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Chemical Evidence for Oxide Films on Platinum Electrometric Electrodes

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Chemical analysis of the films formed on oxidized platinum electrodes has provided direct evidence of their reality and composition. The films comprise both PtO and PtO_2. The amount of oxidized platinum found by chemical analysis agrees with the amount of electrode oxidation as measured by the chronopotentiometric technique. The oxide films present on oxidized platinum anodes inhibit oxidation of other substances at the electrode.

Platinum electrodes, as used in electrometric measurements, commonly are assumed to behave "nobly" and thus to serve only as a means of electron transfer without participating in electrode reactions. Plausible though it may be in solutions of relatively low oxidation potential, this concept is untenable in solutions whose oxidation potential is larger (more oxidizing) than the potentials of platinum–platinum ion couples in the particular solution. Why does platinum appear to obey the Nernst equation in solutions in which it is thermodynamically unstable and susceptible to oxidation? This is still a moot question, but one tentative answer is that the platinum surface is protected by a film of a platinum oxide, which prevents more than superficial oxidation of the platinum and yet permits electron transfer processes involving other substances. The substantiation of this interpretation requires a conclusive demonstration that films of platinum oxides are indeed formed on platinum electrodes subjected to either electrochemical or chemical oxidation in aqueous solutions, and this is the point with which this paper is concerned.

Several investigators,[1–10] employing various electrometric techniques, have observed phenomena consonant with the postulate that a film of platinum oxide is formed on platinum electrodes subjected to anodic polarization. Although persuasive, this evidence nonetheless is indirect and has never been verified by direct chemical tests. Conceivably, the observed electrochemical phenomena could result from some process other than the formation of actual platinum oxide films. Indeed, Butler, *et al.*,[2] have attributed some of the observed phenomena to the formation of adsorbed oxygen on the platinum surface, rather than actual production of platinum oxides.

In the present investigation the oxidation of platinum electrodes has been studied by the chronopotentiometric technique whose principles have been reviewed by Delahay[11] and Lingane.[12] The reality of formation of platinum oxide films, rather than adsorbed oxygen, has been substantiated by direct chemical analysis of the surface of oxidized electrodes. The quantity of platinum which can be chemically stripped from oxidized electrodes agrees with the quantity of electrode oxidation indicated by the chronopotentiometric measurements. The chemical analyses demonstrate that both PtO and PtO_2 are present on the surface of an oxidized electrode, and the ratio of the two is approximately the same regardless of whether the electrode has been oxidized by anodic polarization or with various chemical oxidants.

Experimental

The experimental arrangement for the chronopotentiometric measurements has been described previously.[13]

A mercury–mercurous sulfate reference electrode was used, but the potentials are referred to the more familiar saturated calomel electrode. Special precautions were taken to prevent mercury from contaminating the test solutions. Air was removed from the test solutions with nitrogen.

The data for the anodic and cathodic transition times for electrode oxidation and reduction, respectively, were obtained manually with a 6 cm.^{2} electrode. Whether or not the solution was stirred between successive trials had no effect on the transition time, as is to be expected when the transition time is determined by formation of an oxide film rather than by diffusive transfer.

For the chronopotentiometric measurements platinum foil electrodes with areas of 2, 6 and 60 cm.^{2} (both sides) were used, prepared from the purest commercial platinum foil. The chemical analyses were performed only with the largest electrode, in order to obtain enough platinum in solution to measure. The total quantity of platinum oxides present was of the order of 0.5 mg./60 cm.^{2}

Various solutions were investigated for the chemical stripping experiments. The aim was to employ a solution which would dissolve the oxide film, without altering the ratio of +2 and +4 platinum, and in which the concentrations of +2 and +4 platinum could be determined spectrophotometrically. A stripping solution composed of 0.2 *M* hydrochloric acid and 0.1 *M* sodium chloride proved to be suitable. PtO and PtO_2 both are soluble (slowly) in such a solution, and the resulting $PtCl_4^{=}$ and $PtCl_6^{=}$ ions have sufficiently different absorption spectra to permit their individual determinations.[14]

The stripping was performed by placing the oxidized, and thoroughly washed, electrode (area 60 cm.^{2}) in 100 cc. of the stripping solution from which air had been removed with nitrogen. The solution was boiled gently until most of the oxide film was stripped. From 20 to 60 min. was required. The concentrations of $PtCl_4^{=}$ and $PtCl_6^{=}$ in the solution were then determined spectrophotometrically (Beckman DU spectrophotometer with 10 cm. silica cells). The concentrations were only about 2×10^{-6} *M*, but, using cells with a 10 cm. light path, an accuracy of about ±10% was possible.

The required extinction coefficients were evaluated with known concentrations of K_2PtCl_4 and $(NH_4)_2PtCl_6$. Measurement of $PtCl_6^{=}$ was made at 262 mμ, and $PtCl_4^{=}$ was measured at 230 mμ.

Stripping for as long as an hour in the air-free, boiling hydrochloric acid solution removed most, but not all, of the

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[1] F. P. Bowden, *Proc. Roy. Soc.* (*London*), **A125**, 446 (1929).

[2] J. A. V. Butler, *et al.*, "Electrical Phenomena at Interfaces," Methuen and Co., Ltd., London, 1951.

[3] A. Hickling, *Trans. Faraday Soc.*, **41**, 333 (1945).

[4] B. Ershler, *Disc. Faraday Soc.*, 1, 269 (1947).

[5] S. Altmann and R. Busch, *Trans. Faraday Soc.*, **45**, 720 (1949).

[6] S. El Wakkad and S. Emara, *J. Chem. Soc.*, 46 (1952).

[7] B. Baker and W. MacNevin, THIS JOURNAL, **75**, 1476 (1953).

[8] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 632 (1954).

[9] J. Ross and I. Shain, *ibid.*, **28**, 548 (1956).

[10] J. K. Lee, R. N. Adams and C. N. Bricker, private communication.

[11] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

[12] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., Revised Ed. 1957.

[13] F. C. Anson and J. J. Lingane, THIS JOURNAL, **79**, 1015 (1957).

[14] J. Kirkland and J. Yoe, *Anal. Chim. Acta*, **9**, 441 (1953).

oxide film. The amount of oxide coating remaining was estimated by washing the stripped electrode and then recording a *cathodic* chronopotentiogram in 1 *M* sulfuric acid.

Results and Discussion

Chronopotentiometric Measurements.—Curve 1 in Fig. 1 is a typical anodic chronopotentiogram obtained with a previously reduced (by cathodization, or treatment with a chemical reductant) electrode polarized with a constant anodic current in 1 *F* sulfuric acid. Curve 2 resulted when the trial was repeated without re-reducing the electrode. The anodic transition time of curve 1 (*i.e.*, the time that the constant current passes before the potential inflection occurs and oxygen evolution commences) is a measure of the amount of electrode oxidation.

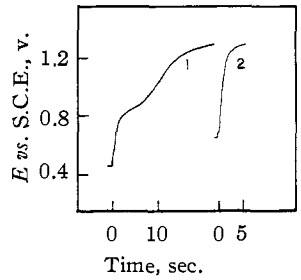

Fig. 1.—Anodic chronopotentiogram showing oxidation of platinum anode in an air-free sulfuric acid solution at a current density of 0.2 milliamp./cm.^{2}: (1) previously reduced electrode; (2) resulted when trial was repeated without re-reducing the electrode.

When the oxidized electrode is made the cathode in an oxygen-free 1 *F* sulfuric acid solution a cathodic chronopotentiogram results, as shown by curve 1 of Fig. 2. When the trial is repeated without re-oxidizing the electrode, curve 2 results. Curve 1 results from the reduction back to the metal of the platinum oxides on the oxidized electrode, and its transition time is a measure of the quantity of these oxides. It will be noted that the cathodic transition time (curve 1, Fig. 2) is defined more sharply than the anodic transition time (curve 1, Fig. 1). Quite likely the anodic transition time includes a small contribution from oxidation of water. This is also indicated by the fact that anodic transition times are consistently about 15% greater than cathodic transition times. We regard the cathodic transition time as the more nearly correct measure of the quantity of oxidized platinum.

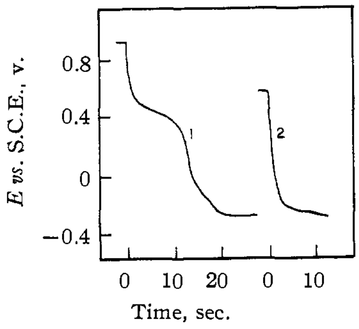

Fig. 2.—Cathodic chronopotentiogram showing reduction of an oxidized platinum electrode in an air-free 1 *M* sulfuric acid solution at a current density of 0.2 milliamp./cm.^{2}: (1) previously oxidized electrode; (2) resulted when trial was repeated without re-oxidizing the electrode.

Representing the transition time (sec.) by τ and the constant current (amp.) by i, the total number of equivalents of platinum oxides is given by $i\tau/96{,}493$.

Table I summarizes the results of anodic and cathodic chronopotentiometric measurements in solutions of various *p*H. Dilute sulfuric acid was used for *p*H's of 0 and 1, an acetate buffer for *p*H 4.3, a phosphate buffer for *p*H 6.5, a borax buffer for *p*H 8.5, and potassium hydroxide for *p*H 13. The potentials *vs.* S.C.E. for the inflections corresponding to the transition times are indicated. In neutral and alkaline media the anodic inflection is less well defined than in acid medium. It is seen that the *p*H of the solution has little or no influence on the quantity of oxide film formed. These results are in quantitative agreement with data obtained by Hickling[3] by a different technique.

TABLE I

EFFECT OF *p*H ON ANODIC AND CATHODIC TRANSITION TIMES

Platinum electrode area 6 cm.^{2} Constant generating current was 600 microamp.

Soln. *p*H	E_{an}, v. *vs.* S.E.C.	$\tau_{an.}$ sec.	E_{cat}, v., *vs.* S.C.E.	τ_{cat}, sec.
0	1.23	10.3	+0.08	9.8
1	1.13	11.8	+ .03	9.2
4.3	0.98	11.2	− .17	9.5
6.5	.88	13.0	− .32	10.8
8.5	.78	13.9	− .52	13.2
13	.53	12.2	− .72	11.9

Chemical Analysis of Oxidized Electrodes.—To verify the hypothesis that an oxidized platinum electrode acquires an actual film of platinum oxides, direct chemical analysis of the oxidized electrodes was carried out.

This was accomplished by stripping the oxidized platinum from the electrode by treating it with a 0.2 *F* hydrochloric acid–0.1 *F* sodium chloride solution which was de-aerated and heated to boiling. The resulting solution was then analyzed spectrophotometrically for $PtCl_4^=$ and $PtCl_6^=$.

That chloroplatinate and chloroplatinite ions are the species present was established by comparing the absorption spectrum of the solution from a stripping experiment with a solution containing known concentrations of chloroplatinate and chloroplatinite ions.

A typical chemical stripping experiment consisted of oxidizing the electrode in one of several different ways, chemically stripping the oxidized film from the electrode, measuring the amount of any unstripped film by means of a cathodic chronopotentiogram, analyzing the stripping solution for dissolved platinum, and comparing the sum of stripped and unstripped platinum with the amount of electrode oxidation measured by the cathodic transition time for the reduction of the freshly oxidized electrode.

The length of time the electrode needed to be treated with the stripping solution in order to dissolve most of the electrode film depended on the oxidizing procedure. When the electrode was only mildly oxidized by anodizing just until the electrode potential reached the inflection point in the anodic chronopotentiogram, or treating the electrode with a 0.1 *F* ceric sulfate solution for 5 minutes, the oxide film was almost completely removed after a 20 minute treatment with the hot stripping solution. When the electrode was more strongly oxidized by prolonged anodic polarization, or treatment with +2 silver or ceric perchlorate solutions, 60 minutes were required for the stripping solution to dissolve most of the oxide film.

Table II summarizes the results of the comparison of the quantity of oxide film indicated by cathodic chronopotentiometry with the quantity actually found by the chemical analyses, following both electrolytic oxidation and chemical oxidation with +2 silver ion, ceric perchlorate and ceric sulfate. The cathodic transition times were all measured with a constant current of 2.00 milliamp. To facilitate comparison, the quantities of +2 and +4 platinum stripped from the oxidized electrodes are expressed in seconds at 2.00 milliamp.

The sums of the equivalents of $PtCl_4^=$, $PtCl_6^=$, and unstripped, oxidized platinum in the last column of Table II agree within experimental reproducibility with the equivalents indicated by the cathodic transition time for the reduction of an oxidized electrode. This agreement leaves no doubt that the oxidized platinum which is dissolved by the stripping solution is also responsible for the potential pauses in the cathodic and anodic chronopotentiograms, and that electrode oxidation does indeed consist in the formation of oxides of platinum. The oxide which is stripped from the electrode corresponds to PtO and PtO_2 in a molar ratio close to 6 to 1.

TABLE II

COMPARISON OF QUANTITY OF PLATINUM OXIDE FILM BY CHRONOPOTENTIOMETRIC AND CHEMICAL MEASUREMENTS

Oxidation process	τ_{cat}, sec. before stripping	Stripping time, min.	Equiv. $PtCl_4^=$ stripped, sec. at 2.00 ma.	Equiv. $PtCl_6^=$ stripped, sec. at 2.00 ma.	τ residual, sec.	Equiv. $PtCl_4^=$ + equiv. $PtCl_6^=$ + $\tau_{residual}$, sec.
a	21.0	20	11.0	3.5	3.8	18.3
a	20.5	20	13.0	4.0	4.9	21.9
a	21.0	20	11.4	3.4	4.4	19.2
b	33.5	20	10.1	3.7	20.8	34.6
b	34.3	20	15.8	5.7	14.9	36.4
b	33.6	60	20.6	6.6	8.6	35.8
b	33.9	60	16.9	8.0	6.4	31.3
c	37.2	20	9.3	3.5	24.5	37.3
c	34.4	20	12.0	4.4	19.0	35.4
c	38.8	60	25.4	8.9	6.1	40.4
c	34.7	60	22.7	9.8	4.4	36.9
d	33.7	60	20.2	7.0	8.1	35.3
d	34.7	60	20.9	8.3	5.2	34.4
e	25.1	20	14.8	5.4	4.7	24.9
e	23.4	20	13.4	4.8	5.7	23.9

[a] Electrode oxidized just until its potential reached the inflection potential, 1.23 v. *vs*. S.C.E., in the anodic chronopotentiogram. [b] Anodization for 5 minutes at 2.00 milliamp. in 1 *F* sulfuric acid. [c] Standing for 5 minutes in 0.01 *F* +2 silver solution in 8 *F* nitric acid. [d] Standing for 5 minutes in 0.3 *F* ceric perchlorate solution in 6 *F* perchloric acid. [e] Standing for 5 minutes in 0.1 *F* ceric sulfate solution in 1 *F* sulfuric acid.

With the more strongly oxidizing conditions of experiments 4 through 13 in Table II the extent of electrode oxidation is a good deal greater than in the other experiments, but the relative proportions of +2 and +4 platinum are the same.

These data constitute the first direct chemical proof for the hypothesis that formation of actual platinum oxides occurs. Heretofore this has been only indirectly indicated by various electrochemical phenomena, which conceivably could have had some other cause.

Because platinum in both the +2 and +4 oxidation states is found in the stripping solutions, does not necessarily mean that PtO and PtO_2 are both actually present on the electrodes. It is possible that one or the other of these oxidation states could have been produced during the chemical stripping, as for example by disproportionation of +2 platinum or partial reduction of +4 platinum. To test this possibility, experiments were performed in which the *unoxidized* platinum electrode was boiled under nitrogen with known solutions of $PtCl_4^=$ and $PtCl_6^=$ having the same concentrations of hydrochloric acid and sodium chloride as the stripping solution. After boiling for two hours—a much longer time than in the actual stripping experiments—the concentration of $PtCl_6^=$ decreased by only 30%, and the concentration of $PtCl_4^=$ increased correspondingly. We conclude, therefore, that PtO and PtO_2 are both present on the oxidized electrodes, but the proportion of PtO_2 may be somewhat larger than the proportion of $PtCl_6^=$ in the stripping solution. This conclusion is substantiated by the fact that the relative proportions of $PtCl_6^=$ and $PtCl_4^=$ in the stripping solution was practically the same with only 20 minutes and 60 minutes stripping time.

Some Effects of Platinum Oxide Films on Oxidations Occurring at the Electrode.—That films of platinum oxide can inhibit oxidations of other substances at a platinum electrode has been suggested by Baker and MacNevin[7] and Hickling and Wilson.[15] We have found the chronopotentiometric technique to be particularly effective in revealing such inhibition. For example, as shown by curve 1 in Fig. 3, the oxidation of iodide ion in a phosphate buffer of *p*H 6.5 produces a definite chronopotentiogram, and the transition time corresponds to oxidation to iodate ion provided the platinum anode has not previously been oxidized. If, however, the trial is repeated with the now oxidized electrode the potential immediately assumes the value at which water is oxidized and there is no chronopotentiometric wave for the oxidation of iodide (curve 2 in Fig. 3). Apparently the presence of the film of platinum oxides on a previously oxidized electrode increases the overpotential involved in the oxidation of iodide ion to such an extent that it does not occur below the potential at which water is oxidized.

The same phenomenon was observed with iodine oxidation to iodate, and oxidation of oxalic acid to carbon dioxide. In both cases the anodic chronopotentiometric wave observed with an unoxidized

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(15) A. Hickling and W. Wilson, *J. Electrochem. Soc.*, **98**, 425 (1951).

platinum anode disappeared after the electrode had become oxidized.

If the platinum anode is only partially oxidized an anodic chronopotentiometric wave is still observed but the transition time is smaller than for an unoxidized anode. This is demonstrated by the chronopotentiograms of iodide ion in Fig. 4 obtained with different degrees of prior oxidation of the anode.

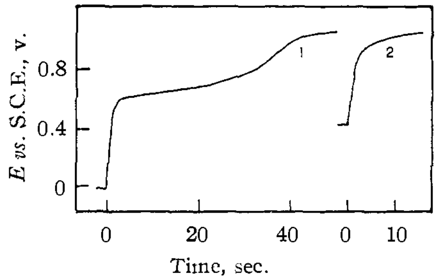

Fig. 3.—Anodic chronopotentiograms for 0.094 milliformal potassium iodide in phosphate buffer at *p*H 6.5 at a current density of 0.3 milliamp./cm.^{2}: (1) with a previously reduced electrode; (2) resulted when the trial was repeated.

Acknowledgment.—Appreciation is expressed to Merck and Co. for sponsoring the Merck Graduate Fellowship in Analytical Chemistry held by one of us (F.C.A.).

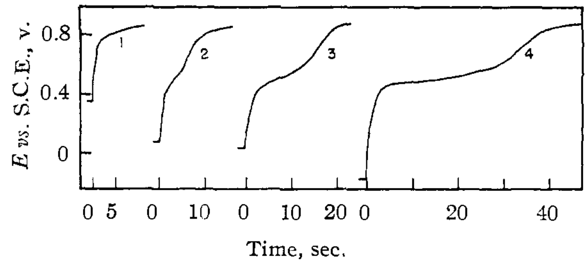

Fig. 4.—Anodic chronopotentiograms for 0.094 milliformal potassium iodide in borax buffer at *p*H 8.5 at a current density of 0.3 milliamp./cm.^{2}: (1) previously oxidized electrode; (2) oxidized electrode cathodized for 6 sec. at 0.3 milliamp./cm.^{2}; (3) oxidized electrode cathodized for 10 sec. at 0.3 milliamp./cm.^{2}; (4) oxidized electrode totally reduced by cathodizing for *ca.* 20 sec. at 0.3 milliamp./cm.^{2}.

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Infrared Spectra of Metallic Complexes. IV. Comparison of the Infrared Spectra of Unidentate and Bidentate Metallic Complexes

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The infrared spectra of sulfato, carbonato, oxalato and acetato metallic complexes in which those ligands coördinate to the metal as an unidentate and as a bidentate have been measured in the range between 5000 and 400 cm.$^{-1}$. From the comparison of the spectra of bidentate with that of unidentate complexes of the same ligands, it has been found that lowering of symmetry of the ligand or frequency shifts of the fundamentals due to coördination is, in general, more remarkable in the former than in the latter.

Introduction

Studies of the effect of coördination on the infrared spectra of metallic complexes afford valuable information on the nature of the metal–ligand bond and the stability of the complex. Coördination usually causes (1) appearance of new bands and splitting of the degenerate modes due to lowering of symmetry, (2) frequency shifts of the bands, and (3) intensification of the spectra. In the previous works,[1] our attention was focussed to the frequency shifts of the ligand fundamentals caused by complex formation. However, a study of the effect of coördination on the symmetry of the ligand is also important. It is well known that the ligands such as CO_3^{--} and $C_2O_4^{--}$ coördinate to the metal as an unidentate and as a bidentate. Therefore, comparison of the infrared spectra of unidentate and bidentate metallic complexes of those ligands will be of considerable interest. The present paper deals with the infrared spectra of sulfato, carbonato, oxalato and acetato complexes.

In discussing the symmetry of the ligand from the spectra obtained in the crystalline state, site group or factor group analysis based on the knowledge of crystal structure is desirable. Unfortunately, for most of the compounds discussed here, crystal structural data are lacking. It is anticipated, however, that the effect of coördination upon the ligand absorption is much stronger than the effect of the over-all crystal field. Hence, ignorance of rigorous site group analysis may be justified.

By coördination, all the fundamentals are more or less shifted according to their modes of vibration. As the metal–ligand bond becomes stronger, their shifts to lower or higher frequencies increase. Furthermore, when coördination lowers the symmetry of the ligand, forbidden vibrations of the free ion are permitted, and degenerate vibrations are split. The stronger the metal–ligand bond, the larger the splitting of the degenerate mode. Therefore, frequency shifts, the magnitude of the splitting, and the intensity of newly permitted bands are useful as a measure of the effect of coördination.

As to the change of relative intensity caused by complex formation, it is generally expected that newly developed fundamentals have weak or medium intensity, and other fundamentals active in

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[1] J. Fujita, K. Nakamoto and M. Kobayashi, THIS JOURNAL, **78**, 3295, 3963 (1956); *J. Phys. Chem.*, **61**, 1014 (1957).