The Electrolytic Formation and Dissolution of the Oxide Layer on Rhodium in an Acid Solution

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The surface oxidation of rhodium has been studied in parallel with that of platinum by means of chronopotentiometry,[1] the triangular voltage sweep[2,3] and rest-potential measurement[4]. However, there has as yet been very little study aimed at giving a coherent mechanism of the formation and dissolution of the surface oxide under the conditions of controlled current electrolysis.

The present paper will describe the results obtained with rhodium electrodes using techniques similar to those applied to the platinum electrode in this laboratory.[5]

Experimental

The electrical circuit and the electrolytic cell used were fundamentally similar to those previously described.[4] The electrode was a smooth rhodium wire 0.5 mm. in diameter and 10.3 mm. long. The electrode was stored in 10 N nitric acid when not in use. The counter electrode was a platinum cylinder placed concentrically around the test electrode. The electrolytic solution was 2 N sulfuric

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[1] M. Breiter, C. A. Knorr and W. Völkl, *Z. Elektrochem.*, **59**, 681 (1955).

[2] F. G. Will and C. A. Knorr, ibid., **64**, 270 (1960).

[3] W. Böld and M. Breiter, *Electrochim. Acta*, **5**, 169 (1961).

[4] J. P. Hoare, *J. Electrochem. Soc.*, **111**, 232 (1964).

[5] S. Shibata, This Bulletin, **37**, 410 (1964).

acid, which had been freed from dissolved oxygen by passing purified nitrogen gas through, unless otherwise stated.

The experiments were made in an all-glass, double-wall cell which allowed the electrolyte to be thermostated and also permitted the bubbling of nitrogen gas. All experiments were made at 25 ±0.1°C.

The reference electrode was a mercury-mercurous sulfate electrode in 2 N sulfuric acid. The values of the potential described in this paper are on the standard hydrogen scale.

Results and Discussion

Charging Curves.—Typical charging curves for oxygen- and hydrogen-free solutions are shown in Figs. 1A and 2A.

A constant current is passed through, and the potential of the electrode is followed as a function of the time. The potential rises slowly (the α_a region) until all the hydrogen adsorbed on the electrode has been oxidized. The potential then rises rapidly through the region, β_a, where the only process is the charging of the electrical double layer. At 0.6 V. an anodic process begins, and the potential increases more gradually through the γ_a region. Eventually the oxygen evolution potential is reached, causing a leveling off of the potential (the δ_a region). If the current is reversed and the electrode thus anodized is made the cathode, the cathodic charging curve of Fig. 2A is observed. The potential drops very rapidly to about 0.5 V., where there is a plateau (the γ_c region) due to the reduction of the oxide layer formed in the γ_a region of the anodization. The potential drop is slow in both the γ_c and γ_c' regions, and the difference in the slopes of these curves is so small that the starting potential of α_c is not satisfactory determined. The δ_c region is attributed to the evolution of hydrogen.

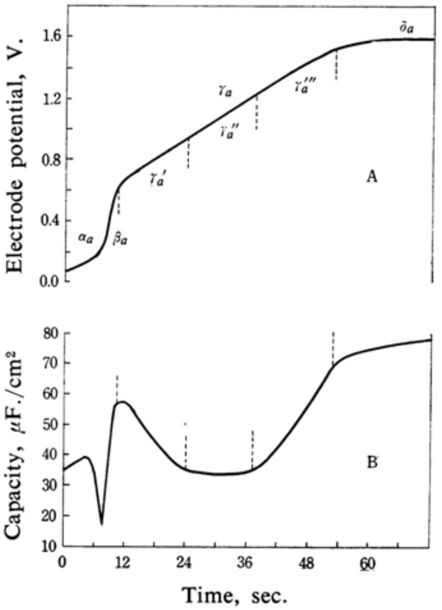

Fig. 1. Comparison of charging and capacity curves.

A Anodic charging curve. i_a=46 μamp./cm²

B Differential capacity curve recorded simultaneously with curve A.

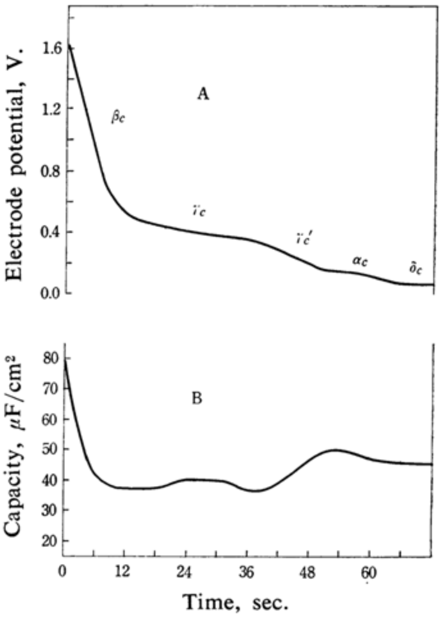

Fig. 2. Comparison of charging and capacity curves.

A Cathodic charging curve of the oxidized electrode. i_c=46 μamp/cm²

B Differential capacity curve recorded simultaneously with curve A.

The anodic and cathodic charging curves do not have the same shape. If the difference in their shapes were due to the effect of the polarization as the result of a slow reaction, the curves would become more similar as the current density is decreased. However, a very low current density study showed that the hysteresis is not decreased significantly by a decrease in the current density. Such an intrinsic hysteresis suggests a reaction which is so irreversible that the oxidation and reduction occur by different mechanisms.

A comparison of the anodic and cathodic curves shows that the γ_a region is always larger than the $\gamma_c+\gamma_c'$ region, indicating that more electricity is used to form the oxide than is required to remove it. (The γ_c region is also the reduction stage of the oxide layer. Its experimental evidence will be given later.) This inequality in electricity can be explained without inconsistency if, in the course of cathodization, the reduction of the oxide to hydrogen peroxide is assumed.⁶⁾ However, it was shown in a previous paper⁵⁾ that this hypothesis is not applicable to platinum. It is necessary to examine whether or not the hydrogen peroxide theory is true for rhodium.

The Variation in Double Layer Capacity during the Anodic and Cathodic Polarizations.— The differential double layer capacity of the rhodium electrode was measured by the galvanostatic pulse method previously described.⁵⁾ The pulse-rise time was 0.2 μsec., and the duration was 5 μsec. 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 pulse current was so adjusted that ΔE was 1—4 mV. at a Δt of 5 μsec. To prevent the lowering of the double layer capacity by the traces of surface-active impurities adsorbed on the electrode, the electrode was first anodized in order to eject the impurity.⁷⁾ The clean electrode was then reduced before measurements made.

The value of the double layer capacity thus observed showed an interesting mode of time change during the constant current anodic and cathodic polarizations, as may be seen in Figs. 1B and 2B respectively. These results suggest that the γ_a region of the anodic charging curve can be divided into three regions, γ_a', γ_a'' and γ_a''', in spite of its simple tone. Starting with the oxygen deposition potential of 0.6 V., the first stage, γ_a', is characterized by a fall of the double layer capacity with an increase in the potential until 0.9 V. The second stage, γ_a'', is marked by a constant minimum value of 34 μF./cm² in the potential from 0.9 to 1.2 V., and the final stage, γ_a''', by an increase in the value until the potential of 1.5 V., at which the evolution of oxygen begins.

It has been suggested by Llopis and Colum⁸⁾ that the cause of the increase in the electrode capacity at the anodization is the presence of such dipoles as M⋯O or M⋯OH at the electrode-solution interface. These dipoles would replace the water molecules and the ions which form the electrical double layer at the reduced electrode surface. The behavior of the electrode capacity due to the anodization seems to give us some information about the mechanism of the surface oxidation. In the first stage, γ_a', with the high capacity value, highly polar groups may be expected to exist at the metal-solution interface of the electrode, which may be represented as Rh⋯OH. In the γ_a'' stage, these polar groups of the hydroxyl radical may be converted into non-polar groups or into the definite oxide, and in the final stage, γ_a''', the polar groups may be adsorbed on this oxidized surface.

The capacity change during the cathodization of the oxidized electrode is monotonic compared with that during the anodization.

The Electrode Reaction in the γ_c' Region.— For the platinum electrode, the oxide layer is reduced exhaustively at the one stage of 0.8 V. which corresponds to the plateau, γ_c, of 0.5 V. for the rhodium electrode. When all of the oxide on the platinum has been reduced, the potential drops rapidly to about 0.3 V., where the deposition of hydrogen begins. However, for the rhodium electrode, following the γ_c plateau a slow linear fall of the

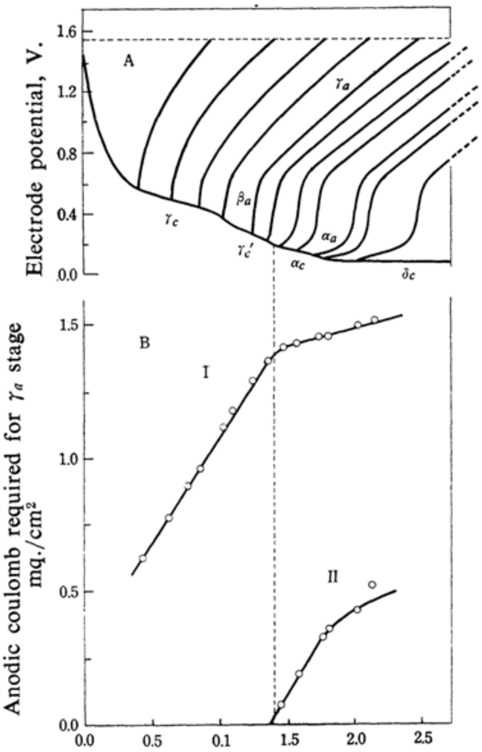

Fig. 3. A. Anodic charging curves from various initial potentials. $i_a=94$ μamp./cm².

B. Plot of anodic coulombs required for the stages of γ_a (curve I) and α_a (curve II) of the anodic charging curves for the electrode which was polarized from various initial potentials vs. cathodic coulombs used to polarise the oxidized electrode to these initial potentials.

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6) K. J. Vetter and D. Berndt, *Z. Elektrochem.*, **62**, 378 (1958).

7) H. A. Latinen and C. G. Enke, *J. Electrochem. Soc.*, **107**, 773 (1960).

8) J. Llopis and F. Colum, "Proceedings of the International Committee on Electrochemical Thermodynamics, Eighth Meeting, 1958," Butterworths, London, p. 414—427.

potential, γ_c', is observed. In order to look into the reaction taking place in this region, the following measurements were carried out.

The electrodes oxidized by a constant current anodization up to the potential of 1.55 V., which is the end potential of the γ_a region, were polarized cathodically with a constant current up to various potentials, and then the current was reversed immediately. The charging curves obtained by these procedures are shown in Fig. 3. In general, following the initial steep ascent of the potential (β_a), the potential curves turn to a slow linear rise, γ_a. However, when the cathodic current was reversed at the potential below 0.2 V., the α_a plateau, the ionization stage of the adsorbed hydrogen, appears on the anodic curves. As long as the quantity of electricity, which has been passed through the oxidized electrode at the cathodization, q_c, does not suffice to reduce the oxide layer exhaustively, the quantity of electricity, q_a, which is required to restore the thus-cathodized electrode to the oxidized state will increase as q_c is increased. The number of coulombs required to oxidize a given electrode from the completely reduced state into the completely oxidized state would be constant. Consequently, it may be seen from the comparison of the potential curve in Fig. 3A with the coulombic curve I in Fig. 3B that the γ_c' region, together with the γ_c of the cathodic charging curve corresponding to the steeper branch of the curve I, can be attributed to the reduction of the oxide layer. The α_c region, corresponding to the less sloped branch of curve I and to curve II, can be ascribed to the adsorption of hydrogen on the electrode after the completion of the reduction of the surface oxide.

The fact that the oxide layer is reduced in two regions by the consecutive cathodization suggests that the oxide layer consists of two different species of oxide or that it is removed subsequently through two-stage reactions.

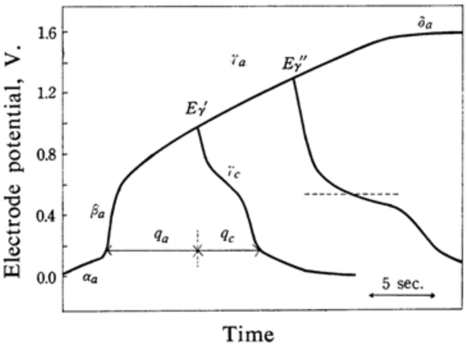

Fig. 4. Alternating anodic-cathodic charging curves when the current was reversed at potentials, E_γ' and E_γ''. $i_a = i_c = 94$ μamp./cm²

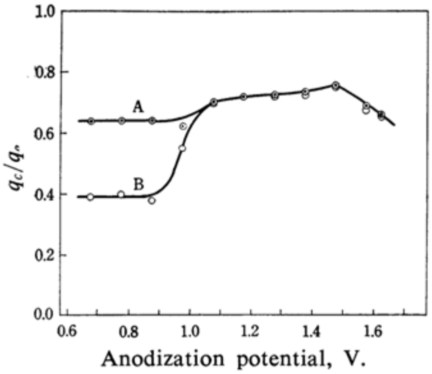

Fig. 5. Plots of the anodic and cathodic coulomb ratio vs. the potential at which the current was reversed or turned off. $i_a = i_c = 94$ μamp./cm²

Curve A, immediately reversed.

Curve B, allowed to remain at open circuit for 1 min. in stationary solution before the cathodic polarization starts.

The Anodic and Cathodic Coulombs. — The applied anodic current is immediately reversed at various potentials, E_γ's, in the γ_a region. The charging curves thus obtained are shown in Fig. 4. The ratio of q_a, the quantity of electricity used in the region from the initial potential of γ_a to the potential, E_γ, on the anodic curve, to q_c, that used from E_γ, to the end potential of γ_c' on the cathodic curve, was traced against E_γ; the results are represented by curve A in Fig. 5. Furthermore, the anodic and cathodic charging curves were taken in the same manner as above except that the circuit was let stand open for one minute after the anodic polarization up to E_γ till the outset of the cathodic one. The results thus obtained are represented as curve B in Fig. 5. The spontaneous decrease in the q_c/q_a ratio for the electrode anodized up to potentials in the γ_a' region indicates that the oxygen deposited in this potential region is unstable and less tightly bound with the metal than the oxygen in higher potential regions, γ_a'' and γ_a'''.

The Reduction Potential of the Oxide Layer, the Open Circuit Potential and the Quantity of Electricity Required for the γ_c' Stage as a Function of the Pre-anodization Potential.— The potential of the γ_c plateau, i. e., the reduction potential of the oxide layer on the electrode, varies with the potential at which the electrode is pre-anodized, as is shown in Fig. 6. This curve can be divided into three linear sections corresponding to three potential regions, γ_a', γ_a'' and γ_a''', of the anodic charging curve.

When the pre-anodization potential was taken in the γ_a' region, the slope of the

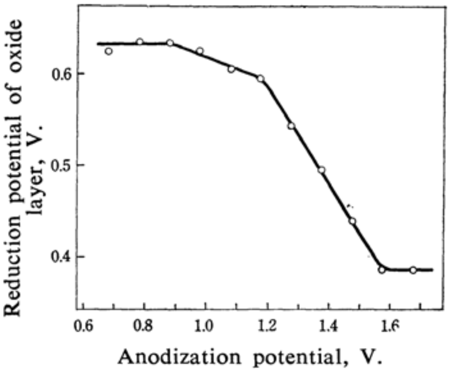

Fig. 6. Plot of the reduction potential of oxide layer at the stage γ_c vs. the pre-anodization potential.

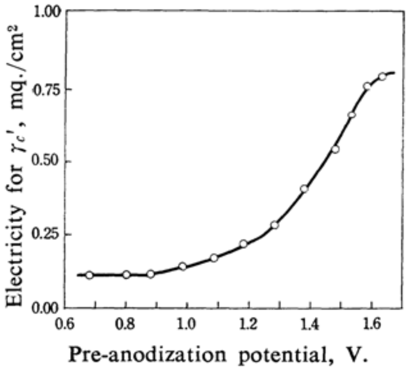

Fig. 7. Plot of the quantity of electricity required for the region γ_c' vs. the pre-anodization potential.

curve γ_c', for this electrode was almost equal to that of the curve, β_a, which is attributed only to the charging of the double layer. Consequently, under this pre-anodization the current passing through the electrode in the γ_c' region should be nonfaradaic. However, the slope of γ_c' decreases and the electricity required for this stage increases with an increase in the pre-anodization potential in the region of γ_a''', as may be seen in Fig. 7. This plot indicates that only when the electrode is polarized at potential above 1.2 V. is the stable oxide which is reduced at a more negative potential formed.

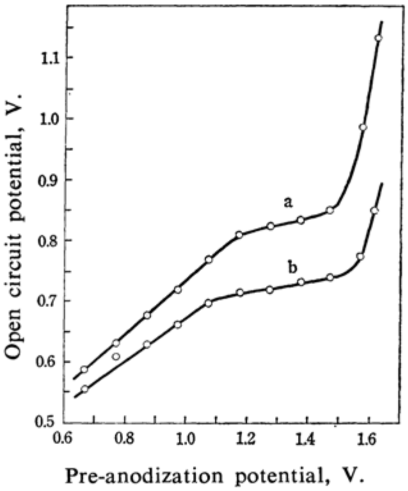

Fig. 8. Plots of the open circuit potential vs. the pre-anodization potential.
Curve a, 1 min. after the pre-anodization current was turned off.
Curve b, 5 min. after the pre-anodization current was turned off.

When the current is turned off after the anodic polarization, the electrode potential drops rapidly at first, but more slowly as time elapses. The open circuit potential of the electrode was measured 1 and 5 min. after the circuit was broken. The open-circuit potential increases linearly with an increase in the pre-anodization potential up to about 1.2 V., and then it remains approximately constant in the region of the pre-anodization potential from 1.2 to 1.5 V. corresponding to the γ_a''' (Fig. 8).

The Cathodic Behavior of the Electrode in the Solution Containing Hydrogen Peroxide.— If the hydrogen peroxide theory[6] is correct as to the cause of the inequality between the quantity of electricity required for the γ_a stage and that for $\gamma_c+\gamma_c'$, the hydrogen peroxide formed during the cathodization of the oxidized electrode and also the oxygen which may be produced by the decomposition of hydrogen peroxide would diffuse away from the surface of the electrode into the solution, without being further reduced cathodically to water at the reduction potential of the oxide layer. In other words, the reduction potential of hydrogen peroxide or oxygen molecules on the electrode should be sufficiently less positive than that of the oxide layer.

To find the reduction potential of hydrogen peroxide and oxygen on the rhodium electrode, the cathodic charging curves were measured with a smooth rhodium wire in a 2 N sulfuric acid solution containing each of these substances. The mesurements were started one minute after the electrode had been introduced into the solution in order to keep the solution quiescent.

Curve a in Fig. 9 is the cathodic curve obtained with a reduced electrode in the solution containing hydrogen peroxide of 3.7×10^{-4} mol./l. The potential was confined at a constant value of 0.65 V. during the electrolysis. Curve b is for the oxidized electrode. From a comparison of curve d, which is the reduction curve of the oxidized electrode in the solution freed from both hydrogen peroxide and oxygen, with curves a and b, it is evident that the remaining of constant potentials on curves a and b can be attributed to the reduction of the hydrogen peroxide. The chronopotentiometric reduction potentials of hydrogen peroxide on the reduced and oxidized electrodes are 0.65 and 0.45 V., while those of oxygen on the reduced and oxidized electrodes are 0.62 and 0.41 V. respectively. All of these potentials are more positive than the reduction potential of the oxide layer. When electrodes are polarized with a larger current density, the potential falls after a definite time, τ (the transition time), as may be seen in curves c and c′ of Fig. 9.

For chronopotentiograms with a wire electrode, Eq. 1 has been derived theoretically:⁹⁾

$$\frac{i\tau^{1/2}}{C}=\frac{\pi^{1/2}nFAD^{1/2}/2}{1-\pi^{1/2}D^{1/2}\tau^{1/2}/4r+D\tau/4r^2-3\pi^{1/2}D^{3/2}\tau^{3/2}/32r^3} \quad (1)$$

where i is the constant current; C, the concentration of the electroactive substance in the bulk solution; D, the diffusion coefficient; n, the number of electrons per molecular unit of reaction; F, the Faraday constant; A, the area of the electrode, and r, the radius of the electrode.

If a completely-reduced electrode is used, the oxide will be formed by the direct reaction between the metal and the hydrogen peroxide included in the solution while the electrode is let stand in the cell before the measurement starts. When the oxide thus formed is reduced at the same time as the hydrogen peroxide, it is necessary to make a correction for the value of the observed current, i_{obs}, in the chronopotentiometry. The value of the current, i, used to reduce the hydrogen peroxide during the transition time can be estimated by substracting the current for the reduction of the oxide from i_{obs}. The values of i were calculated by assuming that the amount of the oxide formed during the standing time of the electrode is constant and that the current resulting from the reduction of the oxide remains constant during the entire time of transition.

$$i=i_{obs}-q/\tau \quad (2)$$

where q is the quantity of electricity used to reduce the oxide. The value of q was selected by trial and error.

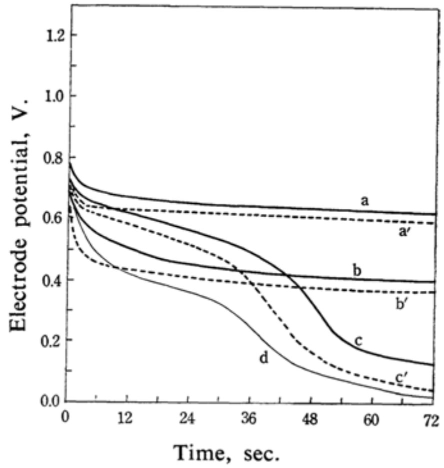

Fig. 9. Cathodic curves.

Solid lines: in the solution containing hydrogen peroxide

Curve a, for the reduced electrode $i_c=47$ μamp./cm²

Curve b, for the oxidized electrode $i_c=47$ μamp./cm²

Curve c, for the reduced electrode $i_c=73$ μamp./cm²

Broken lines: in the air saturated solution

Curve a′, for the reduced electrode $i_c=47$ μamp./cm²

Curve b′, for the oxidized electrode $i_c=47$ μamp./cm²

Curve c′, for the reduced electrode $i_c=83$ μamp./cm²

Fine line: curve d, for the oxidized electrode in the solution freed from hydrogen peroxid and oxygen. $i_c=47$ μamp./cm²

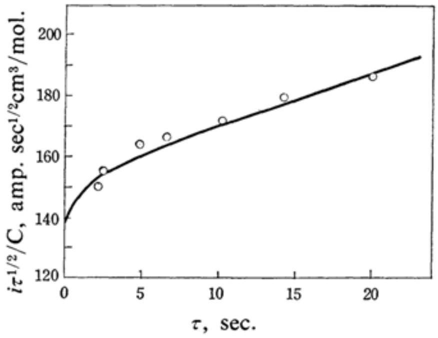

Fig. 10. Variation of $i\tau^{1/2}/C$ with transition time τ for the reduction of hydrogen peroxide in 2 N sulfuric acid; $C=3.76\times10^{-4}$ mol./l., $r=0.025$ cm., $A=0.195$ cm², $i=i_{obs}-11.3/\tau$. The solid line is the theoretical curve according to Eq. 1.

The corrected values of $i\tau^{1/2}/C$ were plotted against τ and are represented as tiny circles in Fig. 10. The solid line in the same figure is the theoretical curve according to Eq. 1 using the

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9) J. J. Lingane, *J. Electroanal. Chem.*, **1**, 379 (1960); **2**, 1, 46 (1961).

diffusion coefficient of hydrogen peroxide (1.71×10^{-5} cm./sec.) reported by Kern.[10] The agreement of the observed values with those predicted by the theoretical equation shows that, in chronopotentiometry, hydrogen peroxide on the electrode is quantitatively reduced to water at a potential which is not less positive than the reduction potential of the oxide layer. Consequently, even if the oxide might be reduced to hydrogen peroxide during the cathodization, or even if this peroxide might be decomposed on the surface, these products should be further immediately reduced to water. Thus the hydrogen peroxide theory described above is not applicable to the rhodium electrode.

The fact that more electricity is used for the γ_a stage than is required to remove the oxide may be caused by a mixed anodic process where a reaction of oxygen evolution occurs simultaneously with the oxide formation reaction and so consumes some of the electricity.

The Corrosion by Square-wave Alternating-current Electrolysis.—The test electrodes for these experiments were rhodium wires 0.5 mm. in diameter and 4—6 mm. long; a new one was used for every run of measurement. The frequency of the square-wave alternating current was 78 c. p. s., the rise time was 1 μsec., and the output voltage of the generator was 100 V. The square-wave alternating current from the generator was passed through a current-limiting resistor in order to obtain the constant current.

The electrolysis was carried out in a hydrogen-saturated solution. The amplitude of the oscillating-electrode potential during the alternating-current electrolysis increased with the increase in the current density. The minimum value of the potential which appears during negative semicycle of alternating current electrolysis was slightly increased by the hydrogen overpotential when the current density was increased, whereas the maximum potential during a positive semicycle increased rapidly with the increase in the current. The current was so adjusted that this maximum potential was the desired value, E_s, during the electrolysis.

The degree of the corrosion of the surface by alternating current electrolysis may be estimated by measuring the increase in the true area per apparent unit area, i. e., the increase in the roughness factor, because the surface is coarsened by the electrolytic attack. Since the value of the electricity, Q_a (coulombs/apparent unit area), required to form the oxide layer is proportionate to the true area of the electrode, the degree of the corrosion is estimated by the ratio of the Q_a' for the electrode already electrolyzed for one hour to the Q_a^0 for that not yet electrolyzed. The values of the Q_a' and Q_a^0 were obtained from anodic charging curves, which were measured by means of the cathode-ray oscilloscopic technique.

The dependence of the degree of the corrosion on the maximum potential, E_s, was traced; the results are shown in Fig. 11. It can be seen from this curve that the surface does not suffer from the corrosion until the E_s potential reaches a critical value, $E_s^0 = 0.88$ V., but after the potential has exceeded this value, the Q_a'/Q_a^0 ratio rises very rapidly and the bright surface becomes cloudy.

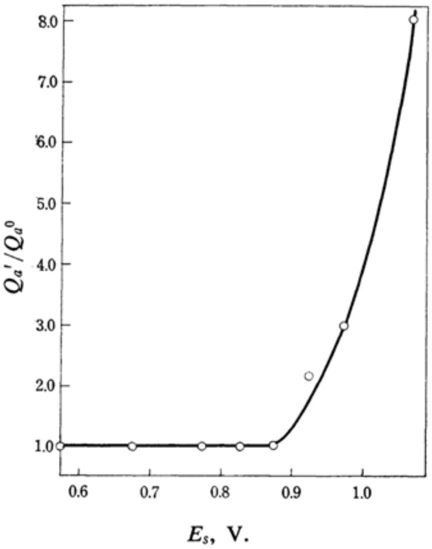

Fig. 11. Plot of the extent of corrosion vs. the maximum value, E_s, of oscillating potential in square wave alternating current electrolysis.
Frequency, 78 c.p.s. Etectrolyzing time, 1 hr.

The corrosion by the alternating-current electrolysis may be attributed to the repetition of the alternate formation and reduction of the "oxide" layer, as has been suggested previously for the platinum electrode.[5] The rearrangement of the rhodium atoms on the surface due to the repeated formation and dissolution of oxide lattices should cause a recrystallization on the surface. The fact that the surface did not suffer from any attack at all until the E_s^0 potential was reached indicates that the oxygen atoms deposited on the surface in the potential region, γ_a', are only in a state of adsorption or are attached to the surface by relaxed bonds so that they

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[10] D. M. Kern, *J. Am. Chem. Soc.*, **78**, 4207 (1954).

are not able to effect a serious change in the Rh-Rh bonds.

On the basis of the observed data for the rhodium electrode, the mechanism of the surface oxidation can be considered. The oxidation is completed through three steps taking place at the different potential regions. The number of coulombs required for each of these regions, γ_a', γ_a'' and γ_a''', are equal to one other.

The first step of the γ_a' region can be attributed to the formation of an intermediate which is adsorbed on the electrode surface. The intermediate may be hydroxyl redicals which come from water with one electron per molecular unit change:

$$\mathrm{Rh} + \mathrm{H_2O} \rightarrow \mathrm{Rh\cdots OH} + \mathrm{H^+} + \mathrm{e^-} \qquad (3)$$

The highly polar group, Rh···OH, thus formed is unstable and may be converted to a less polar group which is close to the oxide, Rh-OH or Rh_2O, as the electrode potential increases.

The second stage, γ_a'', is the reaction in which the "oxide" is formed;

$$\mathrm{Rh\text{-}OH} \rightarrow \mathrm{Rh\text{-}O} + \mathrm{H^+} + \mathrm{e^-} \qquad (4)$$

Sidgwick[11] stated that the only stable oxide formed by rhodium is Rh_2O_3, while Hoare[4] found that the end product formed by the anodic polarization is Rh_2O_3. From the polarization data and the coulombic studies of Butler and Drever,[12] and Böld and Breiter,[3] it seems true that the oxide layers on the rhodium do not grow much beyond a monolayer. Therefore, in the third stage, γ_a''', the following reaction may take place, with an intermediate of a polar group:

$$\mathrm{Rh\text{-}O} + \mathrm{H_2O} \rightarrow \mathrm{Rh\text{-}O\cdots OH} + \mathrm{H^+} + \mathrm{e} \qquad (5)$$

where Rh-O···OH has the same empirical formula as hydrated Rh_2O_3.

At the cathodization, the oxide layer is reduced in two stages of different potentials. As the quantity of electricity required for the first reduction stage, γ_c, is almost twice as much as that required for the second stage, γ_c', which is equal to that for the hydrogen deposition stage, α_c, the first stage seems to be a reducing reaction using two electrons per molecular unit of reaction, and the second stage, one using one electron.

Summary

Surface oxides on the smooth rhodium electrode have been characterized by anodic oxidation and by cathodic stripping with a constant current under various conditions.

The oxidation reaction of the surface should consist of three stages with a characteristic potential region; the adsorption of OH, the formation of an oxide, Rh-O, and, finally, the formation of a higher oxide, Rh_2O_3. The oxide thus formed is cathodically reduced step-by-step in two different potential regions. These mechanisms are supported by the experimental data of the charging curves taken under various conditions, the corrosion by the square-wave alternating-current electrolysis, and the variation in the electrode capacity during the electrolysis.

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[11] N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford Press (1950), p. 1533.

[12] J. A. V. Butler and G. Drever, *Trans. Faraday Soc.*, 32, 427 (1936).