PLATINIZED PLATINUM ELECTRODES

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Received July 29, 1970 (Revised Manuscript Received October 23, 1970)

Contents

I. Introduction

The platinized platinum electrode is the most widely used type of electrode. It makes a regular appearance in conductance cells, forms the basis of the hydrogen reference electrode, and is unsurpassed as an electrocatalyst in fuel cells. Yet the mechanism of the formation of the platinum deposit has been investigated only recently, and information on the properties of the electrode (its appearance, structure, area, and reproducibility), and how these are affected by its method of preparation, is widely scattered and not well known. The main factors are critically assessed in this review.

II. Historical Origins

It is an accident of history that the original recipes for platinum black electrodeposition were devised, not for electrochemical purposes, but in connection with the measurement of radiation. When radiation falls on a black metallic strip the temperature of the strip rises, and the resulting increase in resistance can be determined with a Wheatstone bridge arrangement. Early models of such devices, known as bolometers, made use of[1] platinum strips blackened with soot by means of a petroleum flame. The irreproducibility of this method of blackening led Lummer and Kurlbaum[2] to try instead the electrodeposition of platinum black, since composition of the plating solution, current, voltage, and time can be exactly defined and controlled. But there was one drawback: platinum black electrodeposited from pure chloroplatinic acid solutions did not adhere properly to the electrode. In attempting to overcome this difficulty, Kurlbaum and Lummer[3] recalled that platinum black can easily be precipitated from chloroplatinic acid solution by adding copper or lead, so that such chemically prepared platinum black always contains some copper or lead as well. Accordingly, they tried adding a small amount of copper sulfate, to the extent of about 1% of the chloroplatinic acid present, to the plating solution and found that this regularly produced very good platinum black deposits. Even better results were achieved by adding a small quantity of lead acetate. Their final recipe[3] was 1 part of chloroplatinic acid and 0.008 part of lead acetate to 30 parts of water, the electrolysis being carried out with a potential difference of 4 V between the (platinum) working electrodes which gave a current density of 30 mA cm^{-2} at the cathode. It is this recipe which was shortly afterwards adopted by Kohlrausch[4] for making platinum black electrodes for electrochemical purposes. Kohlrausch, to whom this preparation has at times been incorrectly attributed,[5] stated clearly, but without quoting any literature sources, that the method was that of Lummer and Kurlbaum. Only in a later book[6] is ref 3 specifically referred to. That this historic recipe is quite sound is shown by the results of more modern research which is discussed in the following sections. The main modification desirable is a reduction of the lead acetate concentration by a factor of approximately 5.

In the original bolometric study the platinum compound was referred to[2,3] as "Platinchlorid," but both Kohlrausch[7] and more recent books[8,9] have pointed out that this term was commonly applied to chloroplatinic acid. This loose nomenclature has caused some confusion in the later literature and in many present-day undergraduate laboratory manuals. Even $PtCl_4$ may mean[10,11] chloroplatinic acid unless a special preparation[7] of platinic chloride is given.

III. Electrode Kinetics and Mechanism

The electrodeposition of platinum from chloroplatinic acid solution involves three couples.

$$\mathrm{Pt^{IV}Cl_6{}^{2-} + 2e^- \rightleftharpoons Pt^{II}Cl_4{}^{2-} + 2Cl^-} \qquad (1)$$

$$\mathrm{Pt^{II}Cl_4{}^{2-} + 2e^- \rightleftharpoons Pt + 4Cl^-} \qquad (2)$$

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(1) O. Lummer and F. Kurlbaum, *Ann. Phys. Chem.*, **46**, 204 (1892).

(2) O. Lummer and F. Kurlbaum, *Sitzungsber. Kgl. Preuss. Akad. Wiss.*, 229 (1894).

(3) F. Kurlbaum and O. Lummer, *Verh. Phys. Ges. Berlin*, **14**, 56 (1895).

(4) F. Kohlrausch, *Ann. Phys. Chem.*, **60**, 315 (1897).

(5) G. Jones and D. M. Bollinger, *J. Amer. Chem. Soc.*, **57**, 280 (1935).

(6) F. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," B. G. Teubner, Leipzig, 1898, p 9.

(7) F. Kohlrausch, *Ann. Phys. Chem.*, **63**, 423 (1897).

(8) A. I. Vogel, "A Textbook of Macro and Semimicro Qualitative Inorganic Analysis," 4th ed, Longmans, Green and Co., London, 1954, p 581.

(9) "Platinum," International Nickel Ltd., London, p 11.

(10) G. Hevesy and T. Somiya, *Z. Phys. Chem.*, **171**, 41 (1934).

(11) A. Slygin and A. Frumkin, *Acta Physicochim. URSS*, **3**, 791 (1935).

$$\mathrm{Pt^{IV}Cl_6^{2-} + 4e^- \rightleftharpoons Pt + 6Cl^-} \qquad (3)$$

The electrode potentials have been measured under a variety of conditions, and the results are summarized in Table I. Those of Goldberg and Hepler[12] are the selected best standard values. In general, the emf's of these couples lack reproducibility.[13a] This is not unexpected; reactions 1–3 involve the breaking of several Pt–Cl bonds and must therefore be kinetically slow and possess low exchange current densities.

Table I

Electrode Potentials of the Three Pertinent Platinum Couples (See Text)

Couple	*Temp, °C*	*Supporting electrolyte*	E^0, *V*[a]	*Ref*
1	25	None	0.77 ± 0.05	12
1	25	None	0.68	13b
1	25	1 *M* HCl	0.72[b]	25
1	25	1 *M* $NaClO_4$	0.72[d]	25
1	50	2.5 *M* HCl	0.74	21
1	60	None	0.74_5[c]	20
2	25	None	0.75	12
2	25	None	0.73	13b
2	25	1 *M* $NaClO_4$	0.76[b]	25
2	60	None	0.78_5[c]	20
3	25	None	0.76[e]	12
3	25	None	0.70_5[e]	13b
3	25	1 *M* $NaClO_4$	0.74[b]	25
3	60	None	0.76_5[c]	20

[a] All potentials in this review are given on the NHE scale, unless stated otherwise. Values given on the SCE scale have been converted by using *E*(SCE) = 0.245 V at 25°. [b] Originally measured *vs.* a 1 *M* NaCl calomel electrode (NaCE). The cell SCE|1 *M* $HClO_4$|NaCE had an emf of 65 mV; hence *E*(NaCE) = 0.310 V if the large liquid junction potential is ignored. [c] Measured *vs.* SCE at 18° with a KCl salt bridge. [d] Calculated from the corresponding values for couples 2 and 3. [e] Calculated from the corresponding values for couples 1 and 2.

Reference is occasionally made to the extent to which $PtCl_6^{2-}$ hydrolyzes in solution. The hydrolysis kinetics have been investigated,[14–17] and the reaction has been found to be catalyzed by a product of the hydrolysis,[15] light,[15–18] and platinum black.[15] In fact, most plating solutions are acid (usually HCl is added), and the evidence strongly suggests that under these conditions the major species present is $PtCl_6^{2-}$. Only in neutral aqueous solutions of K_2PtCl_6 or $PtCl_4$ should there be significant concentrations of hydrolyzed species and these, too, are reduced cathodically to platinum.[19]

A. IN THE ABSENCE OF LEAD

The earliest electrochemical studies of the plating of platinum from $PtCl_6^{2-}$ solutions appeared[20,21] more than one-third of a century after the process itself had been introduced.[2–4,6] That $PtCl_4^{2-}$ participated was shown by two main lines of evidence. First, the current–voltage curves, of which an example is given in Figure 1, exhibited not one but several waves, the last steep rise being caused by hydrogen evolution. The quantitative concordance between the curves obtained by early[20,21] and later[22,23] workers is relatively poor, partly because the compositions and temperatures of the plating solutions varied and also as a result of the different speeds with which the curves were drawn. The slower the experiment, the greater the area of the platinized platinum deposit, and so the lower the real current density. Grube and Reinhardt's results[20] are not atypical and encompass a wider range of conditions than most: their initial deposition potentials with 0.1 *M* H_2PtCl_6 at 18°C were 0.45 V in the absence of HCl and 0.12 V in 5*M* HCl and, at 60°, 0.54 and 0.36 V, respectively. Comparison with Table I shows that the initial electrode process (almost certainly reaction 1) is irreversible and this, as has already been pointed out, is not unexpected. The shift to more anodic deposition potentials as the temperature is raised demonstrates the anticipated increase in exchange current density.

The second reason for pointing to the participation of $PtCl_4^{2-}$ came from the analysis of the electrode products after various times. Initially there was preferential reduction to $PtCl_4^{2-}$, as shown also by the fact that the solution color turned from lemon yellow to dark red, to be followed by the deposition of platinum metal. This change with time was particularly pronounced at higher temperatures.[20]

Another third of a century passed before more quantitative information appeared with the advent of sophisticated electrochemical techniques. The most useful of these to date has been thin-layer voltammetry[24] where the peak currents are a few microamperes only and the amount of platinum deposited during the course of each run is manageably small.[19] Lau and Hubbard[25] applied slow voltage sweeps to a cell 26 μm thick containing either $PtCl_6^{2-}$ or $PtCl_4^{2-}$ solutions, and fitted the resulting current–voltage curves to theoretical rate equations. The derived rate constants *k* are listed in Table II. In agree-

Table II

Rate Parameters[a] for the Reduction of $PtCl_6^{2-}$ to $PtCl_4^{2-}$ (k_1, $\alpha_1 n_1^0$) and of $PtCl_4^{2-}$ to Platinum (k_2, $\alpha_2 n_2^0$) at 25°C from Ref 25

[NaCl], M[b]	$\alpha_1 n_1^0$	k_1, *cm sec*$^{-1}$	$\alpha_2 n_2^0$	k_2, *cm sec*$^{-1}$
0	0.29	6.1×10^{-6}	0.38	8.1×10^{-6}
0.01	0.37	3.5×10^{-6}	0.32	3.4×10^{-6}
0.10	0.37	1.5×10^{-6}	0.32	1.6×10^{-7}
0.30	0.45	5.9×10^{-7}		$\leqslant 2 \times 10^{-9}$
1.00	0.44	5.7×10^{-7}		$< 1 \times 10^{-9}$

[a] The parameters were derived from the basic equation $i = nFkC_{ox} \exp[-\alpha n^0 F(E - E^0)/RT]$ relating current density *i* to potential *E*. The E^0 terms were taken as standard and not as formal potentials, the values used being $E_1^0 = 0.40$ (NaCE) and $E_2^0 = 0.45$ (NaCE) V at all chloride concentrations. [b] In addition to the NaCl concentration indicated, the solutions contained 1 m*M* $PtCl_6^{2-}$ or $PtCl_4^{2-}$, 0.01 *M* $HClO_4$, and sufficient $NaClO_4$ to adjust the ionic strength to 1.01.

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(12) R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, **68**, 229 (1968).

(13) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952: (a) p 204; (b) p 343; (c) p 341.

(14) E. Sonstadt, *Proc. Chem. Soc., London*, **14**, 25 (1898).

(15) E. H. Archibald, *J. Chem. Soc.*, 1104 (1920).

(16) A. D. Westland and L. Westland, *Proc. Int. Conf. Coord. Chem., 7th, 1962*, 251 (1962).

(17) R. Dreyer, I. Dreyer, and D. Rettig, *Z. Phys. Chem. (Leipzig)*, **224**, 199 (1963).

(18) E. Sonstadt, *Proc. Chem. Soc. (London)*, **14**, 179 (1898),

(19) A. T. Hubbard and F. C. Anson, *Anal. Chem.*, **38**, 1887 (1966).

(20) G. Grube and H. Reinhardt, *Z. Elektrochem.*, **37**, 307 (1931).

(21) O. Stelling, *ibid.*, **37**, 321 (1931).

(22) H. Yamamoto, Y. Kobaku, T. Nagai, and T. Takei, *Denki Kagaku*, **33**, 804 (1965); *Chem. Abstr.*, **64**, 13747*h* (1966).

(23) C. Bernard, *Electrochim. Acta*, **15**, 271 (1970).

(24) A. T. Hubbard, *J. Electroanal. Chem.*, **22**, 165 (1969).

(25) A. L. Y. Lau and A. T. Hubbard, *ibid.*, **24**, 237 (1970).

ment with most emf and the early voltammetry evidence, both reactions 1 and 2 are seen to be electrochemically irreversible. The addition of chloride has an adverse effect, to such an extent that the reduction of $PtCl_4^{2-}$ to platinum in 1 *M* chloride solutions takes place at potentials so cathodic that solvent reduction occurs simultaneously. At low chloride concentrations, on the other hand, conversion of $PtCl_6^{2-}$ to $PtCl_4^{2-}$ is rapidly followed by the latter's reduction to the metal, and the electrode process appears to be simply reaction 3. The reaction

$$\mathrm{PtCl_6^{2-} + Pt + 2Cl^- \rightleftharpoons 2PtCl_4^{2-}} \qquad (4)$$

should play a negligible role since it takes 500 hr at 60° to come to equilibrium.[20]

The following discussion is based on the values of the rate constants as listed in Table II although, as one of the referees pointed out to us, their magnitudes and particularly the trends they display depend strongly on the E^0 assignments (see footnote *a* of Table II). As the chloride concentration rises, k_1 decreases at first and then reaches a steady value, whereas k_2 decreases more and more rapidly. Their behavior is therefore qualitatively different. The potentials of reduction of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ in low chloride media are similar and the charges of the ions are identical; their shapes, however, are not, $PtCl_6^{2-}$ being octahedral and $PtCl_4^{2-}$ planar. This fact has already been invoked to explain why, at mercury cathodes, the reduction of $PtCl_6^{2-}$ (and of many other large anions) is much more sensitive to the presence of cations than is that of $PtCl_4^{2-}$. If, as Frumkin has suggested,[26] the transition states of the flat $PtCl_4^{2-}$ ions are located close to the electrode surface, while the $PtCl_6^{2-}$ ions to be discharged are linked to it by cationic bridges, the behavior at mercury electrodes becomes comprehensible. A similar situation may obtain at platinum. A flat $PtCl_4^{2-}$ ion will then require a group of at least five adjoining surface atoms to be free of adsorbed chloride for discharge to be possible, and this becomes increasingly difficult as the chloride concentration rises,[25] hence the sharp fall in the values of k_2. Another test of the Frumkin hypothesis could be made by measuring k_1 and k_2 in the presence of supporting electrolytes containing different cations. Some information on this aspect is already available. According to Table II, when Na^+ is almost the sole counterion, k_1 is constant as the chloride ion concentration changes from 0.3 to 1 *M*, whereas, in the presence of 3 *M* H_2SO_4, k_1 varies inversely[27] with sodium chloride concentration over the range 0.4–1 *M*. In the original paper[27] the authors deduced from the latter finding that the step determining the rate of the cathodic process involves the complex $PtCl_5^-$, formed by the preceding reversible reaction

$$\mathrm{PtCl_6^{2-} \rightleftharpoons PtCl_5^- + Cl^-} \qquad (5)$$

However,[25] the rate of a reaction such as eq 5 or the equivalent reaction producing $Pt(H_2O)Cl_5^-$ is too small to account for the observed rates of reduction.

Table II records also the values of αn^0, the product of the cathodic transfer coefficient and the number of faradays involved in the formation of 1 mol of activated complex. Although it did not prove possible[25] to separate these two parameters, the results suggest that both n_1^0 and n_2^0 are unity. This implies that transient Pt(III) and Pt(I) species, respectively, are produced in the electrode reaction. Lingane,[28a] in an earlier chronopotentiometric study of $PtCl_6^{2-}$ reduction kinetics in 1 *M* HCl on slightly platinized electrodes, found the curve to fit, very roughly, a diffusion-controlled one-electron process. He interpreted this as an initial reduction of Pt(IV) to Pt(III), followed by the latter's disproportionation to Pt(IV) and Pt(II). Although the evidence is as yet far from convincing, it is worth noting that short-lived Pt(III) and Pt(I) species have recently been formed[28b] in aqueous solutions by electron pulse radiolysis.

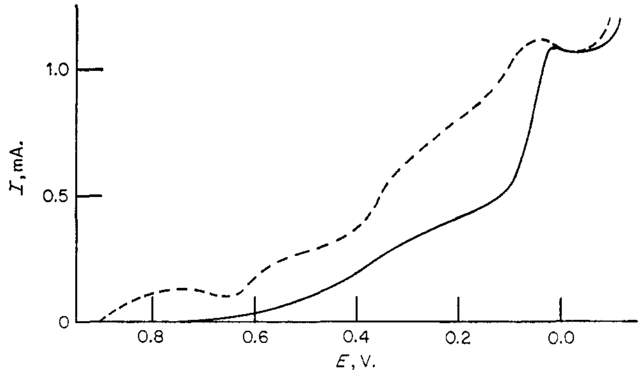

Figure 1. Current (*I*) *vs.* voltage (*E*) curves for the platinization of platinum from a 0.05 *M* chloroplatinic acid solution with no added HCl: no lead acetate, —; 2.7 × 10^{-4} *M* lead acetate, ---. The area of the electrode was not given (from ref 23).

There is considerable evidence in the literature that the platinizing process is a more complex one than the thin-layer voltammetry results in Table II lead one to suppose. In Lingane's chronopotentiometric experiments,[28a] no discrete reduction wave for $PtCl_6^{2-}$ in 1 *M* HCl occurred on "clean" platinum electrodes but only on those covered with a visible coating of platinum black. Lingane concluded that metallic platinum must participate in the reduction process in a much more specific way than merely serving as an inert electron source, and proposed an initial chemical reduction of the oxidant by platinum metal. Another chronopotentiometric finding was an ageing effect. If the slightly platinized electrode was allowed to stand in the deoxygenated 1 *M* HCl test solution for 2 days (a medium in which the extent of hydrolysis should be slight), a four-electron reduction wave was recorded, corresponding to reaction 3. This is in marked contrast to the thin-layer results which showed the reduction steps Pt(IV) → Pt(II) and Pt(II) → Pt to be well separated in 1 *M* chloride solutions. Whether the pH difference of 2 between the solutions of Lingane (pH ≈ 0) and those of Lau and Hubbard (pH ≈ 2) is in part responsible for these considerable differences is not known, but it does seem clear that the state of the surface plays a major role in the electrode kinetics.

Two other puzzling observations in the early literature bear this out. Certain curious behavior, such as strong potential fluctuations in one region of the current–voltage curve, was said[20] to point to the formation at the electrode surface of a poorly conducting layer which changed as the electrolysis continued. A peak at the beginning of a chronopotentiogram was

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[26] A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).

[27] V. I. Kravtsov and B. V. Simakov, *Electrochim. Acta*, **9**, 1211 (1964).

[28] (a) J. J. Lingane, *J. Electroanal. Chem.*, 7, 94 (1964); (b) G. E. Adams, R. B. Boszkiewicz, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 1256 (1968); A. S. Ghosh-Mazumdar and E. J. Hart, *Int. J. Radiat. Phys. Chem.*, **1**, 165 (1969).

also interpreted in this way,[21] although it is more likely to have been caused by slow nucleation.[29] A second unexpected phenomenon during platinization was the evolution of hydrogen at potentials more positive by up to 0.14 V than that calculated for the reversible hydrogen electrode.[20,21] Lingane[28a] too observed this and attributed it to simultaneous reduction of $PtCl_6^{2-}$ and H^+, the latter forming hydrogen at a very low partial pressure. One is led to wonder if some electrochemical synergistic effect is involved here. It is interesting to recall that long ago Kohlrausch[7] suggested that at high current densities, solutions of $PtCl_4$ (not H_2PtCl_6) produced platinum at the cathode by the formation of hydrogen which subsequently reduced the platinic chloride. Further study in this area should prove interesting.

B. IN THE PRESENCE OF LEAD

In the preceding section we have seen how little is understood of the electrode kinetics of platinum deposition from chloroplatinic acid solutions. Considerably less is known of platinum deposition from lead-containing solutions, an astonishing fact when we bear in mind that the process is now three-quarters of a century old and is in daily use around the world.

Virtually the first attempt at an electrochemical study was[23] in 1970, and it produced some unexpected results. First, a solution containing no platinum but 0.01 *M* in lead acetate and 0.1 *M* in HCl showed a reduction wave on a platinized platinum electrode beginning at +0.74 V, although the standard potential of the $Pb^{2+}|Pb$ electrode[13c] is −0.126 V. This is almost certainly related to the fact that a lead-containing platinized platinum electrode in a lead ion solution exhibits[30] a potential of *ca.* 0.83 V. This potential does not obey the Nernst equation, and the facts suggest a very low lead activity coefficient in the deposit, indicative either of strong lead–platinum bonding or steric or diffusion-limited imprisonment of lead in the platinum lattice.

The presence of small amounts (10^{-4}–10^{-3} *M*) of lead acetate in chloroplatinic acid plating solutions strongly affects[23] the cathodic current–voltage curve (*cf.* Figure 1). The curve alters shape and shifts anodically by 100–200 mV, and the current at a given potential increases. Lead therefore decreases the overpotential, and increases the rate, of the reduction of $PtCl_6^{2-}$. This, incidentally, contradicts a theory[31a] that states that, in cases of codeposition, the rate of reduction is lowered for the metal with the more positive value of the potential of zero charge. E_{pzc} is +0.15 V for platinum and −0.65 V for lead.[31b] Current–voltage curves in the presence of lead,[32] as in its absence,[20] can fluctuate strongly. The current increases with stirring.[32]

Bernard[23] believes, on rather skimpy evidence, that the lead is not deposited concurrently on the platinum but is adsorbed on the electrode. In this way it inhibits the growth of crystals and favors the creation of new crystallites, but it is not clear how the lead comes to be incorporated into the deposit. Electrocrystallization studies coupled with structural probing would prove most enlightening. The other function of the lead could be[23] inhibition of the evolution of hydrogen and so an increase in the coulombic efficiency of platinum deposition.

C. COULOMBIC EFFICIENCY

The coulombic efficiency will be unity if reaction 3 alone describes the plating process or if both reactions 1 and 2 are involved with reaction 2 the fast step. The kinetic data of Lau and Hubbard[25] suggest that the latter may be true in the absence of any additives. At low chloride concentrations the production and accumulation of $PtCl_4^{2-}$ decreases the coulombic efficiency on the anodic side, and the evolution of hydrogen decreases it at the cathodic end. A maximum would therefore be expected in between. The drop at the cathodic end was recently confirmed[33] in plating experiments from solutions 0.041 *M* (2%) in chloroplatinic acid and 1.5 *M* in sulfuric acid, where the coulombic efficiency was roughly constant at 90–95% for deposition potentials from +250 to +50 mV (RHE: *i.e.*, with respect to the reversible hydrogen electrode in the same solution) and then steadily decreased to 44% at a deposition potential of −50 mV (RHE). In the presence of much chloride, the coulombic efficiency should rise from a very low level as the potential decreases to the point where simultaneous $PtCl_4^{2-}$ reduction and hydrogen evolution set in, and may reach a plateau level. A test of these predictions by means of literature data (Table III) is difficult because in the literature it is usually not potentials of deposition but rather current densities that are cited. It is of course true that currents of reduction processes rise as the potential becomes more cathodic, but there is no simple correlation because, at a given current, the potential of deposition depends on the stirring conditions. The second difficulty is our ignorance about the effect of lead on the electrode kinetics, and virtually all workers in the literature have added lead in various amounts, and sometimes HCl, to the plating solution (*cf.* Table III). For the time being, therefore, the figures in Table III must act as an empirical guide, and it is interesting to notice that the coulombic efficiencies listed pass through a maximum as the current density of plating increases

D. SUBSTRATE PRETREATMENT

Platinized platinum deposits formed on untreated platinum substrate electrodes are more fragile[34] than those formed on annealed or sandblasted surfaces. Electron microscopy showed[34] that a smooth platinum surface was roughened, to an increasing degree, by thermal etching, sandblasting, and etching with aqua regia. On a roughened surface the initial real current density will be lower than for a smooth one, at constant geometric current density. This is likely to produce more adherent deposits, as is well known in electrofinishing. The other effect of these treatments, particularly etching by heat or with aqua regia, is to remove impurities, such as grease, from the substrate surface.

Some interesting information is provided by a nucleation study[35] of mercury on platinum single crystals. Here, platinum

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(29) M. Fleischmann and H. R. Thirsk, *Advan. Electrochem. Electrochem. Eng.*, **3**, 123 (1963).

(30) A. M. Feltham and M. Spiro, *J. Electroanal. Chem.*, **28**, 151 (1970).

(31) (a) K. M. Gorbunova and Yu. M. Polukarov, *Advan. Electrochem. Electrochem. Eng.*, **5**, 249 (1967) (see p 263); (b) P. Delahay," Double Layer and Electrode Kinetics," Interscience, New York, N. Y., 1965, p 128.

(32) A. M. Feltham and M. Spiro, unpublished work.

(33) V. I. Podlovchenko and R. P. Petukhova, *Elektrokhimiya*, **6**, 198 (1970); *Sov. Electrochem.*, **6**, 185 (1970).

(34) H. A. Roth and W. R. Lasko, *Amer. Chem. Soc., Div. Fuel Chem., Prepr.*, **11**, 241 (1967).

(35) S. Toschev and B. Mutaftschiew, *Electrochim. Acta*, **9**, 1203 (1964).

Table III

Coulombic Efficiency Data for the Platinization of Platinum

Current density,[a] *mA cm*$^{-2}$	*[Chloroplatinic acid]*[b] *%*	*10*^{3} *M*	*[Lead acetate]*[b] *%*	*10*^{3} *M*	*[HCl], M*	*Coulombic efficiency, %*	*Ref*
10[c]	2.5	51	0.0–0.2	0.0–5.3	0	40	44
10	3.5	72	0.2	5.3	0	60	30
30	3.5	72	0.005	0.13	2	100	30
120	5	103	0.02	0.53	0	78	60
170	5	103	0.03	0.79	0	34	86
625	1	21	0.00–0.15	0.0–4.0	0.1	3[d]	52

[a] These and subsequent current densities are all given per geometric area of the substrate electrode. [b] Most workers have given solute concentrations in per cent (w/v). These have been converted to molarities on the basis that chloroplatinic acid is 40 mass % platinum,[9] and that the lead acetate has a stoichiometry of $Pb(CH_3CO_2)_2 \cdot 3H_2O$ (molecular mass 379.35). Subsequent concentrations will be given in both forms for convenience. [c] With current reversal every 1.5 min. [d] Cited in ref 44, although examination of ref 52 revealed no mention of coulombic efficiency.

was anodized to intense oxygen evolution in mercurous nitrate solution and subsequently soaked in 0.09–1.3 *M* nitric acid for 5–60 sec. The electrolytic nucleation of mercury from mercurous nitrate solution was then observed. The critical overpotential for nucleus formation diminished substantially with increasing time of soaking and nitric acid concentration. Cathodic prepolarization in nitric acid after the anodization produced an even more active electrode, and it was concluded that the dilute nitric acid removed the surface oxide layer. At concentrations below about 2 *M*, nitric acid has[36] virtually no oxidizing power and there is the possibility[37a] that the Pt–O layer is unstable in acid solution in the absence of dissolved oxygen. However, in the nucleation work[35] no mention was made of deaeration.

The pretreatment that proved most effective for deposition of mercury on platinum, namely anodization followed by cathodization, is similar to that conventionally recommended[38] for the platinization of platinum. This is, in brief, washing the platinum substrate in either warm concentrated nitric acid or in aqua regia, followed by nitric acid, and subsequent cathodization in very dilute sulfuric acid. There is some foundation for this procedure. Concentrated nitric acid produces an oxide film on the platinum surface,[37a] and some workers believe[37b] that cathodization of a preanodized electrode (*i.e.*, oxide covered) produces an invisible film of platinum black. Lingane[28a] has shown (section III.A) that the formation of such a film is essential for rapid reduction of $PtCl_6^{2-}$. The electrode kinetics of $PtCl_6^{2-}$ reduction on platinum substrates subjected to various electrochemical pretreatments have not yet been studied. It is known that the exchange current densities of a few couples are greater on preanodized platinum surfaces, while those of most couples are higher on precathodized surfaces.[37b,39,40]

IV. Electrodeposition

No thorough electrocrystallization study has been carried out. In general, the work that has been done has been purely empirical in approach. Rather more attention has been paid to platinization from solutions containing a metal additive, usually lead acetate.

A. DEPOSIT APPEARANCE

Nearly all papers in which platinized platinum electrodes are employed describe their appearance. The presence of additives in the plating solution can have a startling effect and the range of textures obtainable is wide.

1. In the Absence of Lead

Platinization with solutions containing no additive has always given gray deposits. In many cases[2,5,10,41,42] these were not adherent and tended to flake off. Adherent deposits have, however, been prepared from solutions containing no lead acetate by one of the following procedures: platinizing only slightly[5] (nonadherency occurred after intense platinization); employing a low current density[43,44] (10 mA cm^{-2}); or holding the platinum cathode[45] at +50 mV, instead of the more usual galvanostatic conditions. It is interesting to note that a common factor in all but one[44] of these procedures was the addition of HCl to the platinizing solutions. The first mentioned[5] employed 0.025 *M* HCl and obtained only moderately good deposits; the other two used 2 *M* HCl[43] and 1 *M* HCl[45] and completely satisfactory deposits resulted. This might be due to the kinetic inhibitory effect of chloride. Indeed, in chloroplatinic acid solutions 6.0–10.7 *M* in HCl smooth ductile platinum deposits can be obtained.[46]

A similar inhibitory effect occurs[47] with the additive cetylammonium bromide and leads to highly uniform smooth deposits. Bright platinum deposits can be obtained[48] from solutions of chloroplatinous acid. The possibility of obtaining

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(37) J. P. Hoare, "The Electrochemistry of Oxygen," Interscience, New York, N. Y., 1968: (a) Chapter II; (b) pp 171–175.

(38) G. J. Hills and D. J. G. Ives in "Reference Electrodes," D. J. G. Ives and G. J. Janz, Ed., Academic Press, New York, N. Y., 1961, pp 106–108.

(39) F. C. Anson, *Anal. Chem.*, **31**, 1451 (1959).

(40) W. D. Cooper and R. Parsons, *Trans. Faraday Soc.*, **66**, 1698 (1970).

(41) S. Popoff, A. H. Kunz, and R. D. Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

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(44) R. Thacker in "Hydrocarbon Fuel Cell Technology," B. S. Baker, Ed., Academic Press, New York, N. Y., 1965, p 525.

(45) R. Woods, *Electrochim. Acta*, **13**, 1967 (1968).

(46) R. H. Atkinson, *Trans. Inst. Metal Finish.*, **36**, 7 (1958–59).

(47) K. S. Indira, S. Sampath, and K. S. G. Doss, *Metal Finish.*, **67**, 44 (1969); abstracted in *Platinum Metals Rev.*, **13**, 156 (1969).

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

bright deposits[49] from solutions of chloroplatinic acid, or better, alkaline chloroplatinate solutions, was later disclaimed[48] and attributed to the presence of chloroplatinous acid produced as a result of overheating the platinic compound during its preparation. This effect of chloroplatinous acid on chloroplatinic acid plating solutions was later noted again,[46] but just why bright deposits should result under these circumstances when $PtCl_4^{2-}$ is an intermediate in platinum black plating is not at all clear, and should be looked into. The commercial systems for bright platinum plating onto noble and base metal substrates have been reviewed.[50]

2. In the Presence of Lead and Other Additives

Adherent deposits, usually black, are best produced by adding lead acetate to the platinizing solution, as Kurlbaum and Lummer discovered[3] long ago. Other additives have been studied, but none has been employed as extensively as lead acetate. Copper[3,51] and mercury[51] were found to be acceptable substitutes for lead, and gold and thallium gave[10] deposits of good quality. Cadmium, zinc, nickel, and iron have given[10,51] gray inferior deposits. The effects of a host of metal additives on the appearance and on the X-ray diffraction patterns of platinized platinum deposits have been examined[52] (see later).

The final appearance and texture of a platinized platinum electrode depends on the concentration of lead acetate in the plating solution and the current density of deposition. The minimum concentration of lead acetate required to give a good black deposit from a 0.062 *M* (3%) chloroplatinic acid solution 0.5 *M* in HCl at 13.5 mA cm^{-2} was found[41] to be 2.5×10^{-4} *M* (0.01%). A black, velvety texture is usually associated with lead-containing platinized platinum electrodes, although at higher lead acetate concentrations they become gray and smooth (Table IV). Kurlbaum,[53] speculating as to why platinized platinum deposits were black, compared them to an end-on view of a collection of aligned shiny knitting needles. Internal reflection reduces net reflection. Experimental support for this picturesque illustration is apparent in Table IV, where the blackest deposits have the highest roughness factors, *i.e.*, the highest areas.

Table IV

Data on Platinization for Varying Lead Acetate Concentrations[a]

[Lead acetate] % w/v	[Lead acetate] 10^4 M	Appearance of deposit	Coulombic efficiency, %	Pb/Pt atomic ratio	Roughness factor
0	0	Gray, compact		0	358
0.003	0.8	Black, very powdery	40.6	0.0021	534
0.01	2.6	Black, very powdery	35.9	0.0041	509
0.05	13	Black, powdery	37.2	0.0143	261
0.075	20	Gray, compact	41.6	0.0208	229
0.1	26	Gray, compact	41.6	0.0230	296
0.15	40	Gray, compact	39.8	0.0247	
0.2	53	Gray, compact	38.4	0.0256	296

[a] Using 0.051 *M* (2.5%) chloroplatinic acid at 10 mA cm^{-2} for 1 hr with current reversal every 1.5 min; from ref 44.

Table V

Variation of Appearance of Platinized Platinum Electrodes with Lead Acetate Concentrations[a]

[Lead acetate] % w/v	[Lead acetate] 10^4 M	Appearance of deposit
0	0	Dark gray, compact
0.002	0.5	Black, compact
0.01	2.6	Black, compact
0.02	5.3	Black, compact[b]
0.05	13	Black, very powdery
0.08	21	Black, very powdery
0.1	26	Black, very powdery
0.15	40	Black, very powdery

[a] Using 0.021 *M* (1%) chloroplatinic acid in 0.1 *M* HCl at 625 mA cm^{-2} for 10 min; from ref 52. [b] The deposits were black and compact up to 625 mA cm^{-2} but black and powdery with current densities in the range 850–1250 mA cm^{-2}.

Comparison of Tables IV and V suggests that the appearance of the platinized platinum deposit also depends on the current density of platinization. Footnote *b* in Table V confirms this. The powdery deposits obtained at high current densities, and therefore at rather cathodic potentials, are no doubt attributable in part to pitting by the simultaneous hydrogen evolution (this could perhaps be reduced by strong stirring). However, this conclusion seems oddly at variance with the findings in Table IV, where a very low current density was employed and yet, at a lead acetate concentration of 5.3×10^{-4} *M* (0.02%) (the same as in footnote *b* of Table V), a black and powdery deposit was found. A possible explanation is that the current reversal used in Table IV was harmful and the chlorine evolved caused gas pitting, although it has been found[41,48] that current reversal has no effect. Potter,[54] on the other hand, claims it is beneficial and decreases the amount of occluded gases. Current reversal is certainly convenient for the platinization of the two electrodes in a conductance cell. An alternative suggestion is that the formation of a black compact deposit at 5.3×10^{-4} *M* (0.02%) lead acetate in Table V but not Table IV is a consequence of the higher lead acetate/chloroplatinic acid ratio in the plating solution. Yet this idea, too, is inadequate, for Table V shows that black compact deposits are produced at low rather than at high lead acetate/chloroplatinic acid ratios, at least at a very high current density.

The information on appearance in Tables IV and V is supplemented by isolated observations. Deposits obtained[34] from a 0.1 *M* (4.9%) chloroplatinic acid plus 2×10^{-3} *M* (0.076%) lead acetate solution at 10 mA cm^{-2} were smooth and gray (consistent with Table IV), but at 100 mA cm^{-2} they were coarser in appearance and characteristic of a dendritic structure. Similar behavior was observed[32] for a 0.072 *M* (3.5%) chloroplatinic acid plus 5.2×10^{-3} *M* (0.2%) lead acetate solution on changing the current density from 10 to 30 mA cm^{-2}. Yet with 0.072 *M* chloroplatinic acid, 2 *M* HCl, and 1.3×10^{-4} *M* (0.005%) lead acetate, 30 mA cm^{-2} gave[32] a velvety black deposit. Best results were obtained at the diffusion-limited current. Clearly, further systematic work linking appearance with current density, solution composition, and

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(49) H. T. Beans and L. P. Hammett, *J. Amer. Chem. Soc.*, 47, 1215 (1925).
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(51) W. M. MacNevin and M. Levitsky, *Anal. Chem.*, 24, 973 (1952).
(52) G. Bianchi, *Ann. Chim. (Rome)*, 40, 222 (1950).
(53) F. Kurlbaum, *Ann. Phys. Chem.*, 67, 846 (1899).
(54) E. C. Potter, "Electrochemistry," Cleaver-Hume Press, London, 1956, p 102.

other variables is required before any systematic relationship can be formulated.

Most appearance studies were carried out at constant current, but at least one report[55] refers to potentiostatic work. In this, using a solution 0.05 *M* (2.4%) in chloroplatinic acid plus 2.7×10^{-4} *M* (0.01%) in lead acetate, deposits obtained at potentials more anodic than +395 mV (very low current densities) were gray, while those obtained at still more anodic potentials were not adherent or reproducible. Deposits formed at potentials slightly more cathodic than +145 mV (high current densities) were finely divided and very black.

Appearance is the most obvious and direct way of characterizing the texture of a surface, but Kohlrausch[4] also examined the wettability of black platinized platinum electrodes prepared according to Kurlbaum and Lummer's recipe.[8] He found that generally they were easily and well wetted with water. However, a large lightly platinized electrode became deactivated when allowed to become dry and was then no longer wetted by water. Optical experiments indicated the presence of an air layer between the platinum particles. The wettability was restored by adding a drop of alcohol to the electrode. In contrast, the smooth gray electrodes prepared from solutions high in lead were found[32] to shed water quite readily. The capillary nature of the black deposits is obviously responsible for their enhanced wettability.

B. DEPOSIT GROWTH

A most important aspect of platinization that has yet to be properly investigated is the nucleation and growth of the deposit. Electrocrystallization studies have been carried out[56] on the deposition of platinum on mercury (where it forms an amalgamated two-dimensional layer which changes to a three-dimensional structure as the Pt(IV) concentration exceeds 10^{-4} *M*) and on glassy carbon. Here thick platinum deposits grew, the nuclei being essentially hemispherical, but with small protruding dendrites, which points to mass transport control. Growth of platinum on platinum might well follow a similar path to that on a carbon substrate,[57] but little direct work has been done.

1. *In the Absence of Lead*

Electrocrystallization studies in general have shown[29,58] that rates of nucleation are strongly dependent on overpotential. On a surface with a high density of dislocations ($\sim 10^{10}$ cm^{-2}), no nucleation is possible[58] unless cathodic overpotentials exceed 150 mV. At overpotentials below this value the growth occurs at the dislocations. Platinization on platinum requires high cathodic overpotentials (section III.A), and indeed nucleation has been favored[34,53,59] as the mode of deposit growth. Most experimental work, however, has been done galvanostatically.

Deposits on platinum obtained[34] from a 0.041 *M* (2%) chloroplatinic acid solution at 100 mA cm^{-2} were found by replication electron microscopy to form as randomly distributed particles which grew laterally to cover the electrode surface. The same general growth pattern occurred for various substrate topographies (untreated, metallographically polished, sandblasted, and etched by heat, molten sodium carbonate, and aqua regia), but with minor variations. On an untreated platinum substrate the deposit thickness growth rate was not linear and obeyed the equation

$$d = Dt^{\delta} \tag{6}$$

where d is the thickness at time t, and D and δ are constants whose values were not given.[34] Optical microscopy revealed these surfaces to be rough and without any distinguishing features, and cross-sectional microscopy showed that they appeared as solid films with vertical cracks. The latter technique was also applied to similarly prepared deposits at 10 mA cm^{-2} and the same features emerged. The deposit thickness growth rate on an untreated platinum substrate was 2×10^{-4} mm sec^{-1}.

The lattice constant of platinized platinum[33] deposited from 0.041 *M* (2%) chloroplatinic acid solution 1.5 *M* in sulfuric acid was 3.915 ± 0.005 Å, independent of the deposition potential from 0 to +250 mV (RHE). The accepted value for platinum metal is 3.924 Å.

2. *In the Presence of Lead*

It has been shown[34] by electron and optical microscopy that more nuclei were formed from solutions containing lead than from those without. In the same work, cross-sectional studies revealed a transition from a closely packed deposit prepared from a solution of 10^{-4} *M* (0.0038%) lead acetate to a dendritic type deposit prepared from a solution of 10^{-2} *M* (0.38%) lead acetate (using 0.1 *M* (4.9%) chloroplatinic acid and 100 mA cm^{-2}). The visual texture changed correspondingly from fine grains to a coarse open structure.

At 100 mA cm^{-2} a 0.1 *M* (4.9%) chloroplatinic acid plus 2×10^{-3} *M* (0.076%) lead acetate solution gave [34] a constant deposit thickness growth rate of 2.8×10^{-3} mm sec^{-1}. At 10 mA cm^{-2} this solution produced rapid initial growth followed by a linear one after approximately 200 sec. In another study,[60] a 0.103 *M* (5%) chloroplatinic acid plus 5.3×10^{-4} *M* (0.02%) lead acetate solution at 120 mA cm^{-2} gave a deposition rate of 2.8 mg cm^{-2} min^{-1}, which is equivalent to 2×10^{-5} mm sec^{-1} if the density of platinum is taken as 21.45 g cm^{-3}. This suggests that a small change in plating conditions causes a vast change either in coulombic efficiency or, less likely, in the density of the deposit. A repetition of these growth experiments under potentiostatic conditions should clarify the situation.

3. *Occlusion of Reagents*

Kohlrausch[4] observed that after platinization several days of washing was required before the conductivity of the rinsing water stabilized. If a thoroughly washed platinized platinum electrode was immersed for a long time in platinizing solution the phenomenon was not repeated, so Kohlrausch suggested that the solute was occluded only during platinization. Similarly, there was an overwhelming tendency[49] to occlude acid during platinization and subsequently, if in neutral solution, to emit such acids slowly but continuously. The trouble caused by solute adsorption on platinized platinum used for a hydrogen electrode in unbuffered solutions has been discussed.[38]

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(55) C. Bernard, *Electrochim. Acta*, 14, 143 (1969).

(56) R. R. Giles, J. A. Harrison, and H. R. Thirsk, *J. Electroanal. Chem.*, 20, 47 (1969).

(57) J. A. Harrison, personal communication, 1970.

(58) J. O'M. Bockris and A. Damjanovic, *Mod. Aspects Electrochem.*, 3, 224 (1964).

(59) D. F. A. Koch, Extended Abstracts, 131st National Meeting of the Electrochemical Society, May 1967, p 32, No. 174.

(60) I. R. Jonasson, Ph.D. Thesis, University of Adelaide, 1967, p 148.

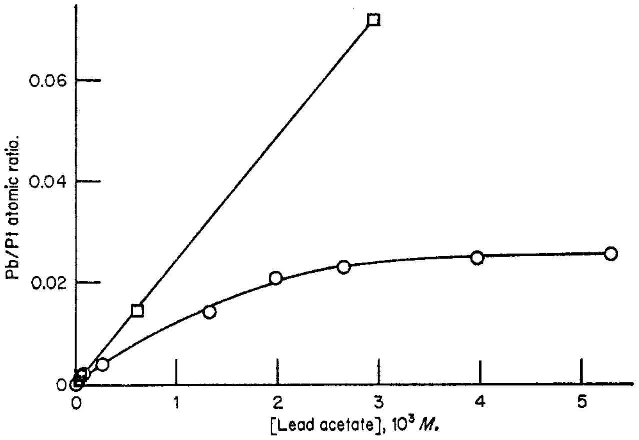

Figure 2. Dependence of the lead content of a platinized platinum deposit on the lead acetate concentration in the plating solution, at 10 mA cm^{-2}: (○) ref 44, 0.051 M (2.5%) chloroplatinic acid, current passed for 1 hr with reversal every 1.5 min; (□) ref 10, 0.062 M (3%) chloroplatinic acid in 0.2 M hydrochloric acid. Time of platinization was not given, and the current density was stated to be 10 cm^2, probably a misprint for 10 mA cm^{-2}.

C. CONSTITUTION OF LEAD-CONTAINING DEPOSITS

1. Composition

As the concentration of lead acetate in the plating solution increases, so does the amount of lead included in the platinized platinum deposit. The available data are plotted in Figure 2, from the radiotracer work of Hevesy and Somiya[10] and the nondestructive X-ray fluorescence spectroscopy of Thacker.[44] The latter's figures are also incorporated in Table IV. The striking disagreement in the diagram is somewhat difficult to explain. The only apparent difference in preparation was that Thacker used current reversal, whereas Hevesy and Somiya did not. Since the anodization potential (on current reversal) is probably high enough to impede[30] loss of lead in the acid solution, the reason almost certainly does not lie here. A very puzzling feature of Hevesy and Somiya's paper is that they claimed to have measured the lead content of deposits by the α-particle activity of a thorium B (^{212}Pb) indicator, but thorium B does not emit α particles and is a β^--particle emitter. The only lead α-particle emitter is radium D (^{210}Pb). Values of lead content were estimated by comparison with lead dioxide containing the tracer, and multiplying by, among other quantities, the inverse of the ratio of the α-particle ranges in the two solids. Thus, change in this ratio can vastly affect the final results. It would therefore seem that Thacker's results are the more trustworthy of the two.

In another investigation[34] it was found that the lead contents of the deposits obtained from a 0.1 M (4.9%) chloroplatinic acid plus 2×10^{-3} M (0.076%) lead acetate solution passed through a maximum as the current density i increased from 0 to 100 mA cm^{-2}, the total amount of electricity being kept constant by adjusting the time t. Equation 7 expresses the results. The magnitudes of the constants k and ξ were not

$$\%\ \text{Pb in deposit} = kt(i/t)^{\xi} \qquad (7)$$

stated, nor was the method of estimating the lead contents of the deposits.

Recent work[30] throws some doubt on all these results and may explain the discrepancy in Figure 2. When a lead-containing platinum deposit was immersed in 1 M perchloric acid solutions, much of the surface lead in the deposit dissolved within a few minutes. This lead appeared to be present as an oxide, probably PbO, and when reduced by hydrogen to lead, it did not dissolve in acid. Since plating solutions are always acidic, some lead will have dissolved if the electrodes were kept in the aerated solution after platinization and before the lead content of the deposit had been measured. It is evident that if reliable estimates of the lead contents of platinized deposits are to be obtained, they must not be allowed to come into contact with acid in the presence of oxygen before the analysis.

Indications as to the physicochemical state of the lead in platinized platinum deposits come from several directions. From X-ray diffraction work it has been deduced both that the lead is[44,52] in solid solution and that it is not[10] in solid solution. The equilibrium platinum–lead phase diagram[61] suggests that all the lead is present as Pt_3Pb dispersed in a matrix of Pt; while the emf *vs.* composition curves[62] of cast alloys indicate a compound of stoichiometry PbPt in Pt, and this has been verified[62] by microscopy. However, it is essential to point out that[31] the phase state of alloys produced by electrolysis often does not correspond to that of the equilibrium phase diagram.

Hevesy and Somiya[10] examined the retention of lead by electrodes at high temperatures using the both the α(?) particle and γ-ray activity of the thorium B tracer. According to the α-particle activity the lead started to sublime out of the deposit at about 600°C and 85% of it had been removed after 16 hr at 720°. However, the γ-ray activity indicated that only 42% of the lead had been lost after 16 hr at 690°. Since γ-rays are more penetrating than α particles it was concluded that lead had vaporized only from a surface region, as deep as the range of the α particles in the deposit. This would be expected, as the rate of sublimation of lead from the bulk of the deposit would be limited by the slow rate of diffusion. A similar situation applies[30] to the leaching of lead from platinized platinum electrodes by 1 M perchloric acid, as already mentioned. Only the lead in the first two or three atomic layers could be dissolved and then only when present as an oxide.

2. Structure

It was noted in the previous section that platinized platinum deposits containing lead have been examined with X-rays. Debye–Scherrer diffraction patterns were obtained, indicating the deposits to be crystalline, for deposits formed from solutions of up to 2.9×10^{-3} M (0.11%)[10] and 5.3×10^{-3} M (0.2%)[44] lead acetate, with 0.062 M (3%) and 0.051 M (2.5%) chloroplatinic acid, respectively, at 10 mA cm^{-2}. Lead acetate concentrations[52] below 2.1×10^{-3} M (0.08%), with 0.021 M (1%) chloroplatinic acid at 625 mA cm^{-2}, also gave deposits which exhibited Debye–Scherrer patterns, but when, at this high current density, higher lead acetate concentrations of 2.1×10^{-3} M (0.08%) to 4.0×10^{-3} M (0.15%) were used, no diffraction lines were observed. This was attributed to the deposit being in a state of colloidal dispersion.

In these diffraction patterns[44,52] an appreciable line broadening, which tended to increase with lead content, suggested that the crystallite sizes were smaller in the higher lead-containing deposits. One would suppose, therefore, that the latter

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(61) M. Hansen, "Constitution of Binary Alloys," 2nd ed, McGraw-Hill, London, 1958, p 1096.

(62) N. A. Puschin and P. N. Laschtschenko, *Z. Anorg. Chem.*, 62, 34 (1909).

possessed larger specific areas,[59,63] yet the reverse is true for the higher lead contents (see Figure 7). The situation is obviously more complicated than appears at first sight, and indeed, electron microscopy[64] indicated that there is not a continuous distribution of crystallite size about a mean value but rather two cubic types of crystallite, each with a distribution of size about its own mean value. The lattice constant of the lead-containing deposits[44,52] was greater than that of pure platinum, but whether it increases with an increase in the lead content is in dispute.[44,52]

Other metal additives that produced a widening of the platinum crystal lattice[52] in the electrodeposit were Hg, Cd, and Tl, while Cr, Mn, Fe, Co, Ni, Cu, Zn, and Pd caused a contraction, and Sb, Sn, Bi, As, and Au, although they modified the nature of the deposit, did not alter the platinum lattice dimensions. No correlation can be seen between the effect of these metals on the lattice dimensions and the appearances of the deposits discussed earlier, brought about by their inclusion in the plating solution.

D. THE EFFECT OF ALTERNATING CURRENT

Platinum black surfaces can be produced on smooth shiny platinum in an inert aqueous solution by several minutes of ac polarization. The conditions used have been[65] 0.5 *M* sulfuric acid at 60 Hz and with an amplitude sufficient to reduce and oxidize the surface without substantial gas evolution; after such polarization platinum has also been found[66] in solution. Others have used[67] either 1 *M* perchloric acid or 3 *M* nitric acid with a 30-Hz square wave of 500 mV amplitude centered on 950 mV. Here the reflectance of the electrode began to decrease before visible darkening, and the time of blackening shortened with increasing frequency. Strangely, it was only in alkaline solution that darkening of the electrode was first noted[68] on the application of a square-wave pulse. Moreover, under certain conditions, with the application of ac a roughened electrode can be smoothed.[66,69]

There is controversy over the mechanism of this darkening. On the one hand[37b] it has been attributed to the repeated penetration and removal of hydrogen caused by the cathodic parts of the pulses, with the resultant expansion and contraction of the platinum lattice breaking up the metal surface. Other workers[66,69] have focused attention on the anodic parts of the pulses, and it has been suggested[66] that the formation of strong Pt–O chemisorption bonds weakens the platinum–platinum interactions. A relevant observation[70] is that the electrolytic formation and reduction of thick bulk oxide layers, repeated several times, increased the roughness factor of a platinum electrode by 100 times or more. Perhaps both mechanisms are admissible under appropriate conditions.

V. *Surface Area*

The prime aim of platinization is to obtain a large area. The concept of *true* area on a microscopic scale is somewhat arbitrary, and especially so with electrochemical systems. Thus it has been argued[71] that the area determined in the dry state, *e.g.*, by the BET method, may be much greater than that associated with electrochemical processes, because the inside surfaces of many pores and cavities of a highly porous surface are not effective in, or contribute but slightly to, the transfer of charge in an electrochemical process. Since all investigations of the areas of platinized platinum electrodes have used electrochemical methods of estimation, the principles of these methods will be outlined first. As will be seen, the correlation between gas adsorption and electrochemical methods of area determination is reasonable for platinized platinum electrodes.

The results of area measurements have unfortunately been presented in the literature in a wide variety of ways, and we must begin by defining the many terms used. The simplest measure is the *surface area* itself, *S*. The area lacks significance on its own and is never used in this review. For electrodes, the most useful quantity is *roughness factor* ϕ. It is dimensionless and defined by

$$\phi = S/A \qquad (8)$$

where *A* is the geometric area of the substrate electrode. The specific area is also used, although this is generally more useful for powders than electrodes. Two types of specific area have been employed and are described by different names in this review to avoid ambiguity. First, the *mass specific area*, σ_m, is given by

$$\sigma_m = S/m \qquad (9)$$

where *m* is the mass of the *deposit*. Note that this does not include the mass of the underlying substrate. Second, *coulombic specific area*, σ_c, is defined by

$$\sigma_c = S/q \qquad (10)$$

where *q* is the amount of electricity passed in deposition. It is necessary to use σ_c because some investigators have characterized the amount of deposit only by recording the number of coulombs passed during platinization, and 100% coulombic efficiency cannot be assumed. For the deposition of platinum with complete coulombic efficiency, a mass specific area of 1978 $cm^2\ g^{-1}$ is equivalent to a coulombic specific area of 1 $cm^2\ C^{-1}$. Division of the roughness factor by the amount of deposit, or of specific area by geometric area, gives the corresponding *specific roughness factor*, in reciprocal grams or reciprocal coulombs. There is no advantage in using this quantity, and it will not be employed here.

Another useful quantity is the degree of platinization of electrodes. Like specific area, it is quoted in two forms. The *mass degree of platinization*, ω_m, is defined as

$$\omega_m = m/A \qquad (11)$$

and the *coulombic degree of platinization*, ω_c, is defined by

$$\omega_c = q/A \qquad (12)$$

For 100% coulombic efficiency, a mass degree of platinization of 1 g cm^{-2} is equivalent to a coulombic degree of platinization of 1978 C cm^{-2}. It follows from the above that

$$\phi = S/A = \sigma_m\omega_m = \sigma_c\omega_c \qquad (13)$$

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(63) A. A. Balandin, V. I. Spitsyn, L. I. Barsova, A. E. Agronomov, and N. P. Dobrosel'skaya, *Zh. Fiz. Khim.*, **41**, 2623 (1967); *Russ. J. Phys. Chem.*, **41**, 1420 (1967).

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

(66) T. Biegler, *J. Electrochem. Soc.*, **116**, 1131 (1969).

(67) A. Bewick and A. M. Tuxford, personal communication, 1969.

(68) A. Hickling, *Trans. Faraday Soc.*, **41**, 333 (1945).

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A. ELECTROCHEMICAL DETERMINATION

There are three basic electrochemical methods for estimating the surface area of platinum electrodes: the determination of the amount of electricity equivalent to the formation of a monolayer of hydrogen and of that equivalent to a monolayer of oxygen, and the measurement of the double-layer differential capacitance. Each of these three methods refers to a fairly well-defined region of the charging (potential–charge) curve of platinum in some inert electrolyte solution (usually sulfuric or perchloric acid), as shown in Figure 3. The solution is saturated[37a] with an inert gas, such as N_2 or He, so that the system is not complicated by the ionization of adsorbed hydrogen or the reduction of adsorbed oxygen. Anodization[37a,72] from the potential of hydrogen evolution gives a slow increase in potential as adsorbed hydrogen is ionized to approximately 0.35 V (RHE). Then a sharp rise occurs while most of the charge passed goes into charging the double layer, to approximately 0.8 V (RHE). Finally, there is a slow linear increase, during which a layer of adsorbed oxygen is formed, to oxygen evolution at about 1.6 V (RHE). Subsequent cathodization[37a] removes the adsorbed oxygen; as this process involves a high activation energy the potential drops sharply to an almost horizontal region at about 0.7 V (RHE). The potential then decreases further to the hydrogen evolution region. The flatter regions up to gas evolution are known as arrests.

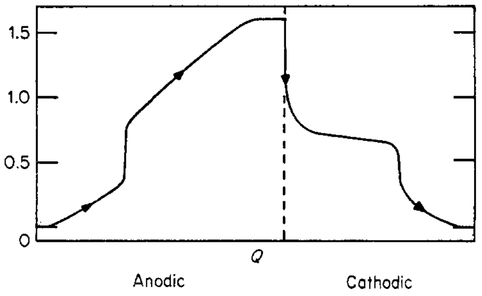

Figure 3. Schematic charging curve for platinized platinum in an inert electrolyte. Potentials (E) are *vs.* the reversible hydrogen electrode (RHE) for the solution used. Under galvanostatic conditions, the charge passed (Q) can be replaced by the time of charging.

If on anodizing the potential is not allowed to exceed about 0.8 V (RHE), the subsequent cathodic charging curve is identical with the anodic one[11,73] and there is no hysteresis. This fact is made use of in area determinations using the hydrogen arrest. The electricity equivalent to a monolayer of hydrogen is found[72] from the length of the hydrogen arrest in the charging curve. The necessary correction for double-layer charging can be simply achieved by extrapolating the linear double layer portion to 0 V (RHE). The charging curve can be determined either anodically or cathodically (see above), and it was claimed by the originators[74] of this technique that, provided the solution was free from oxygen and "negative metal impurities", these were the same. They also recommended that the current density should be high enough to make leakage currents negligible. However, on the whole two different schools of measurement have evolved and will be dealt with separately.

Anodic measurement of the hydrogen arrest was developed in Russia and has been thoroughly investigated for platinized platinum and platinum black. The measurements are carried out galvanostatically and are best[11] at *moderate* current densities (*ca.* 0.1 mA cm^{-2}) where little or no hysteresis is found and the system is virtually in equilibrium[73] all the time. Comparison of the areas of various electrodes obtained by the krypton BET method with the lengths of the anodically determined hydrogen arrests has shown that the latter require 280 μC cm^{-2} for platinized platinum[75] in 0.5 *M* sulfuric acid and for platinum blacks[76] in 0.05 *M* sulfuric acid, and 218 μC cm^{-2} for platinized platinum in 1 *M* HCl and in 1 *M* KBr plus 0.03 *M* HCl[75] and for platinum blacks in 0.5 *M* sulfuric acid.[63] The accuracy of these measurements was reckoned[75] to be ±16%. Nevertheless, it has been argued[77] that the anodic measurement of the hydrogen arrest is unsatisfactory as a routine determination because allowance has to be made for the molecular hydrogen generated at the reversible hydrogen potential, as was found[78,79] for a Teflon-bonded platinum black electrode. The results in fact depended on the starting potential. It must be noted that in most of the Russian charging curve work[72] the potential did not go below approximately 10 mV (RHE), so no molecular hydrogen would have been formed. However, in none of the experimental area calibrations[63,75,76] was the lower limit of potential stated.

The cathodic measurement of the hydrogen arrest was developed chiefly in the United States but has not been experimentally tested like the anodic measurement. Galvanostatic charging[45,77,80] at *high* current densities (*ca.* 100 mA cm^{-2}), where the areas were independent of the current, and cyclic voltammetry[66,81,82] have been used. In the latter the areas of the appropriate current–voltage (time) regions are evaluated. Assuming that at the reversible hydrogen potential there was one atom of hydrogen per surface platinum atom it was calculated[77] that 210 μC cm^{-2} was required. With 1 *M* perchloric acid or 0.5 *M* sulfuric acid as electrolyte, this figure has been used for smooth[45,66,77,80,81] and platinized[45] platinum.

The analogous use of the oxygen arrests is not so straightforward as for the hydrogen ones since[83] a condition of full coverage by oxygen is difficult to define. This is because[83] surface oxides of differing thickness and/or formal valencies are produced (a full discussion on the nature of these surface oxides is given in ref 37a and 82, but contention still exists[84,85]).

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The correction for double-layer charging in the oxygen anodic arrest can be carried out by extrapolating the steep double-layer line to the potential just before oxygen evolution commences. For the cathodic arrest this correction must be calculated from capacitance data but is very small because the potential range covered is short. Measurement under galvanostatic conditions was satisfactory,[37a] although in one case[77] roughening of the electrode resulted (see section IV.D). A fairly high current density was always necessary;[37a] otherwise the lengths of the cathodic and anodic arrests differed. During the anodization there is a danger of oxygen dissolving in the platinum, but the effect of this can be circumvented[37a] by making fast cathodic measurements only. To reduce this danger even further, some workers have not cathodized from oxygen evolution but from 1.24 V,[86] 1.10 V (RHE),[78] and 1.05 V (RHE);[79] in the first case the electrolyte was 1 *M* sulfuric acid at 25°, so the potential corresponds to *ca.* 1.10 V (RHE), and for the other two cases the electrolyte was 85% orthophosphoric acid at 150°. It was found[86] that for cathodization from 1.24 V in 1 *M* sulfuric acid to be consistent with krypton BET measurements, 272 μC cm^{-2} was required for platinized platinum, as opposed to 347 μC cm^{-2} by comparison with smooth platinum, and 355 μC cm^{-2} for Teflon-bonded platinum black electrodes. A very similar figure of 357 μC cm^{-2} was obtained[79] for Teflon-bonded platinum black electrodes in 85% orthophosphoric acid at 150° when cathodization was started at 1.05 V (RHE). Some workers have used values calculated from the packing density of platinum by assuming that a complete monolayer of oxygen is formed with a 1:1 O:Pt stoichiometry, giving[87] 420 μC cm^{-2} and[44] 513 μC cm^{-2}, according to the packing densities used. The charge equivalent to oxygen coverage has also been determined by cyclic voltammetry.[44,82]

Finally, the double-layer differential capacitance as a measure of surface area has been investigated in some detail. The classical ac bridge technique is not suitable for determining the capacitances of platinized platinum electrodes because their areas, and thus their capacitances, are too large. In essence, the method has been to take the slope of the charging curve in the (linear) double layer region. The differential capacitance, *C*, is then given by

$$C = \int_0^{\Delta t} I\mathrm{d}t/\Delta E \qquad (14)$$

where *I* is the current which causes a change in potential of ΔE in a time Δt. Usually galvanostatic conditions[11,74] have been employed so the slope could be measured directly and eq 15 used. Ershler[73] recommended that moderate current

$$C = I\Delta t/\Delta E \qquad (15)$$

densities be used; otherwise the system is not in equilibrium. If the potential is changed too quickly some of the current is still used for the hydrogen arrest (in the case of anodic charging) or the oxygen arrest (cathodic charging). In a later modification[88,89] applied to platinized platinum, the starting potential was fixed by auxiliary dc polarization and a square-wave signal of low amplitude ($\leqslant$ 20 mV) and frequency (2 Hz) was applied. The change with time of the potential across the test electrode was recorded on a cathode ray oscilloscope. In more recent work,[87] short constant-current pulses of less than 10-μsec duration are employed so as to eliminate any faradaic contribution.

While the differential capacitance method is good[44,59,89] for smooth platinum, it is not usually satisfactory[44,59,75] for finely divided platinized platinum (although it has been successful on some occasions[42,88]) or for Teflon-bonded platinum black fuel cell electrodes[78] and platinum black.[63,76] Its usefulness appears to be limited[44] by the texture of the electrode, and deposits of high roughness factor and specific area may give anomalous results because[63] the values of the capacitance in narrow pores are too high compared with those of a smooth surface. For platinized platinum the best figures, from comparison with the krypton BET method, are: 36 ± 5 μF cm^{-2} in 0.5 *M* sulfuric acid,[75] 20 ± 3 μF cm^{-2} in 1 *M* HCl or 1 *M* KBr plus 0.03 *M* HCl,[75] and 20.1 ± 0.7 μF cm^{-2} in 1 *M* sodium sulfate solution.[88] The experimental conditions pertaining to the last figure were dubious. Measurements were taken using a square wave of frequency 2 Hz and of amplitude 20 mV centered on 445 mV or about 0.86 V (RHE). Since this is a little above the upper limit of the double-layer region, oxygen adsorption would affect the value of the capacitance measured. Values of about 20 μF cm^{-2} have been criticized[82] for smooth platinum as being too low, and attributed to contamination.

B. DEPENDENCE ON PLATING CONDITIONS

The roughness factors reported in the literature vary over an enormous range. Extreme values as high as 3900 or even 20,000 were said[88] to be obtained by a "standard" platinization procedure. However, usual values[32,42,44,86] are 200–500, although roughness factors in excess of 2000 have been claimed,[42,45] in one instance[42] with the proviso that this was true only with large deposits (approximately 1 g of deposit per square centimeter of electrode). The actual value obtained depends on the amount of deposit, the composition of the plating solution, the current density of deposition, and the temperature. The first three have been investigated at ambient temperatures only, but temperature itself seems to have been somewhat neglected. Moreover, experiments designed to test the effect of the composition of the plating solution have all in fact just examined the effect of the lead acetate concentration.

1. Degree of Platinization

The areas of platinized platinum electrodes increases[11,34,55] with degree of platinization, although the rate of this increase usually drops[11,34,42] as the platinization continues, or even attains[5] a maximum value. The available data are plotted in Figures 4, 5, and 6.

The roughness factors of Figure 6 are almost ten times greater than those in Figure 4 and these, in turn, are some ten times greater than the ones in Figure 5. The ϕ values in the last case might be expected to be well below the true values, partly because[90] of a faradaic contribution to the measured capacitance and partly because of the very small current density (0.7 mA cm^{-2}) of platinization. This would normally lead to a low coulombic efficiency and the accumulation of $PtCl_4^{2-}$ in the plating solution, except that here the chloroplatinic acid concentration was correspondingly small. It is therefore a moot point whether the coulombic degree of platinization here is a fair guide to the mass degree of platinization. The exceed-

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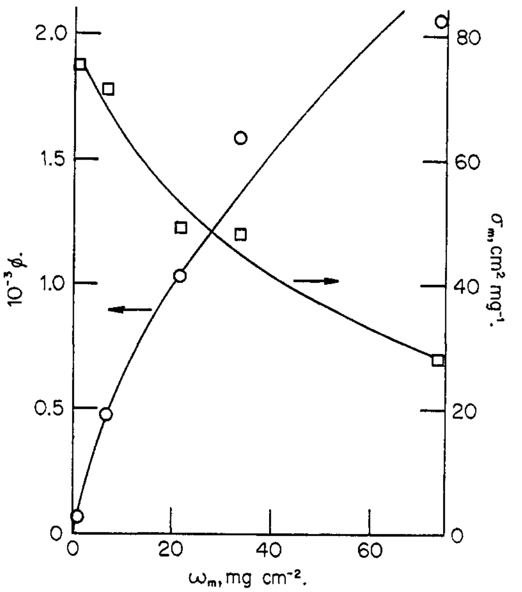

Figure 4. Variation of roughness factor ϕ (○) and mass specific area σ_m (□) of a platinized platinum deposit with mass degree of platinization ω_m. Obtained from a 0.041 M (2%) chloroplatinic acid solution at 2.9 mA cm^{-2} (from ref 11). Electrode surface areas were given in coulombs obtained from the anodically measured hydrogen arrest in 0.5 M sulfuric acid. They were converted to square centimeters by dividing by 280 μC cm^{-2} (see section V.A). The geometric area was 34 cm^2.

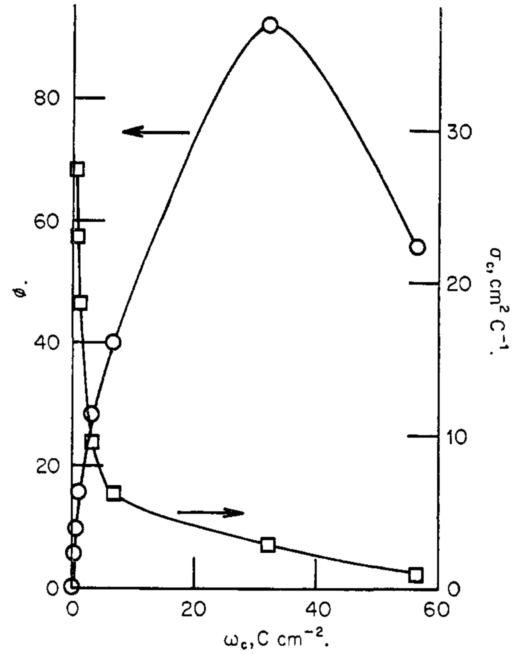

Figure 5. Variation of roughness factor ϕ (○) and coulombic specific area σ_c (□) of a platinized platinum deposit with coulombic degree of platinization ω_c. Obtained from a 0.006 M (0.3%) chloroplatinic acid plus 6.6 × 10^{-4} M (0.025%) lead acetate solution, 0.025 M in hydrochloric acid, at 0.7 mA cm^{-2} for 10 min with current reversal every 10 sec (from ref 5). The experimental data were polarization capacitances, at 700–3070 Hz, in a conductance cell containing two circular platinum electrodes of 3-cm diameter and 0.85 cm apart, with the plating solution as electrolyte. The resulting parallel plate capacitance is negligible (*ca.* 60 pF) compared to the polarization capacitances (30–8000 μF) with which it is in parallel.[90] Values obtained at[91] 1 kHz were doubled (two electrodes in series) and divided by 20 μF cm^{-2} to give areas. Roughness factors were obtained by using A = 14.14 cm^2. This gives ϕ = 0.26 for the unplatinized electrode, and a better area measure might therefore be obtained by multiplying all values by 4.

ingly high roughness factors of Figure 6 may not be very reliable, as they are based on double-layer differential capacitance measurements[92] which, as already pointed out (section V.A), can be anomalously high.

Not only the magnitudes but also the shapes of the plots in the three diagrams differ markedly. The maximum in the roughness factor curve in Figure 5 is not encountered elsewhere, and the complete linearity shown in Figure 6 might be a consequence of the potentiostatic, as opposed to galvanostatic, plating conditions. A more likely explanation is proposed below. In a more recent and quantitative study,[34] in which electrode area was measured by anodization in the hydrogen region, eq 16 was found to relate roughness factor to deposition

$$\phi = bt(1 - e^{-\beta t}) \tag{16}$$

time, t, at 100 mA cm^{-2} for the first 400 sec of plating from a 0.041 M (2%) chloroplatinic acid solution. The values of b and β varied from about 0.3 to 1.3 sec^{-1} and from about 0.0006 to 0.003 sec^{-1}, respectively, depending on the pretreatment of the platinum substrate. For platinization from a 0.1 M (4.9%) chloroplatinic acid plus 2 × 10^{-3} M (0.076%) lead acetate solution at 100 mA cm^{-2} the area increased linearly with time (as in Figure 6) or with mass of deposit. From the figures given we calculate that after t sec

$$\phi = (3.8 \times 10^{-3})t \tag{17}$$

by dividing the rate of area increase, found by the hydrogen arrest method, by 280 μC cm^{-2}. The pretreatment of the substrate had no effect in this case.

At 10 mA cm^{-2}, with the same lead-containing solution, the relationship between area and time or mass of deposit was no longer linear. The deposition rate varied with electrode pretreatment, and the rate of increase in surface area decreased with deposition time, as in Figures 4 and 5. The experimental data followed the equation

$$\sigma_m = g(i/t)^{\gamma} \tag{18}$$

where i is the current density of 10 mA cm^{-2}, and g varies from about 650 to 850 and γ from about 0.3 to 0.4, depending on the nature of the substrate surface. Equations 17 and 18 taken together suggest that at high current densities specific area is approximately constant with time of plating (or degree of platinization), whereas at low current densities specific area decreases with time of plating. This is confirmed by Figures 4–6, for the potentials of deposition of Figure 6 are of a magnitude[32] to give current densities higher than those of Figures 4 and 5.

As expected, this general rise in area with degree of platinization (with the exception of Figure 5) is reflected in a continued enhancement of electrode activity as more platinum is deposited. An example is found[93] in the electrooxidation of methanol.

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(92) C. Bernard and J. Clavilier, *C. R. Acad. Sci., Ser. C*, **263**, 1340 (1966).

(93) M. Prigent, *Rev. Gen. Elec.*, **74**, 69 (1965).

2. Lead Acetate Concentration

The concentration of lead acetate used in the plating solution affects the roughness factor of the final deposit. The mass specific areas of deposits[34] prepared at 100 mA cm^{-2} from 0.1 *M* (4.9%) chloroplatinic acid solutions decreased as the lead acetate concentration was raised from 10^{-4} *M* (0.0038%) to 0.05 *M* (1.9%). The magnitude and type of decrease were not specified. On the other hand, Thacker,[44] who had used only 10 mA cm^{-2}, found that the area, measured by the oxygen arrest technique, was a maximum at a Pb/Pt atomic ratio of 0.0021, which corresponds to a lead acetate concentration of 8×10^{-5} *M* (0.003%). This is shown in Table IV and Figure 7. Rather more indirect evidence on the area-lead content relationship is provided by the measurements of Hevesy and Somiya.[10] From their cathodic polarization data we have estimated a measure of the surface area as described under Figure 8. The diagram displays an area maximum at a Pb/Pt atomic ratio of approximately 0.005–0.01 which corresponds to a lead acetate concentration of *ca.* 2.5×10^{-4} *M* (0.01%), but there is no minimum at higher lead acetate concentrations as there is in Figure 7. This work[10] and Thacker's[44] taken together indicate that the area would be maximized by employing a lead acetate concentration of about 1.3×10^{-4} *M* (0.005%). These two pieces of work are augmented by a study[93] on the variation of electrode activity, to methanol oxidation in 2 *M* MeOH + 3 *M* H_2SO_4 solution at 25°C, with the lead acetate concentration of the plating solution. For a 0.103 *M* (5%) plating solution of chloroplatinic acid and deposition at a constant potential of 250 mV (RHE), maximum activity of the electrode occurred for a lead acetate concentration of 5.3×10^{-4} *M* (0.02%); however, at deposition potentials of +50 or −50 mV, monotonic increases in electrode activity with lead acetate concentration were found up to 4×10^{-3} *M* (0.15%). Unfortunately this work is not strictly comparable with that discussed above, partly because a different property was measured and partly because of the potentiostatic conditions of preparation. The potentials employed probably correspond[32] to current densities rather larger than the 10 mA cm^{-2} used by Thacker[44] and by Hevesy and Somiya.[10]

It should be added that both the area and the activity measurements were carried out in acid solution. Introduction of oxygen at any stage would have resulted[30] in some leaching of the lead from the surface layer and a possible concomitant change in area.

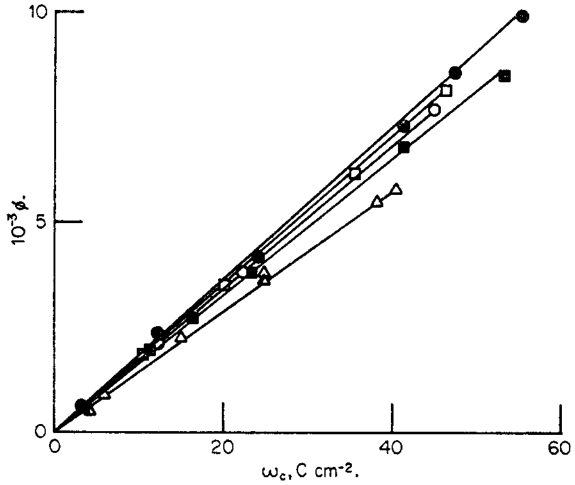

Figure 6. Variation of roughness factor ϕ of a platinized platinum deposit with coulombic degree of platinization ω_c. Obtained from a 0.05 *M* (2.4%) chloroplatinic acid plus 2.7×10^{-4} *M* (0.01%) lead acetate solution at a series of constant potentials; from ref 55: ○, 195 mV; ●, 220 mV; □, 245 mV; ■, 295 mV; △, 345 mV. The experimental data, in farads per geometric square centimeter in 0.05 *M* KCl solution, were converted to roughness factors by dividing by 20 $\mu F\ cm^{-2}$.

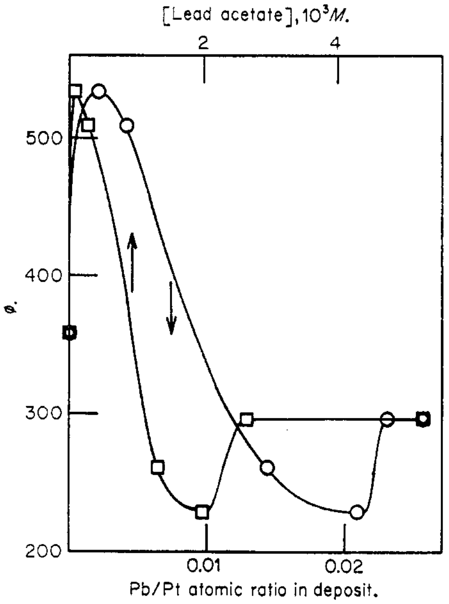

Figure 7. Variation of roughness factor ϕ of a platinized platinum deposit with lead content (○) and with the lead acetate concentration of the plating solution (□); obtained with a 0.051 *M* (2.5%) chloroplatinic acid solution at 10 mA cm^{-2} for 1 hr with current reversal every 1.5 min; from ref 44.

3. Current Density

When the solution composition as well as the mass of deposit are kept constant, the area can clearly be seen to depend upon the current density employed (Figure 9). The type of information conveyed in Figure 10, though superficially similar, differs because in the paper in question[42] the masses of deposit ranged from 1 to 23 g, and the specific area varies with the mass of deposit (*cf.* Figures 4 and 5). A third piece of information can be deduced from a set of current–voltage curves[64] for platinized platinum electrodes carried out in 1 *M* HCl under 1 atm of hydrogen. The composition of the plating solution was not stated. According to the legend of Figure 8, the initial slopes of current *vs.* voltage should be approximately proportional to area. Estimation of the slopes is made difficult by the small size of the graph on which the results are plotted,[64] but the diagram does show that the area tended to increase with current density of platinization up to a value of 45 mA cm^{-2}. There is no evidence of any maximum.

Roth and Lasko,[34] who used a solution 0.1 *M* (4.9%) in chloroplatinic acid plus 2×10^{-3} *M* (0.076%) in lead acetate, presented their area results in two forms. For a constant quantity of electricity during platinization, ϕ was plotted against *i*. The form of this plot was essentially the same for all platinum substrates in spite of various pretreatments

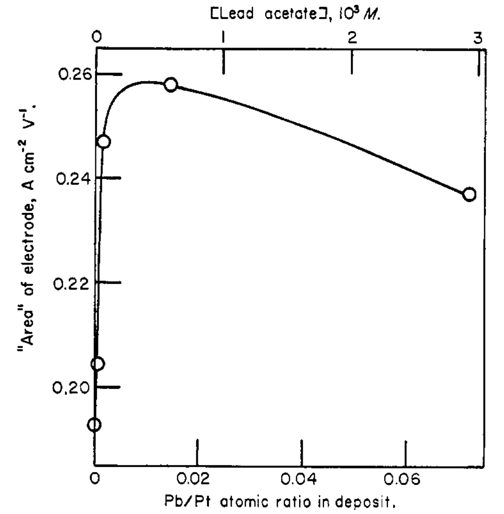

Figure 8. Variation of the "area" of a platinized platinum deposit with lead content and with the lead acetate concentration of the plating solution. Obtained from a 0.062 M (3%) chloroplatinic acid solution 0.2 M in HCl. The current density was stated to be 10 cm^2, probably a misprint for 10 mA cm^{-2} (from ref 10). A measure of the area has been derived from cathodic overpotential measurements in 0.5 M sulfuric acid at a constant current density of 20 mA/cm^2 of geometric area. Current (I) *vs.* overpotential (η) curves are functions of the exchange current density (i_0) or the exchange current ($I_0 = i_0S$). At constant current, η increases as I_0 decreases, and (if i_0 is constant) the smaller I_0, the smaller is the area S. In the special case when overpotentials are <*ca.* 20 mV, $I/\eta = \mathrm{d}I/\mathrm{d}\eta = I_0(nF/\nu RT) = i_0\,S(nF/\nu RT)$, where n = number of electrons, ν = stoichiometric number. Thus, at constant current and small overpotentials, $S \propto I/\eta$. In this way measures of "area", in A V^{-1} cm^{-2} of geometric area, have been deduced from the data in ref 10.

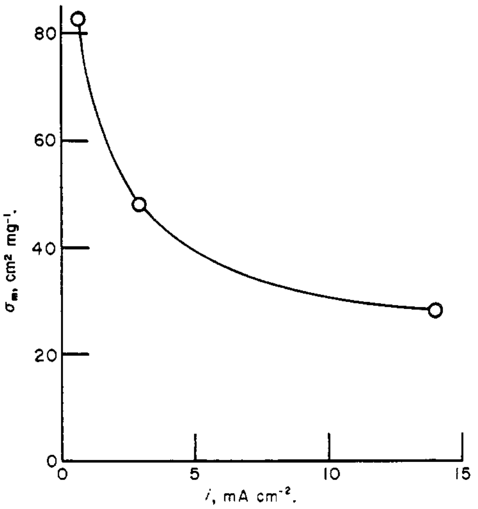

Figure 9. Dependence of the mass specific area σ_m of a platinized platinum deposit on the current density of platinization, i; obtained from a 0.041 M (2%) chloroplatinic acid solution, giving a constant mass of deposit of 0.71 g (from ref 11).

(section IV.B.1) and showed a maximum roughness factor of about 200 at i = 20 mA cm^{-2} (using the conversion factor employed for eq 17). Since the coulombic efficiency varies with current density, the results cannot be directly related to those of Figures 9 and 10. However, the results were fitted[34] in terms of mass specific area to the equation

$$\sigma_m = ht(i/t)^{\epsilon} \qquad (19)$$

where it = constant, and from their logarithmic plot of σ_m/t against i/t, ϵ is close to 0.5. It follows that σ_m is almost independent of current density.

These four area–current density determinations seem united only by their diversity. In one case[11] the mass specific area decreases monotonically as i increases, in another[42] it increases monotonically, in a third[42] it passes through a maximum at 250 mA cm^{-2}, and in yet another[34] it is altogether independent of current density. Of the two studies of roughness factor, one[64] shows ϕ increasing continuously with i and the other[34] records a maximum in ϕ at 20 mA cm^{-2}. One's scientific morale is sustained only by the thought that these differences may have arisen as a result of the diversity of plating conditions, and by the hope that further, carefully planned, studies may disentangle the variables. It is strongly recommended that, in the future, workers always describe their surfaces in terms of roughness factors as well as specific areas.

Some complementary evidence is available from plating experiments carried out under potentiostatic conditions. The dependence of roughness factor on the (constant) potentials[66] of platinization, shown in Figure 6, points to a maximum roughness factor at a potential of approximately 230 mV. This is illustrated more clearly in Figure 11, in which the slopes of the lines in Figure 6 (*i.e.*, the coulombic specific areas) have been plotted against the potentials of platinization. Since lower (more cathodic) plating potentials correspond to higher current densities, it follows from Figure 11 that the roughness factor should pass through a maximum with increasing current density. The decrease in coulombic specific area shown at deposition potentials more anodic than 230 mV may be explained as being due to a decrease in coulombic efficiency as $PtCl_4^{2-}$ is produced and accumulates. The researches below confirm that, at potentials up to +230 mV, higher areas are obtained at more positive potentials.

In one such study,[33,94] in which deposits were prepared from 0.041 M (2%) chloroplatinic acid solution 1.5 M in sulfuric acid, the mass specific area (measured by the hydrogen arrest technique) rose from 40–70 cm^2 mg^{-1} when deposited between −50 and +50 mV (RHE) to 170–200 cm^2 mg^{-1} when deposited at potentials above +150 mV (RHE). The activities of these electrodes to the electrooxidation of methanol increased by factors of 8–10 when the deposition potential was changed from −50 to +250 mV (RHE), and most of this change occurred for potentials between −50 and +50 mV (RHE). However, the mass degree of platinization ranged from 5 to 15 mg cm^{-2}, and this detracts from the usefulness of the above observations. A similar trend was found[93] for electrodes prepared from a 0.103 M (5%) chloroplatinic acid plus 5.3×10^{-4} M (0.02%) lead acetate solution, but here most of the change in activity occurred between +50 and +250 mV. In a fourth paper,[59] the electrodeposition from a 0.051 M (2.5%) chloroplatinic acid solution 1 M in HCl was studied at the controlled potentials 0, 50, and 150 mV; both the areas determined by the hydrogen arrest technique and by differential capacitance at 0.6 V showed a very large increase for a given mass of deposit when the deposition potential was changed from 0 to 50 mV, and this was confirmed visually from electron micrographs. X-Ray diffraction line broadening indicated[59] particle diameters of 24 and 15 nm, respectively, for these two de-

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(94) B. I. Podlovchenko and R. P. Petukhova, *Elektrokhimiya*, **5**, 380 (1969); *Sov. Electrochem.*, **5**, 349 (1969).

position potentials, and it was concluded that at the lower potential a high coverage of hydrogen on the platinum surface inhibited the nucleation process, with a consequent increase in particle size and a smaller surface area. Furthermore, in deposition from 0.041 *M* (2%) chloroplatinic acid solution 1.5 *M* in sulfuric acid, the platinized platinum crystallite diameters were found[33] by X-rays to be *ca.* 30 nm at a deposition potential of 0 mV (RHE) (*ca.* −20 mV (NHE)) and *ca.* 20 nm at +250 mV (RHE). The platinum lattice constant did not change with deposition potential.[33]

It is easier to explain the phenomena observed during electrodeposition if constant potential rather than constant current is employed, but, however the plating is carried out, whether potentiostatically or galvanostatically, both potentials and current densities should be reported. Although the value of the uncontrolled variable will change[32] somewhat during the course of plating, an average value, with the range of variation if it is significantly large, would provide valuable information for subsequent workers.

4. *Temperature*

The effect of the temperature of deposition on the area of platinized platinum electrodes has received but little attention. Electrodes prepared[88,94] from a 0.041 *M* (2%) chloroplatinic acid solution 1.5 *M* in sulfuric acid at −20, +4, and +80°C displayed the same type of dependence of activity (to the electrooxidation of methanol) on deposition potential as did that prepared at +20°C. Deposits obtained at 200–250 mV (RHE) (180–230 mV) in the temperature range −20 to +80°C had similar values of mass specific area and practically the same activity despite a 30-fold variation in deposition currents. Since mass specific area depends on current density as well as on degree of platinization, these two factors appear to have compensated one another.

C. REPRODUCIBILITY

In the literature there are widely differing reports about the reproducibility of platinized platinum electrodes. The data in Figure 12, for example, show a reproducibility of 5–10%. Electrodes prepared[95] from 0.103 *M* (5%) chloroplatinic acid plus 5.3 × 10^{-4} *M* (0.02%) lead acetate solution at 120 mA cm^{-2} gave activities for the Tl^{I}–Tl^{III} electron exchange catalysis which were reproducible to 5%. Even better consistency was obtained[51] in work on the anodic polarography of dextrose; rotating disk electrodes prepared from 0.062 *M* (3%) chloroplatinic acid plus 1.6 × 10^{-3} *M* (0.06%) lead acetate at 152 mA cm^{-2} and 1300 rpm gave polarographic currents reproducible to 2%. In contradistinction, Joncich and Hackerman[42] found that platinization was only "reproducible" when no lead acetate was added. Using a solution 0.049 *M* (2.4%) in chloroplatinic acid and 2.5 × 10^{-5} *M* (0.001%) in lead acetate, and 210 mA cm^{-2}, they obtained samples of specific areas 8.9 and 15 $cm^2\ mg^{-1}$ after 30 min of plating and samples of specific areas 2.9 and 6.8 $cm^2\ mg^{-1}$ after 120 min. A solution of 0.09 *M* (4.4%) chloroplatinic acid containing no lead acetate, with a current density of 150 mA cm^{-2}, gave samples of specific areas 1.5 and 2.0 $cm^2\ mg^{-1}$ (or with roughness factors of 350 and 620, respectively); the time of plating was not given. Thus, even these "reproducible" results are not very promising, although the reproducibility of two points in Figure 10 is good to 5%.

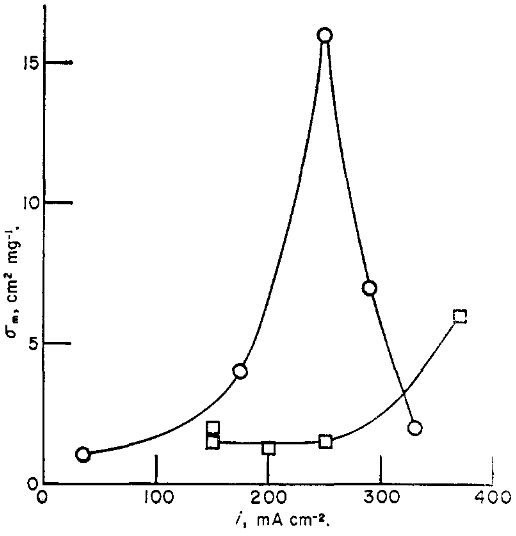

Figure 10. Dependence of the mass specific area σ_m of a platinized platinum deposit on the current density of platinization, *i*; obtained from 0.205 *M* (10.0%, ○) and 0.090 *M* (4.4%, □) chloroplatinic acid solutions 0.86 *M* in HCl, giving deposits of masses from 1 to 23 g (from ref 42).

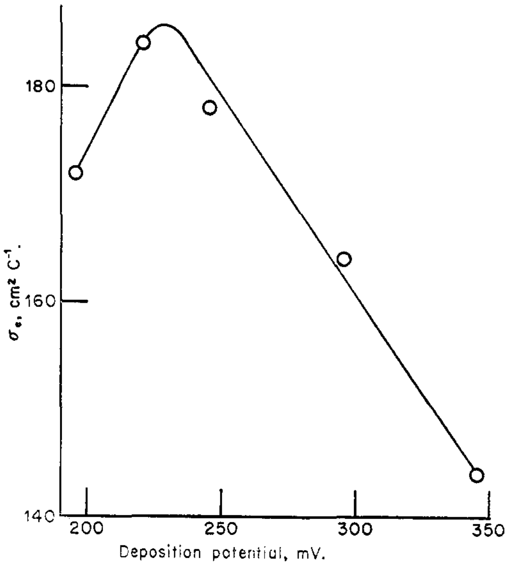

Figure 11. Dependence of the coulombic specific area σ_c of a platinized platinum deposit on the deposition potential of platinization. The plating solution had the same composition as for Figure 6 and the coulombic specific areas were calculated from the slopes of the lines of that figure (from ref 55).

D. DECREASE WITH TIME

It is highly desirable for the area not to change with time. This will be so for surfaces which are not far from thermodynamic equilibrium or which have a low surface self-diffusion coefficient, D_s. Its value for platinum, over all orientations, was found[96] from the interference microscopic observation of

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[95] I. R. Jonasson and D. R. Stranks, *Electrochim. Acta*, **13**, 1147 (1968).

[96] J. M. Blakely and H. Mykura, *Acta Met.*, **10**, 565 (1962).

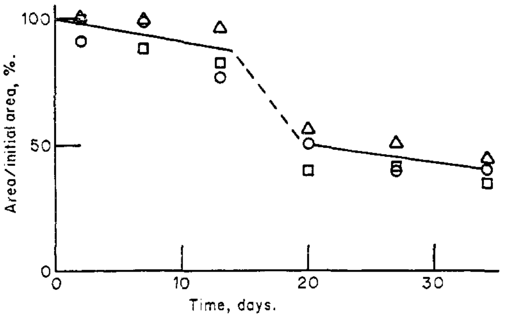

Figure 12. The decrease in area with time of platinized platinum electrodes. They were immersed in 5 *M* orthophosphoric acid and maintained at 25°C for the first 12 days and at 80°C for 7 hr/day on 13 of the remaining 22 days. All three electrodes (○, □, △) were prepared from a 0.051 *M* (2.5%) chloroplatinic acid plus 8×10^{-5} *M* (0.003%) lead acetate solution, at 10 mA cm^{-2} for 1 hr with current reversal every 1.5 min (from ref 98).

the decay of sets of parallel scratches on platinum crystal surfaces, and obeyed eq 20 between 890 and 1310°C, where

$$D_s = D_0 \exp(-Q/RT) \tag{20}$$

$D_0 = 4 \times 10^{-3}$ cm^2 sec^{-1} and $Q = 108 \pm 10$ kJ mol^{-1}. The coefficients were strongly orientation dependent. The Arrhenius equation was also verified[97] by field-electron emission microscopy in the temperature range 823 to 1123°C, and the activation energy of 123 ± 13 kJ mol^{-1} is in quite good agreement with the previous value. If eq 20 applies down to room temperature, D_s at 25° is 4.7×10^{-22} cm^2 sec^{-1}; this corresponds to a mean diffusion distance for a single atom of 3×10^{-11} cm/sec or 2.6×10^{-6} cm/day. Whether there is any net movement of material in a given direction will depend on the existence of a gradient of chemical potential on or up to the surface. Such a gradient might well be present on a freshly prepared platinized platinum deposit, and appreciable sintering would then be expected. For the evidence we must turn to the literature.

An electrode freshly prepared[11] from a 0.041 *M* (2%) chloroplatinic acid solution decreased in area by about 30% in 2–3 months, which averages out as 0.4% per day. The changes of area with time[98] of three identically prepared platinized platinum electrodes in 5 *M* orthophosphoric acid at 25 and 80°C are shown in Figure 12. The decrease in area is only about 0.8% per day at 25° but becomes ten times as large when the temperature is kept at 80° for 7 hr a day. A Teflon-bonded platinum black electrode[79] lost 4.4% of its area per day when stored in 85% orthophosphoric acid at 150°C.

These long-term linear decay results stand in constrast with other observations which point to rapid initial decay which levels off. A platinized platinum electrode, prepared as described in Figure 6 but with the potential of deposition not mentioned, was periodically immersed[65] in 0.05 *M* KCl solution and the double-layer differential capacitance measured after 10 min and again after 18 hr. Between each such pair of measurements the electrode was stored in air in an antidust container for many weeks. After only 1 day of ageing the differential capacitance decreased by 20% during the 18 hr of immersion, but the subsequent rate of decrease was only 13% over the next 6 months, or an average of 0.07% per day. It is not clear whether the initial drop was caused by a genuine contraction in area or by a process of equilibration (perhaps involving adsorption) at the interface. Deactivation by contamination is also a distinct possibility, although Bernard[65] discounted this on the grounds that the solutions were very pure. Evidence for incidental contamination comes from the observation[66] that severe poisoning of a smooth platinum electrode occurred when it was left in "pure" 1 *M* sulfuric acid for long periods (hours) at open circuit or held at potentials below about 0.9 V. Also, the mass specific area of precipitated platinum black[63] found from double-layer capacitance in 0.5 *M* sulfuric acid decreased sharply, while the (lower) value determined by benzene adsorption changed only slightly. The period of time involved and the storage environment were not stated. Further support for the initially rapid type of decay comes from catalysis studies. On a platinized platinum rotating disk electrode (of unspecified preparation) the cathodic hydrogen diffusion current *I* was measured[99] and found to vary with the rotation speed ω according to

$$\frac{1}{I} = a + \frac{b}{\sqrt{\omega}} \tag{21}$$

The existence of the intercept *a* was ascribed to the fact that the active site density *p* on the surface was not infinite and, from *a*, values of *p* were derived. They were found to decrease from $>10^{11}$ cm^{-2} immediately after platinization to 1.3×10^{10} cm^{-2} 6 days later and 0.6×10^{10} cm^{-2} after 12 days. In fuel cell work,[93] electrodes deposited from 0.103 *M* (5%) chloroplatinic acid plus 5.3×10^{-4} *M* (0.02%) lead acetate solution displayed activities to methanol oxidation which stabilized in approximately 3–6 weeks to values which were only 20–30% of the initial activities. Perhaps the essence of this type of decay lies in the interaction of the surface with gases. It was noted long ago[100] that prolonged exposure of platinized platinum to air destroyed its activity for use as a hydrogen electrode and also reduced its wettability.[4] The type of gas is important too: the area (as measured by the hydrogen arrest) of a platinized platinum electrode (of unspecified preparation) decreased[101] in 2 hr by 8% when maintained at 100°C in air and by 50% at 300°C, but sintering at 300° in hydrogen for 2 hr diminished the area by a factor of 30.

The decrease in area is more rapid if the electrodes are kept in a polarized state. Thus, the roughness factor of a platinum electrode,[45] platinized from 0.041 *M* (2%) chloroplatinic acid solution 1 *M* in HCl at 50 mV, dropped from 2380 to 97 in 100 hr when kept at 0.6 V in 0.5 *M* sulfuric acid plus 1 *M* acetic acid at 94°C. Similarly, an electrode[38] that was being anodically polarized at 5 mA cm^{-2} at 80°C, and which had been plated from 0.041 *M* (2%) chloroplatinic acid solution 1.5 *M* in sulfuric acid at 20°C, lost 69% of its initial surface in 48 hr. However, the area lost was only 28% in 48 hr if the electrode had been prepared instead at 80°C. It was suggested[38] that more regular crystals had been formed at 80°C and that these recrystallized less on standing.

Bright-plated electrodes, obtained by using chloroplatinous acid, were initially active[48] as hydrogen electrodes but lost their activity rather rapidly, especially when stored in hydrogen.

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VI. Survey of Recommended Platinizing Procedures

Both undergraduate laboratory textbooks and certain research monographs recommend procedures for obtaining good platinized platinum electrodes. We shall now examine these in the light of the evidence presented in the previous sections.

Standard American and British undergraduate texts for practical physical chemistry list a variety of procedures. Daniels, Mathews, Williams, Bender, and Alberty[102] recommend a 0.021 M (1%) solution of platinum chloride, the use of two dry cells, and the passing of current for several minutes. Shoemaker and Garland[103] instruct the student to use a 0.062 M (3%) solution of platinum chloride plus 5.3×10^{-3} M (0.2%) lead acetate, with two dry cells and a rheostat to give slow gas evolution, the current to be stopped as soon as the electrodes are sooty black. Findlay and Kitchener[104] advocate a solution 0.041 M (2%) in platinum chloride and 5.3×10^{-4} M (0.02%) in lead acetate for conductance electrodes,[104a] and a solution 0.021 M (1%) in platinum chloride and no lead acetate for emf electrodes,[104b] two accumulators, and a rheostat to give only a moderate stream of gas, the current being reversed every 0.5 min for approximately 10 min. A very similar preparation to the former[104a] is given by James.[105] Of these recipes two[102,104b] do not mention lead acetate, one[103] advocates excessive lead acetate, two others[104,105] support the needless[41,43] procedure of current reversal, none specify the current density, and only Findlay and Kitchener give a time of platinization (but again without stating a current density). All the above books incorrectly call the main chemical platinum chloride instead of chloroplatinic acid, so perpetuating a source of confusion found in the older literature (*cf.* section II).

Probably the most widely used research procedure is that of Bates,[106] as recommended by Hills and Ives.[38] This consists of passing a current of 100–200 mA/cm^2 of substrate for 1–3 min in a solution of 0.021–0.062 M (1–3%) chloroplatinic acid plus 2.1×10^{-3} M (0.08%) lead acetate. Bates[106] claims that with a "properly prepared" solution the conditions of plating are not critical. In the light of the evidence available, we believe that the lead acetate concentration recommended is too high, and that the range of other conditions given is too broad.

There are three main uses of platinized platinum electrodes: as hydrogen reference electrodes, as inert surfaces of high area in conductance work, and as catalysts and electrocatalysts. For routine platinization applicable to all three uses, we recommend the use of the following conditions: a solution of 0.072 M (3.5%) chloroplatinic acid plus 1.3×10^{-4} M (0.005%) lead acetate, at a current density of 30 mA cm^{-2} for up to 10 min. A deposition time of 5 min should be adequate for hydrogen emf[38,100] and for conductance[5] electrodes, for here a smaller deposit speeds equilibration and reduces adsorption. Good stirring is essential and no gas should be evolved at the platinum cathode. The chlorine evolved at the anode can easily be prevented from interacting with the cathode by employing a salt bridge or an H-type plating cell. If other considerations dictate the use of a one-compartment plating cell, the evolution of chlorine can be avoided by making the electrolyte 2 M in HCl and employing a large silver anode, previously lightly chloridized to prevent oxidation by chloroplatinate ions.[32]

Potentiostatic platinization, a more definitive method of preparation than galvanostatic deposition, is to be preferred whenever the properties of the electrode play an essential part in the research: in electrocatalytic investigations, for example. Suitable electrodes have been obtained[45] by plating at +50 mV (NHE) from a 0.041 M (2%) chloroplatinic acid solution, 1 M in HCl. There was no simultaneous hydrogen evolution.[107]

For systems sensitive to trace impurities, such as the hydrogen electrode in a medium of neutral pH, platinization without lead additive has been recommended.[38] In this case a low current density (10–20 mA cm^{-2}) is essential for good adherence of the deposit, or else potentiostatic deposition as described above can be used. However, there are two attractive alternatives. One is to add lead acetate as before and, after platinization, to remove the surface lead which is capable of dissolving by soaking the electrode for 24 hr in aerated 1 M perchloric acid.[30] The other is to apply an oscillating signal to the platinum substrate in an inert solution of similar composition to the one to be used. Suitable conditions might be the application of 1 kHz of amplitude 500 mV centered on 0.95 V for 5 min. Bright and highly active electrodes, but of short lifetime, can be prepared[48] by plating from solutions of chloroplatinous acid. The appropriate pre- and post-treatment of the electrodes have been discussed in sections III.D and IV.B.3, respectively.

Acknowledgments. For permission to reproduce figures we are grateful to Academic Press (Figures 2 and 7), the Electrochemical Society (Figure 10), Macmillan (Journals) Ltd. (Figure 12), and Pergamon Press Ltd. (Figures 1 and 6), and we thank the Science Research Council for the award of a Research Studentship to A. M. F.

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