of  $\text{PtO}_3$  unites the views of Foerster and Lorenz: the lower potentials are probably due to different oxides as shown by Lorenz, while the higher potentials are due to different concentrations of  $\text{PtO}_3$  in  $\text{PtO}_2$ . Whether the potential, 1.08 volts, of the platinum-oxygen gas electrode is due to a certain oxide, or whether according to Foerster's view it is due to a balance between the rate of formation and the rate of decomposition of the high oxide which results in such a concentration of the latter that it shows this potential—this is still an open question.

A word may be added here on the details of the evolution of oxygen. Foerster<sup>1</sup> and E. Mueller (8) consider that the evolution of oxygen results secondarily through the formation and decomposition of a high oxide. Although they do not express themselves further, yet we may infer that they believe that oxygen is not evolved except through such an action. It seems to the writer that such a view is not tenable. G. Schulze (16) has shown in his investigation on "valve action" that the formation of oxygen takes place also while

<sup>1</sup> Loc cit.

other oxides are present which are not capable of such decomposition (aluminium oxide, magnesium oxide, etc.). Again the view in question would limit the possible mode of reaction to *one*, which is contrary to our general experience in electrode actions. However, this review is scarce the proper place to argue this question.

After this paper had been finished, there appeared an article by K. Bennewitz (18) which deals with the potential of the anode during the electrolysis of dilute sulphuric acid. Although the theoretical considerations and the experimental procedure present much that is both new and valuable, yet, with the exception of the influence of electric waves which will be mentioned below, he presents no new observations, and hence his results do not help to decide the question in what form the oxygen is present just prior to its evolution. He observed irregularities in the current voltage curve at 0.76, 1.08, and 1.50-1.63 volts respectively, *i. e.*, at points previously observed by other investigators. The irregularities observed at 0.76 and 1.08 volts, Bennewitz ascribes to the formation of oxides, but the potentials 1.50-1.63 volts he ascribes to overvoltage; however, it does not appear that he has considered the possibility of the formation of  $\text{PtO}_3$ , which, as we have seen, accounts very well for this potential.

The new item in the fundamental considerations and method of procedure of this paper is the rotation of the pole with the view of producing a constant "diffusion layer," and the separation of polarization effects due to diffusion from all other effects. In this the author succeeds very well, and he makes a particularly valuable contribution in showing that critical "turns" in the current voltage curve may be ascertained by calculation from *any* of the points in the curve. By this means he located the "turn" at 1.50-1.63 volts (the different values depending upon the surface of the electrode, etc.), and he showed that there is only one such "turn" obtained above 1.08 volts in the electrolysis of dilute sulphuric acid.

When the anode is connected with the antenna of a

Hertzian oscillator, the "turn" in the "current-voltage" curve shows itself just above 1.23 volts—*i. e.*, just above the theoretical reversible potential. This is a very interesting result, but so far it proves or disproves nothing because it has not been shown that under *all* conditions electric waves place the "turn" at this point. And finally, should this prove to be the case, it would not prove that we are dealing with the phenomenon of over-voltage because at this potential the rate of decomposition of  $\text{PtO}_3$ —which according to the oxide theory, is increased by the electric oscillations—may have reached its maximum value, possibly because its formation *begins* at this potential. In this connection we should recall that Lorenz observed a "resting point" at 1.30 volts in his study of anodic discharges.

## LIST OF REFERENCES.

The numbers in parenthesis refer to the following list:

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4. *Zeit. phys. Chem.*, **45**, 216 (1903) or see Foerster: "Elektrochemie wässriger Lösungen," p. 344.
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