The Anodic Oxidation of Metals at Very Low Current Density. Part IV.* Palladium.

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Little work had been done on the anodic oxidation of palladium, and the results are conflicting. These have been clarified by studying the anodic oxidation of palladium in solutions of varying pH values at very low current density. It is shown that $Pd(OH)_2$ is first formed on the surface of palladium in the form of a layer less than unimolecular, followed by $Pd(OH)_4$ at the oxygen-evolution potential. The latter hydroxide or oxide is unstable, decomposing to $Pd(OH)_2$.

THE results of previous work on the anodic oxidation of palladium are conflicting. Jirsa (*Z. Physik*, 1921, **213**, 241) suggested the formation of the oxides Pd_2O, PdO, PdO_2, and PdO_3 on the palladium anode. Müller and Riefkohl (*Z. Elektrochem.*, 1928, **34**, 744; 1930, **36**, 181) believed PdO to be the only oxide formed on the palladium anode. Butler and Drever (*Trans. Faraday Soc.*, 1936, **32**, 427), on the other hand, showed that at quite low current density an adsorbed single layer of oxygen was formed on the anode before evolution of oxygen; at high current density a less than unimolecular layer of the oxide was formed. This oxide was considered to be a peroxide which decomposed spontaneously after the interruption of the current.

In the present investigation this point is clarified by studying the anodic oxidation of palladium at very low current density, El Wakkad and Emara's procedure (*J.*, 1952, 461; 1953, 3504, 3508) being used. With an electrode of large surface area and a very small polarising current, a considerable time is required for the electrode to pass from the hydrogen- to the oxygen-evolution values, and so equilibrium potentials can be measured at each stage of the polarisation. From such a study it is shown that $Pd(OH)_2$ is first formed over the surface of palladium in a layer less than a unimolecular. This is followed by $Pd(OH)_4$ which is formed at the oxygen-evolution potential. The latter hydroxide or oxide is unstable, decomposing to $Pd(OH)_2$.

EXPERIMENTAL

The electrical circuit and the electrolytic cell used were the same as previously used by El Wakkad and Emara (*locc. cit.*). The palladium electrodes were prepared by palladising a platinum foil of 2 sq. cm. apparent area with a smooth and then with a spongy layer. This was carried out in 1% palladium chloride solution in 0·25N-hydrochloric acid. The smooth palladium layer was deposited with a current of 2·5 mA per electrode for 40 min. This was followed by deposition at 150 mA for a further 2 min. to form a spongy layer.

The electrode was washed several times with conductivity water, and then with the solution in which it would be studied, before it was introduced in its compartment in the electrolytic cell. The anode was placed in such a position with respect to the cathode as to ensure uniform distribution of the polarising current at the anode surface. Each experiment was carried out with a freshly prepared electrode.

* Part III, *J.*, 1953, 3508.

Measurements have been carried out mainly with three electrolytes representing the acid, the neutral, and the alkaline pH range. These solutions were 0·1N-sulphuric acid, 0·2M-KH_2PO_4 + 0·2M-Na_2HPO_4 buffer mixture of approximate pH 6·8, and 0·1N-sodium hydroxide, all prepared from " AnalaR " materials and conductivity water. The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen to remove any dissolved oxygen.

The current used was 50 μA per electrode. In each solution three studies were carried out on each electrode—anodic polarisation, cathodic polarisation, and anodic decay.

In the case of the anodic polarisation, the electrode was first polarised cathodically at a current of 2 mA/electrode until hydrogen was evolved and a constant potential was recorded. The polarising current was then reversed to start the anodic polarisation, and owing to the high adsorptive power of palladium for hydrogen, the anodic polarisation started with a polarising current of 1 mA per electrode. The anode potential under these conditions was found to be constant, indicating the removal of the adsorbed hydrogen formed during the cathodic polarisation. This process was continued until the potential of the anode started to change towards more positive values, indicating the approach of the end of this process. The polarising current was then reduced to the value at which the anodic polarisation was required, and the potential of the anode was recorded as a function of time. The cathodic curves were obtained after the electrode had been anodically polarised until oxygen was evolved; the current was then reversed and the potential of the working electrode was measured at suitable times. In the case of anodic decay curves, the electrode was polarised anodically until oxygen was evolved. The current was then interrupted and the potential was measured after various times. All experiments were carried out in an atmosphere of pure nitrogen.

The reference half-cell was a saturated calomel electrode prepared according to Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1943, p. 321). The electrolytic cell and the reference half cell were kept in an air-thermostat at 25° ± 0·01°. The E.M.F. was measured with a Tinsley potentiometer provided with a Tinsley mirror-galvanometer.

RESULTS AND DISCUSSION

Curves *A*, in Figs. 1, 2, and 3, are respectively the characteristic anodic polarisation curve of the palladium electrode at 25° with a polarising current of 50 μA in 0·1N-sulphuric acid, the same anodic polarisation curve in phosphate buffer of pH 6·8, and the anodic polarisation curve in 0·1N-sodium hydroxide. From these curves, which show the variation of the potential of the palladium anode with the quantity of electricity passed, it can be seen that the following three stages take place as the palladium electrode is forced from the hydrogen-evolution to the oxygen-evolution potential.

(*a*) A comparatively long period of constant potential (represented by the dotted line since in this case the polarising current was 1 mA to enhance the removal of the adsorbed hydrogen as was explained before), followed by a slow and somewhat irregular but reproducible rise of potential. (*b*) A rapid build-up of potential. (*c*) A somewhat slow rise of potential accompanied by two steps, the second of which coincides with the potential of oxygen evolution. Stage (*a*) can be attributed to the ionisation of adsorbed hydrogen formed during the cathodic polarisation of the electrode before the anodic polarisation was started. The quantity of electricity passed in this step was very reproducible, amounting to ~1800 mc per electrode in acid medium, and ~1300 mc per electrode in neutral and alkaline solutions; these are respectively equivalent to $1·13 \times 10^{19}$ and $8·2 \times 10^{18}$ atoms of hydrogen. These quantities were found to be independent of the quantity of electricity passed during the previous cathodic polarisation so long as this was greater than 1800 mc per electrode in acid medium, and 1300 mc in neutral and alkaline solutions.

On preparing several palladium electrodes under the standard conditions and determining the quantity of palladium present on each electrode by means of dimethyl-glyoxime, an average value of 0·0019 g. of palladium per electrode was obtained. This is equivalent to $1·09 \times 10^{19}$ atoms of palladium present on each electrode. From these results, it is clear that in acid medium during the cathodic polarisation, the electrode has been transformed to the hydride PdH. The presence of such a hydride was reported by Paal and Gerum (*Ber.*, 1908, **41**, 818).

In neutral and alkaline solutions, on the other hand, the atomic ratio Pd : H is about

1 : 0·7; this, together with the reproducibility of the results, suggests the approach of the formation of the hydride Pd_2H rather than PdH. The presence of the hydride Pd_2H was reported by Gillespie and Hall (*J. Amer. Chem. Soc.*, 1926, **48**, 1207), and by Hanawalt (*Proc. Nat. Acad. Sci.*, 1928, **14**, 953) in his study on the effect of hydrogen on the X-ray absorption spectrum of palladium.

Stage (*b*) can be ascribed by analogy, from the previous studies (El Wakkad and Emara, *locc. cit.*), to the charging of a double layer. Measurement of a large number of polarisation curves in 0·1N sulphuric acid gave an average value of the double layer capacity of
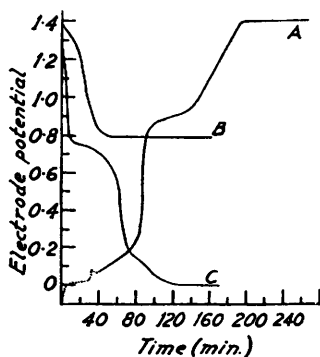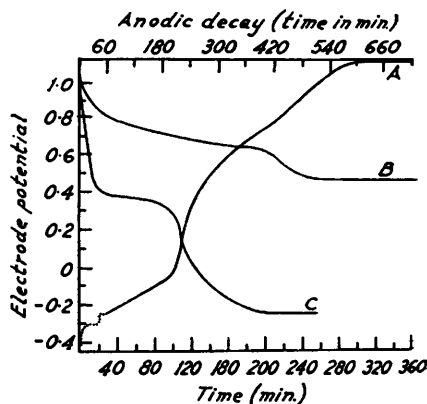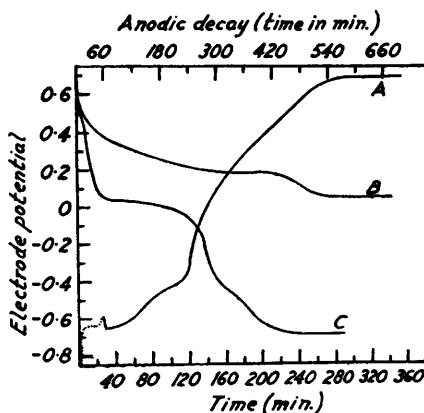
FIG. 1.

FIG. 2.

FIG. 3.

14,175 μF per apparent sq. cm. of our palladium electrode. In phosphate buffer and sodium hydroxide solution the average value was 72,000 μF per apparent sq. cm. The difference can be attributed to the fact that in acid solution the metallic surface was obtained from the oxidation of the hydride PdH, while in the neutral and alkaline solutions the hydride was Pd_2H, as has been shown above. According to Thoma (*Z. physikal. Chem.*, 1889, **3**, 69), palladium electrolytically charged with hydrogen expands equally in all directions; on subsequent removal of hydrogen, the contraction is greater than the previous expansion.

The characteristics of stage (*c*) in the anodic polarisation curves are of great interest. The onset of this stage is well defined in acid medium, but less clear in neutral or alkaline solutions. Thus, after the charging of the double layer, the first step in this stage started at potentials of +0·85, +0·47, and +0·12 v for 0·1N-sulphuric acid, phosphate buffer, and 0·1N-sodium hydroxide solutions, respectively. In the following table the starting potentials of this step in the various electrolytes are compared with the corresponding

equilibrium potentials of the system Pd–Pd(OH)$_2$. The latter values were obtained as follows : The free energy of palladous hydroxide being taken as −70,500 cal., and that of OH⁻ ions as −37,583 cal. (Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions," New York, 1938, p. 190), the free energy change of the reaction Pd + 2OH⁻ = Pd(OH)$_2$ + 2e is $\Delta F = +4670$ cal., and hence E_B° (the potential value at the extreme alkaline range of pH) is *ca.* +0·10 v at 25°. By applying the ordinary equation for the variation of the potential of this system with the pH, the values obtained in col. 3 in the following table are obtained. The very close agreement between these two sets of values strongly suggests that the onset of stage (c) corresponds to the commencement of formation of palladous oxide or hydroxide on the palladium surface.

Solution	Starting potential of the 1st arrest, v	Equilibrium potential of system Pd–Pd(OH)$_2$, v
0·1N-H$_2$SO$_4$	+0·85	+0·88
Phosphate buffer	+0·47	+0·52
0·1N-NaOH	+0·12	+0·16

The quantity of electricity passed from the beginning to the end of the first step was ~120,000 μc in acid solution, and about ~280,000 μc in neutral and alkaline solutions. The quantity of electricity passed in acid medium and in neutral or alkaline solution is sufficient for the liberation of $3\cdot7 \times 10^{17}$ and 9×10^{17} atoms of oxygen, respectively. If the diameter of the palladium atom is taken as $2\cdot44 \times 10^{-8}$ cm. (from the specific gravity) there should be about $1\cdot68 \times 10^{15}$ atoms of metal per true sq. cm. at the palladium surface. A rather rough estimate for the ratio of the real to the apparent area of the palladium electrode under investigation can be obtained from the value of the capacity of the double layer at the electrode. The capacity of a metal anode before oxide formation was estimated as 100 μF per true sq. cm. (El Wakkad and Emara, *loc. cit.*). This gives the real area of our palladium electrode (of 2 sq. cm. apparent area) as 284 sq. cm. in sulphuric acid, and 1450 sq. cm. in both phosphate and sodium hydroxide solutions. This shows that the quantity of electricity passed in the first step corresponds to the formation of less than a unimolecular layer of Pd(OH)$_2$ on the surface of palladium electrode in all the solutions.

From thermal data, Latimer (*op. cit.*) calculated the E_B° value for the reaction 2OH⁻ + Pd(OH)$_2$ = Pd(OH)$_4$ + 2e as +0·71 v.

It is interesting to find that by applying the ordinary equation for the variation of the potential of such a system with pH, and comparing these values with our constant potential values found in the anodic polarisation curves at oxygen evolution, the results shown in the following table were obtained. It is clear that the equilibrium potentials for the system

Solution	Potential (v) obtained from polarisation curves	Equilibrium potential (v) for system Pd(OH)$_2$–Pd(OH)$_4$
0·1N-H$_2$SO$_4$	1·44	1·49
Phosphate buffer	1·12	1·13
0·1N-NaOH	0·72	0·77

Pd(OH)$_2$–Pd(OH)$_4$ are in good agreement with those obtained from polarisation curves, which suggests that oxygen evolution can be attributed to the formation of the higher oxide or hydroxide Pd(OH)$_4$, and, as this potential value is always constant and independent of the time of polarisation as well as of the current density (since a 100-fold increase of the polarising current was accompanied only by an increase of 200 mv in the oxygen evolution potential), it can be concluded that Pd(OH)$_4$ is unstable, giving off oxygen as soon as it is formed by the anodic polarisation. This conclusion can be further proved from both the decay and the cathodic curves. Thus, from curves *B*, Figs. 1, 2, and 3, it can be seen that on interruption of the polarising current when the anode is at the oxygen-evolution potential, the potential did not drop directly to that of the system Pd–Pd(OH)$_2$, but halted for some time at the oxygen-evolution potential or the potential of Pd(OH)$_2$–Pd(OH)$_4$, confirming the existence of the higher oxide or hydroxide over the electrode. However, after a time which varied from one solution to another, as well as the duration of electrolysis after the electrode had attained the value of the oxygen evolution, the potential dropped further to the Pd–Pd(OH)$_2$ value, showing that the Pd(OH)$_4$ formed on the surface of the electrode during its anodic polarisation was rather unstable.

In the cathodic curves C, Figs. 1, 2, and 3, there are also clear steps indicating the reduction of $Pd(OH)_4$ and $Pd(OH)_2$ at their corresponding reversible potential values, and confirming the formation of these two oxides or hydroxides on the palladium electrode as revealed by the anodic curves.

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