

The Electrolytic Formation of an Oxide Layer on Platinum in a Sulfuric Acid Solution

By Shigeo SHIBATA

(Received October 7, 1963)

Although the electrolytic formation of oxide films on the surface of platinum electrodes has been extensively studied,¹⁻²⁸ there are still remain quite a few questions concerning the actual electrode reaction and its mechanism.

Wakkad and Emara⁹ found two plateaus in the oxygen region of a slow anodic charging curve (the variation of potential with the passage of electricity) and suggested that these were to be attributed to definite oxides of platinum(II) oxide and platinum(IV) oxide, on the basis of the fact that the potential of these plateaus were equal to the thermodynamic standard potentials of the platinum-platinum(II) oxide and platinum-platinum(IV) oxide couples respectively.

The construction of the oxide formed on

the platinum surface was estimated by chemical analysis¹⁶ to be a mixture of platinum(II) oxide and platinum(IV) oxide in a molar ratio close to 6:1. Laitinen²³ pointed out that one must be certain that during the chemical attack in this analysis the oxidation state of the platinum has not been changed. Giner²⁰ has examined the question of whether or not the definite oxides are formed on platinum by anodic polarization and has concluded that definite oxides don't exist, only chemisorbed oxygen.

A comparison of the anodic and the cathodic charging curves also shows that more electricity is used to form the oxide than to remove it. Vetter and Berndt¹⁹ attributed the difference in the amounts of electricity to the possibility that some of the oxide or oxygen layer is reduced to hydrogen peroxide, which requires less electricity than the formation of the layer. Laitinen and Enke²³ stressed another possibility, that on the loss of oxygen atoms from the surface oxygen tends to diffuse into the grain boundaries of the platinum.

This study was undertaken in order to obtain further information on the behavior of deposited oxygen and on the oxide-film formation on smooth platinum electrodes by measuring the potential behavior, the electrode capacity and the attack on the electrode surface by the alternating anodic and cathodic polarizations.

The results of the present investigation indicate that the anodic film formation reaction proceeds through two steps: an adsorption step of deposited oxygen, and a step of the formation of a definite oxide film.

Experimental

The electrolyte used was a 1N sulfuric acid solution. Sulfuric acid was distilled twice under reduced pressure, and laboratory-distilled water was further purified by redistillation with alkaline permanganate, followed by double distillations in a quartz still. The electrolyte was pre-electrolyzed with a current of 100 mamp. for at least 23 hr. using platinum electrodes. Unless otherwise stated, the solution was continuously swept with purified nitrogen gas in order to keep it free from dissolved

- 1) F. P. Bowden, *Proc. Roy. Soc.*, **A125**, 446 (1929).
- 2) J. A. V. Butler and G. Armstrong, *ibid.*, **A137**, 605 (1932).
- 3) J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, **1934**, 743.
- 4) A. L. Ferguson and M. B. Towns, *Trans. Electrochem. Soc.*, **83**, 271, 285 (1943).
- 5) A. Hickling, *Trans. Faraday Soc.*, **41**, 333 (1945).
- 6) B. V. Ershler, *Discussions Faraday Soc.*, **1**, 269 (1947).
- 7) A. Hickling and W. H. Wilson, *J. Electrochem. Soc.*, **98**, 425 (1951).
- 8) Ts. I. Zalkind and B. V. Ershler, *Zhur. Fiz. Khim.*, **25**, 565 (1951).
- 9) S. E. S. Wakkad and S. H. Emara, *J. Chem. Soc.*, **1951**, 461.
- 10) I. M. Kolthoff and T. Tanaka, *Anal. Chem.*, **26**, 623 (1954).
- 11) M. Breiter, C. A. Knorr and W. Wolki, *Z. Elektrochem.*, **59**, 681 (1955).
- 12) M. Becker and M. Breiter, *ibid.*, **60**, 1080 (1956).
- 13) K. I. Rosenthal and V. I. Veselowskii, *Doklady Akad. Nauk S. S. S. R.*, **111**, 637 (1956).
- 14) J. W. Ross and I. Shain, *Anal. Chem.*, **28**, 548 (1956).
- 15) F. C. Anson and J. J. Lingane, *J. Am. Chem. Soc.*, **79**, 1015 (1957).
- 16) F. C. Anson and J. J. Lingane, *ibid.*, **79**, 4901 (1957).
- 17) J. K. Lee, R. N. Adams and C. E. Briker, *Anal. Chim. Acta*, **17**, 321 (1957).
- 18) G. Radlein, *Z. Elektrochem.*, **61**, 727 (1957).
- 19) K. J. Vetter and D. Berndt, *ibid.*, **62**, 378 (1958).
- 20) J. Giner, *ibid.*, **63**, 386 (1959).
- 21) B. B. Baker and W. H. Macnevin, *Zhur. Fiz. Khim.*, **75**, 1476 (1959).
- 22) J. Giner, *Z. Elektrochem.*, **64**, 491 (1960).
- 23) H. A. Laitinen and C. G. Enke, *J. Electrochem. Soc.*, **107**, 773 (1960).
- 24) F. G. Will and C. A. Knorr, *Z. Elektrochem.*, **64**, 258 (1960).
- 25) W. Bold and M. Breiter, *Electrochimica Acta*, **5**, 145 (1961).
- 26) A. Kozawa, *This Bulletin*, **35**, 1051 (1962).
- 27) A. Kozawa, *J. Electrochem. Soc. Japan (Denki Kagaku)*, **30**, 720 (1962); **31**, 183, 315, 618 (1963).
- 28) S. W. Feldberg, C. G. Enke and C. E. Briker, *J. Electrochem. Soc.*, **110**, 826 (1963).

oxygen and hydrogen. The presence of oxygen or hydrogen is undesirable; oxygen acts as a depolarizer when the electrode is treated cathodically, while hydrogen reacts chemically with the oxygen on the platinum electrode surface and acts as a depolarizer for anodic electrode treatment.

The test electrodes were cleaned by treating them successively with hot concentrated hydrochloric acid, hot concentrated nitric acid and hot chromic acid, and finally by washing them with distilled water.

As the reference electrode, a saturated calomel electrode was used throughout. The values of the potentials described in this paper are on the standard hydrogen scale. All measurements were made at a constant temperature of $25 \pm 0.1^\circ\text{C}$.

The Charging Curves.—Both the test electrode and the counter electrode were smooth platinum plates 2.0 cm^2 in apparent area, counting both sides. The electrolytic cell was constructed entirely of Pyrex glass, with the two compartments of the test electrode and of the counter electrode separated from one another by a sintered glass disk; each was equipped with a gas inlet tube. The compartment of the test electrode was fitted with a water jacket, through which water regulated at 25°C was circulated.

The circuit for the measurement was of the usual type, equipped with two large B-type batteries of 67.5 V. in series to power the electrolysis circuit. A potentiometer recorder with a high impedance input pre-amplifier (50 M Ω) was used to record the charging curves.

Electrode Capacity.—The test electrode was formed of wire 0.5 mm. in diameter and 5 mm. long; the end of the electrode was covered with a small glass ball to prevent an edge effect of the discharge. The counter electrode of platinum gauze in the shape of a cylinder 20 mm. high and 25 mm. in diameter was placed around the test electrode. The set of these electrodes was placed in a double walled glass vessel, between which two walls there flowed water of a constant temperature. This cell was also used for the measurement of the square-wave alternating-current electrolysis to be described in the next section.

The behavior of the differential capacity of the electrical double layer during forced anodic polarization with a constant current was measured by a fast single-current pulse method. This technique is nearly the same as that described by Schmid and Hackerman.²⁹ The method consists of calculating the capacity from the initial slope of the potential-time curve produced by the pulse under the assumption that the slope of the potential-time curve just before the onset of the pulse is zero. Though this is not true in a strict sense, the slope before the onset of the pulse, not exceeding the order of 10^{-2} V./sec. , can be ignored in comparison with the slope produced by the pulse of the order of 10^2 V./sec.

A block diagram of the electronic apparatus is given in Fig. 1. The potential of the electrode

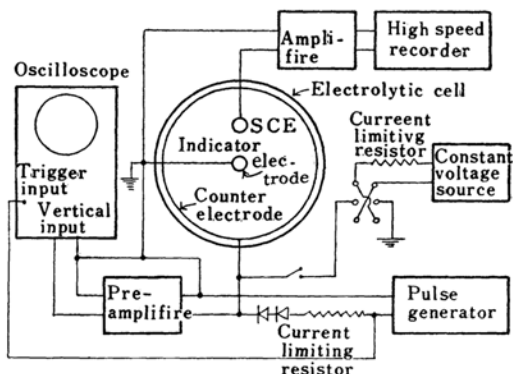


Fig. 1. Circuit diagram.

was measured against the reference electrode through a Luggin capillary by feeding the output of this cell into the recorder. In addition to the steady current, the cathodic pulses were delivered from a generator at the regular rate of 1 pulse every 2.0 sec. The pulses from the generator were passed first through a current-limiting resistor and then through a series of two diodes in order to eliminate a residual direct current from the generator. The pulse-rise time was 0.2 $\mu\text{sec.}$, and the duration was 8 $\mu\text{sec.}$ The ratio of the current to the slope of the potential-time curve, $\Delta E/\Delta t$, gives the double-layer capacity. In practice, the current was so adjusted that ΔE was 1–4 mV. at a Δt of 8 $\mu\text{sec.}$ Since Presbery and Schuldiner³⁰ showed that practically all of the applied current goes to the charging of the double layer in the first 10 $\mu\text{sec.}$, the Faradaic effect is probably negligible. The potential changes of the test electrode caused by these pulses were photographed from the screen of a carefully calibrated cathode-ray oscilloscope (Iwasaki synchroscope, Model SS-5151) equipped with an input pre-amplifier (1 mV./cm.). The beam of the oscilloscope was triggered by the pulse itself, and the curves of the potential change caused by the pulse were successively photographed by means of winding a roll film a little every pulse, the shutter of the camera being kept open.

Square-wave Alternating-current Electrolysis.—This experiment was undertaken to study the effect of the repeated alternate anodic formation and cathodic dissolution of the oxide film on the electrode surface.

The test electrodes for this experiment were platinum wire 0.5 mm. in diameter and 6–4 mm. long; a new one was used for every run of the measurement. The frequency of the square wave was 78 or 40 c. p. s., the rise time was 1 $\mu\text{sec.}$, and the voltage, 100 V.

The electrolysis was carried out in a hydrogen-saturated solution for a given time under the conditions of a constant shape and a constant amplitude of a charging curve resulting from the square-wave current electrolysis. When any change was found on the curve during the electrolysis, which was watched closely with the oscilloscope,

29) G. M. Schmid and N. Hackerman, *J. Electrochem. Soc.*, **109**, 1096 (1962).

30) C. H. Presbery and S. Schuldiner, *ibid.*, **108**, 985 (1961).

the current was increased or decreased slightly so as to restore the curve to its original state. The degree of the attack of the surface may be estimated by measuring the increase in true area per apparent unit area, i.e., the increase in roughness factor, because the surface is coarsened by the electrolytic attack; the increase in the true surface area can be approximated to the degree of the attack, unless the surface suffers too much corrosion. Since the value of the electricity Q_a (coulombs/apparent unit area) required to form the oxide film, which can be measured from the anodic charging curve, is proportionate to the true area of the electrode, the degree of the attack is estimated by the ratio of the Q_a' for the electrode already electrolyzed to the Q_a for that not yet electrolyzed. For this purpose, the charging curves were photographed with the oscilloscope.

Results and Discussion

The Possibility of the Existence of Adsorbed Hydrogen Which is Removed in the Oxygen-deposition Region.—Typical charging curves for an oxygen-hydrogen-free solution with a small current density are shown in Fig. 2. The initial rise of the potential (region α_a) is attributed to the ionization of adsorbed hydrogen. The second rapid linear rise (region β_a) is ascribed to the charging of the double layer, and a final slow linear change (region γ_a), to the deposition of oxygen, which forms a monolayer of oxygen atoms on the surface

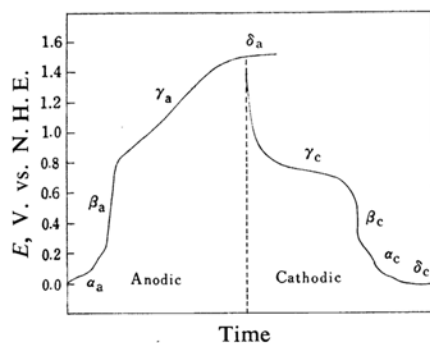


Fig. 2. Charging curves with small current density.

prior to the evolution of gas (region δ_a). When the current is reversed and the anodized electrode is made cathodic, the potential falls very rapidly to a plateau (region γ_c) which corresponds to the reduction of the oxide film formed during the γ_a region of the anodization. When all of the oxide has been reduced, the potential falls again through β_c and the hydrogen deposition (region α_c) prior to the final evolution of gas (region δ_c).

One of possible presumptions we can make as to the cause of the fact that the quantity

of the electricity, Q_e , required to remove the oxide is smaller than that, Q_a , required to form the same substance would be that, in the anodic polarization, some of hydrogen atoms not removed in the α_a region are oxidized at the initial stage of γ_a .³¹⁾ If this is the case, Q_a , the sum of the quantity of electricity consumed to remove the hydrogen and to form the oxide film, should be larger than Q_e , the quantity required only to remove the oxide, and there should be a difference in the shape of the charging curve for the γ_a stage or in the quantity of electricity consumed for this stage in the anodic polarization between the bare electrode and that one covered with adsorbed hydrogen. The BCDEF curve in Fig. 3 is for the electrode polarized

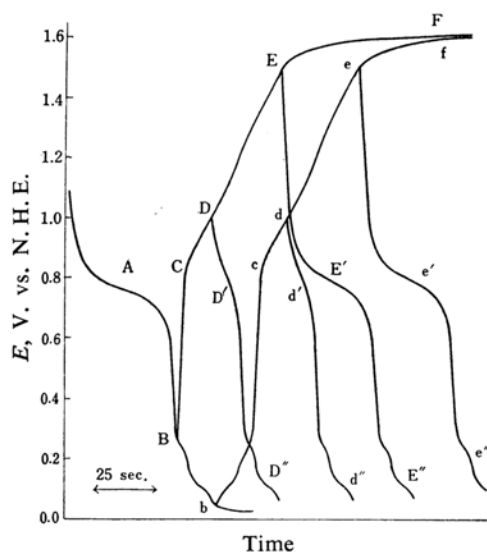


Fig. 3. Anodic and cathodic curves from various initial potentials.
 $i_a = i_k = 20 \mu\text{amp./cm}^2$

from the potential B, where its surface is bare, while the bcdef curve is for the one polarized from the potential b, where its surface is completely covered with adsorbed hydrogen atoms. Between these curves no difference can be found. Moreover, it should be expected that the transition time of γ_c for the DD'D' curve obtained when the current is reversed immediately at the D potential on the ABCD curve is larger than that for the dd'd'' curve reversed at the d potential on the abcd curve, but in practice these two curves, like also EE'E'' and ee'e'', were identical. For these reasons, we cannot accept the above assumption under the conditions of the experiment carried out in this work.

31) T. C. Franklin and S. L. Cooke, *ibid.*, **107**, 556 (1960).

The Detection of Hydrogen Peroxide.—If the presumption of Vetter and Berndt¹⁹⁾ is true as to the cause of inequality between Q_a and Q_c , it should be possible to detect hydrogen peroxide near the electrode during cathodization.

A differential spectrophotometric method using 1,10-phenanthroline³²⁾ was used for the determination of a trace of hydrogen peroxide. This method enables us to detect 0.1 to 2.5 p. p. m. of hydrogen peroxide with satisfactory precision and accuracy.

As the test electrode, a platinum wire 0.1 mm. in diameter and 10 m. long wound on a glass frame was used. According to the above presumption, 0.203×10^{-6} mol. hydrogen peroxide must be produced in the electrolyte during cathodization, because the value of Q_c for this electrode was measured as 4.032×10^{-2} coulombs. Since the volume of the electrolyte used for the measurement was 15 cc., the concentration of the hydrogen peroxide is expected to be 0.474 p. p. m.

Although the analysis was carried out very cautiously several times, the hydrogen peroxide could not be detected in a stationary solution, in an agitated solution, or on a rotated electrode. Consequently, the suggestion of Vetter and Berndt must be rejected.

The Loss of the Oxygen Deposited on the Surface.—In order to study the behavior of the oxygen deposited on the platinum electrode, the anodic and cathodic charging curves were taken under various conditions.

When the anodic current was reversed im-

mediately at a potential, E_a , during the γ_a process, the charging curves shown in Fig. 4 were obtained. The ratios of q_a , the quantity of electricity required for the process from the initial potential of γ_a to E_a on the anodic curve, to q_c , that used for the plateau of γ_c on the cathodic curve taken subsequently, were plotted against E_a , as is shown by curve A in Fig. 5. For E_a exceeding 1.20 V. ($=E_a^0$), the ratio, q_c/q_a , has a constant value, but it decreases below this value.

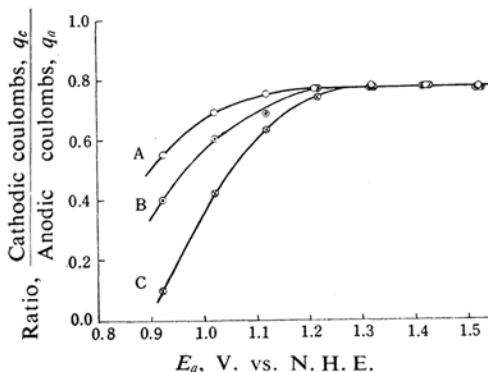


Fig. 5. Cathodic and anodic coulomb ratio as a function of potential, E_a , where the current was reversed.

- immediately reversed
- allowed to remain at open circuit for 2 min. in stationary solution
- ⊗— allowed to remain at open circuit for 2 min. in agitated solution

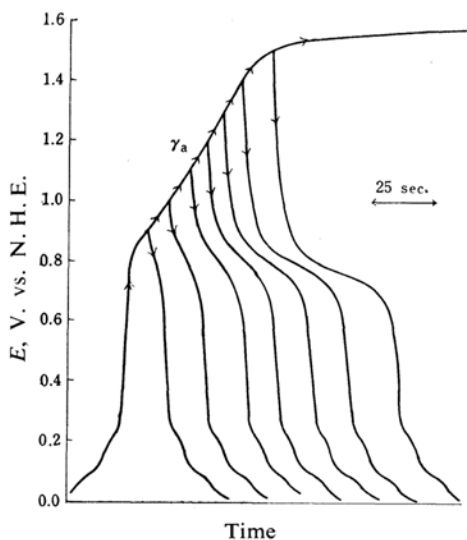


Fig. 4. Alternating anodic-cathodic charging curves when the current was reversed at various potential, E_a .

$$i_a = i_k = 20 \mu\text{amp./cm}^2$$

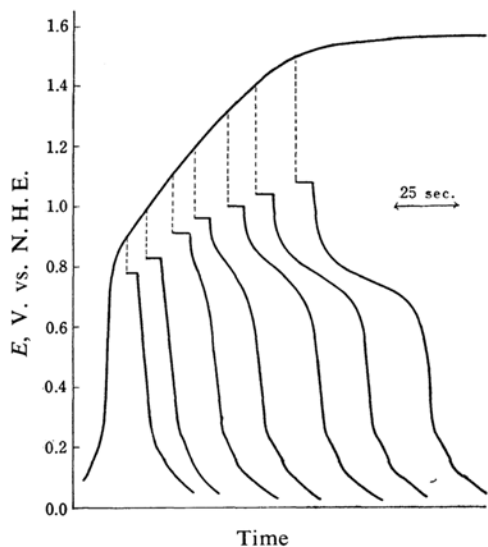


Fig. 6. Cathodic charging curves in stationary solution after anodic polarization till a various potential, E_a , and allowing to remain at open circuit for 2 min. in continuously agitated solution.

$$i_a = i_k = 20 \mu\text{amp./cm}^2$$

32) R. Bailey and D. F. Boltz, *Anal. Chem.*, 31, 117 (1959).

When the solution was agitated vigorously by passing bubbling nitrogen gas through, the value of Q_a increases to 1.4 times that obtained under the stationary solution, whereas the value of Q_c suffers little effect from the agitation. For this reason, it may be presumed that a part of the oxygen deposited in the process of γ_a is very unstable and may be easily removed from the surface. After it is polarized to a given potential, E_a , of the γ_a region with a constant anodic current, the electrode was allowed to remain at an open circuit for 2 min.; then it is polarized cathodically with the same current density. The variation of the ratio, q_c/q_a , thus obtained against E_a is shown by curve B in Fig. 5. If the solution was agitated while the electrode was allowed to stand in this experiment, curve C in Fig. 5 was obtained. When the solution was continuously agitated throughout the anodic polarization and the standing, the curves shown in Fig. 6 were obtained. The plateau, γ_c , of the cathodic curve for the electrode anodized to the potential E_a below 1.05 V. vanished completely, and the potential fell rapidly and immediately reached the hydrogen deposition region.

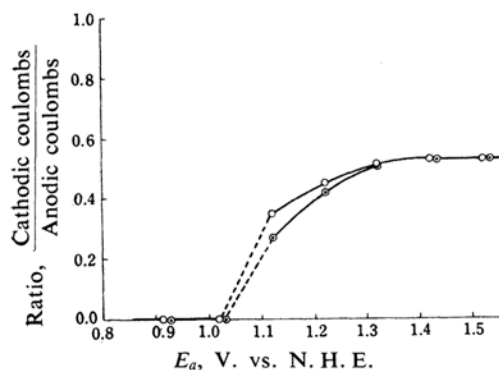


Fig. 7. Cathodic to anodic coulomb ratio as a function of anodically polarized potential, E_a . $i_a = i_k = 20 \mu\text{amp./cm}^2$

- for anodic process in agitated solution and cathodic process in stationary solution after standing for 2 min. in stationary solution.
- ◐—◐ for anodic process in agitated solution and cathodic process in stationary solution after standing for 2 min. in agitated solution.

The data shown in Figs. 5 and 7 suggest strongly that oxygen deposited in the first half of the γ_a region is attached loosely on the surface and is easily removed spontaneously during the standing or by the agitation of the solution.

The inequality between Q_a and Q_c may be

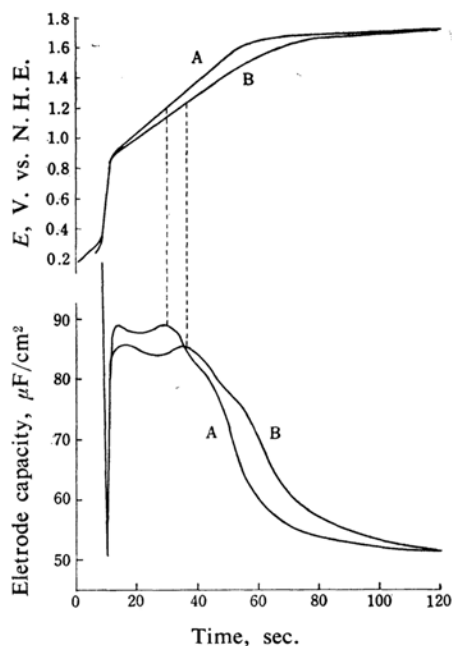


Fig. 8. Electrode potential and double layer capacitance during anodization at $25 \mu\text{amp./cm}^2$ as a function of time.

- A in stationary solution
- B in agitated solution

caused by such a loss of the deposited oxygen from the surface in the initial stage of γ_a .

The Capacity Change in the Course of the Anodic Process.—The potential-time and the capacity-time curves were measured simultaneously during the anodic polarization in the stationary solution, the results being shown in Fig. 8. The capacity-time curve may be divided into three portions: (a) the first portion, which starts with the oxygen deposition potential, where the capacity has a maximum value of approximately $90 \mu\text{F/cm}^2$; (b) the second portion, characterized by a fall of the double layer capacity with time, beginning from 1.15 V. ($=E_w^\circ$), and (c) the third portion, with a stationary capacity value of $50 \mu\text{F/cm}^2$, which is very close to the value found by Laitinen and Enke²³⁾ for an oxidized surface. The result obtained with an agitated solution is shown by curve B in Fig. 8. The maximum value of the capacity is $4\sim5 \mu\text{F/cm}^2$, which is smaller than that for the stationary solution, but the potential at which the capacity value begins to fall coincides with that for the stationary solution.

According to Llopis and Colum,³³⁾ the increase of the electrode capacity of a

33) J. Llopis and F. Colum, Proceedings of the International Committee on Electrochemical Thermodynamics and Kinetics, Eighth Meeting, 1958, Butterworths, London, pp. 414-427.

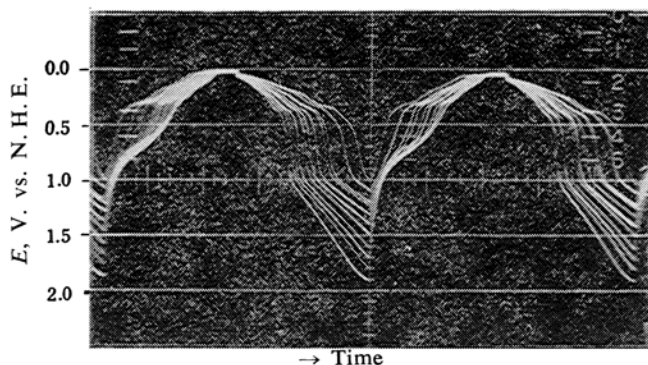


Fig. 9. Oscilloscope traces of electrode potential in square wave current electrolysis of frequency 78 c. p. s. at various c. d.

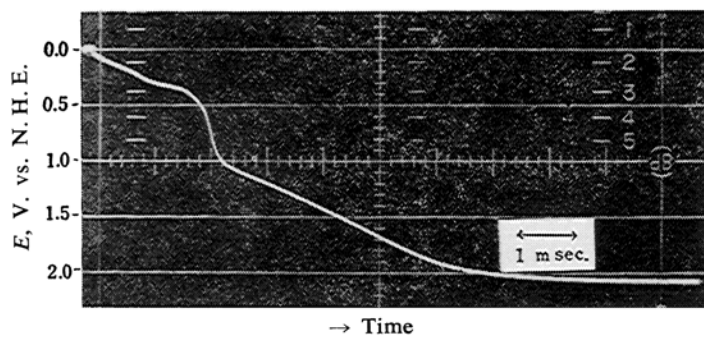


Fig. 10. Typical oscilloscope trace of anodic charging curve.
 $i_a = 190 \text{ mamp./cm}^2$

platinum electrode at the beginning of the surface oxide formation is due to the presence of a dipole such as $\text{Pt}\cdots\text{O}$ at the electrode-solution interface. On the basis of this explanation, it is possible to account for the capacity vs. surface charge curve. Highly polar groups, which might be represented by $\text{Pt}^+\cdots\text{O}^-$, $\text{Pt}^+\cdots\text{OH}^-$ or $\text{Pt}\cdots\text{OH}_2$, may exist at the metal-solution interface on which the initial stage of oxygen deposition is proceeding. These dipoles replace the water molecules and ions which had formed the electrical double layer at the reduced electrode surface. The decrease in electrode capacity that was observed at the potential above E_w^0 may be caused by the decrease in the number of highly polar groups, or by their conversion to non-polar ones, probably to definite oxide molecules.

The Attack by Square-wave Alternating-current Electrolysis.—The mechanism of the change in the structure of a platinum electrode surface caused by repeated alternate anodic and cathodic polarizations calls for our intensive attention. The oscillogram of Fig. 9 shows the charging curves of the test electrode observed when the square-wave current of

various current densities were passed through the cell containing a hydrogen-saturated solution. The amplitude of its oscillation increased with the increase in current density. A square-wave current was so adjusted that the maximum value of the oscillating potential was the desired value, E_s ; the lowest potential, on the other hand, was equal to the hydrogen-evolution potential, which should be slightly increased by the hydrogen overpotential when the current density increases. The oscillogram shown in Fig. 10 is typical of the anodic charging curves photographed in order to determine the increase in true surface area caused by the electrolysis. The degree of the attack resulting from the electrolysis is shown in Fig. 11. It may be found from this figure that the surface of the electrode was not attacked at all as long as the potential did not exceed 1.15 V. ($=E_s^0$), regardless of the electrolyzing duration or the frequency, whereas if the potential exceeded E_s^0 , the ratio Q_a'/Q_a rose rapidly, the bright surface becoming cloudy. The rate of the attack is faster at a frequency of 78 c. p. s. than at one of 40 c. p. s. and the surface is attacked more deeply when the electrolysis is prolonged at a given fre-

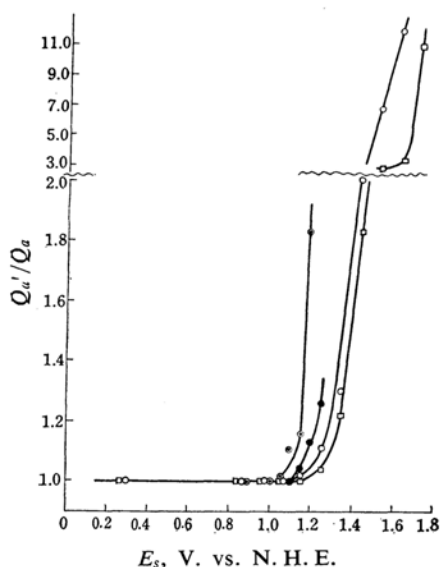


Fig. 11. Relation for maximum value, E_s , of oscillated potential and attack of electrode surface in square wave current electrolysis.

	Frequency c.p.s.	Electrolysing time hr.
□	40	1.0
○	78	1.0
●	78	3.0
⊙	78	6.0

quency. As has been pointed out in previous papers^{34,35} on the sine-wave alternating-current electrolysis, it is clear that the attack of the electrode is not due to the alternate anodic dissolution and cathodic redeposition of platinum itself. Rather, the attack may be attributed to the repetition of the alternate formation and reduction of the oxide film, in which an oxygen atom forms a chemical bond with a surface platinum atom so that the bonds between the oxidized platinum atom and atoms adjoining it are either weakened or ruptured, according to the circumstances. The accumulation of these bond changes due to the repetition of the formation and reduction of the oxide rearranges the platinum atoms to make a recrystallization of platinum on the surface. The fact that surface did not suffer any attack at all the potential below E_s^0 suggests that the oxygen atoms deposited on the surface under that condition are only at a state of the adsorption in which they are not able to effect a serious change in the Pt-Pt bonds.

During the electrolysis at a potential below E_s^0 with a constant current density, the shape

of the charging curve did not change for a long time. The activity of the electrode, however, was lost gradually as the electrolysis was prolonged. At a potential above E_s^0 , the current density had to be increased slowly with time in order to hold the wave shape invariable, because the roughness factor of the surface was increased by the beginning of the attack. In this case, the activity suffered no decay at all for the long period of the electrolysis.

The activation of the platinum surface by the pretreatment of anodic and subsequent cathodic polarization may be attributed to the light platinization due to the formation and reduction of oxide films.³⁶ On the other hand, the loss of the activity with time may be attributed to the settling down of the active platinum atoms on the surface into a stable state^{37,38} as well as to poisoning by the impurities. Consequently, whether or not the activity decays during the alternating-current electrolysis should depend on whether the deposited oxygen is only adsorbed on the surface or whether it forms the oxide with platinum.

When platinum electrodes which have been aged in a hydrogen atmosphere for a long period of time are anodically polarized with a small constant current in a solution containing hydrogen, periodic oscillations of the electrode potential are often observed.^{39,40} This potential-time curve for an acidic solutions shows a transition to a potential ca. +1.0 V., at which the deactivated electrode is reactivated, and then it sweeps down to near the reversible hydrogen potential. The noteworthy fact is found in this experiment that the electrode is not activated at the starting potential of the oxygen deposition process, γ_a , but at the potential nearly corresponding to E_s^0 . This behavior of the electrode may also be interpreted reasonably by the mechanism described above.

Conclusion

The process of the deposition of the oxygen at the anodization has been observed only as a monotonous increase in the potential on the charging curve. However, it has been found that the γ_a region may properly be divided into two portions at the potential 1.15 V.

36) F. C. Anson and D. M. King, *Anal. Chem.*, **34**, 362 (1962).

37) L. P. Hammett and A. E. Lorch, *J. Am. Chem. Soc.*, **55**, 70 (1933).

38) S. Shibata, *This Bulletin*, **36**, 525 (1963).

39) G. Armstrong and J. A. V. Butler, *Discussions Faraday Soc.*, **1**, 122 (1947).

40) D. T. Sawyer and E. T. Seo, *J. Electroanal. Chem.*, **5**, 23 (1963).

34) S. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **79**, 239 (1958).

35) S. Shibata, *ibid.*, **80**, 453 (1959).

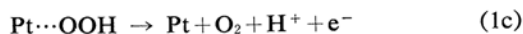
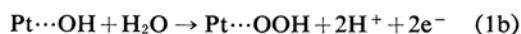
($=E_a^\circ=E_w^\circ=E_s^\circ$), the reaction taking place in different ways in the respective portions.

According to the observed anodic behavior of the electrode, the mechanism of the surface oxidation may be proposed as follows, partly in identical terms with the proposal of Laitinen and Enke.²³⁾

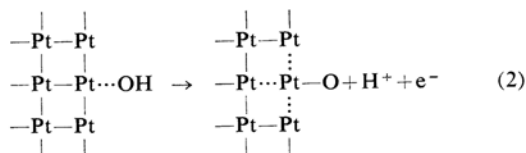
On the first half portion of γ_a ,



some of the $\cdots\text{OH}$ intermediates thus adsorbed weakly on surface platinum atoms can further behave in either of two ways. First, they may be desorbed naturally from the surface, and, secondly, an oxygen evolution reaction may remove the surface hydroxyl, forming a bare platinum site as follows:



On the latter half of γ_a , the surface hydroxyl is converted to a surface oxygen atom which is so firmly bound, producing the definite oxide of platinum, that the bond between the oxidized platinum atom and atoms adjoining it is weakened.



*Department of Chemistry
Faculty of Liberal Arts and Science
Yamagata University
Koshirakawa-cho, Yamagata*