JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 415–420

Studies of platinum electroplating baths
Part I: The chemistry of a platinum tetrammine bath

R. LE PENVEN, W. LEVASON, D. PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, Great Britain

Received 20 June 1991; revised 20 August 1991

The chemistry of a new commercial electroplating bath for platinum, based on a $Pt(NH_3)_4^{2+}$ salt in a phosphate buffer, is investigated using ^{195}Pt NMR and microelectrode techniques. It is shown that the maximum rate of deposition is determined by a homogeneous chemical reaction preceding the electron transfer step; the nature of this homogeneous chemical reaction is discussed.

1. Introduction

Platinum is extensively electroplated onto, for example, some aviation components, turbine blades, electrodes, electronic components and jewellery to improve their properties or appearance. Baumgärtner and Raub [1] have recently reviewed the common electroplating baths for platinum and it is clear that there are still problems with the performance of many of the systems. In 1989, a Johnson Matthey patent [2] and a paper by Skinner [3] described a new bath which gave excellent performance and was suitable for the high rate deposition of thick layers of platinum. It was based on a solution of tetrammineplatinum (II), $Pt(NH_3)_4^{2+}$, in a low concentration, aqueous buffer with a pH in the range 10.0–10.6 and the recommended operating temperature range was 364–368 K. Indeed, it was reported that the current efficiency for platinum deposition improved from 10% to 60% when the temperature was increased from 361 to 363 K. A similar sudden jump in current efficiency has also been reported [1] for Pt-P-salt baths where the platinum source is cis-dinitrodiammineplatinum (II), $Pt(NH_3)_2(NO_2)_2$, although the critical temperature is 333 K. Such a strong dependence of current efficiency on temperature is unusual and the purpose of this work was to understand the factors contributing to these observations.

Platinum NMR uses the naturally occurring isotope, ^{195}Pt ($I = \frac{1}{2}$, natural abundance 33%), and is a powerful technique for confirming the structure of platinum species in aqueous solutions; the fundamentals and application of Pt NMR have been reviewed [4–6]. Potential sweep experiments were carried out at Pt microdisc electrodes. The properties and advantages of microelectrodes have also been widely reviewed [7–10]; in this programme, they were used because their response is relatively undistorted by the effects of *IR* drop and convection (the plating solution has a low ionic strength while convection will be significant as the boiling point of water is approached). It should be emphasized, however, that the current density at a microelectrode cannot be directly compared with that in the plating bath; because of spherical diffusion to the microelectrode, the mass transport coefficient at the microdiscs used in this work could be fifty times higher than that at a flat plate in a poorly stirred solution. On the other hand, the trends in the variation of the current density with bath conditions will be the same at both electrode geometries, especially for kinetically controlled electrode reactions.

2. Experimental details

The voltammetric studies were all carried out in a two electrode, single compartment cell. The 2.5 μm radius platinum microdisc electrode was prepared by sealing a 5 μm platinum diameter wire into glass and polishing the tip; between experiments, it was repolished with several grades of fine alumina on a polishing cloth. The counter/reference electrode was a Radiometer type K401 saturated calomel electrode. Periodically, the radius of the microdisc was checked by measuring the diffusion limited current for the oxidation of ferrocyanide; Equation 1 (below) was then used to estimate *r*, assuming a value for the diffusion coefficient of ferrocyanide of $6.3 \times 10^{-6} cm^2 s^{-1}$. The cell was immersed in a Memmert Model MO200 oil thermostat and the temperature of the experiment was checked with a thermometer within the cell. The solutions were degassed with a fast stream of nitrogen or saturated with oxygen and the gases were preheated by passing them through a copper coil, also immersed in the thermostat. The electroplating experiments were carried out in an open beaker; Pt/Ti gauze anodes were placed on either side of the 5 cm × 2.5 cm copper panels. The microelectrode experiments were performed with a HiTek type PPR1 function generator and a home built current amplifier and the response were recorded on a Gould series 60 000 *x–y* recorder. The constant current electrodepositions were controlled with a HiTek potentiostat model DT2101.

Platinum-195 NMR spectra were recorded at 77.3 MHz on a Bruker AM360 spectrometer, with shifts reported on the δ scale relative to an external solution of K_2PtCl_6 in H_2O/D_2O (10 : 1 v/v). Typically spectra were run in 10 mm outside diameter tubes and averaged over some 50 000 scans (a period of several

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Table 1. Data from ^{195}Pt spectra for the platinum plating solution. External reference compound K_2PtCl_6 (in 10 : 1 v/v H_2O/D_2O).

T/K	$-\delta$/p.p.m.	$\omega_{1/2}$/Hz
293	2576	1000
315	2568	920
333	2562	850
368	2552	800

hours) to improve the signal to noise ratio. The sweep width was 100 kHz, which allowed *ca.* 1000 p.p.m. to be studied at one time; on the other hand, the region of δ from -3500 to -500 p.p.m. was generally examined to check for other platinum resonances.

The solution used throughout this work was 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ in aqueous 28 mmol dm^{-3} Na_2HPO_4, pH 10–11 and it was used as supplied by Johnson Matthey. The only additions were of aqueous sodium hydroxide to modify the pH. The pH of solutions was checked and, if necessary, adjusted after the experimental temperature was reached.

3. Results

3.1. *Solution characterization*

Platinum-195 NMR spectra were recorded at 293 K for the platinum solution used for the electrochemical studies. Under normal conditions of spectral acquisition, a single, broad peak was observed at $\delta = -2576$ p.p.m., consistent with the literature value for $Pt(NH_3)_4^{2+}$ [6]. The peak is broad due both to unresolved coupling to ^{14}N and to the fast relaxation promoted by the quadrupolar nitrogen nuclei [5]. When the temperature of the solution was increased, even up to 368 K, the spectrum is almost unchanged although δ exhibited small high frequency shifts (see Table 1), the effects being reversible on cooling the solution. Hence, it must be concluded that in the temperature range 293–368 K, the platinum is present in solution as $Pt(NH_3)_4^{2+}$ and this is the only detectable platinum species. Confirmation that the solution is, indeed, the tetrammine was obtained by using a very long accumulation time and resolution enhancement techniques, when the characteristic coupling to ^{14}N was resolved, see Fig. 1. The coupling pattern is consistent with coupling to four equivalent ^{14}N nuclei ($I = 1$, 99.6%) which is expected to produce a nine line pattern with relative intensities 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1. The coupling constant, $^1J(^{195}Pt\text{-}^{14}N) = 200 \pm 6$ Hz, may be compared with the value estimated from that reported [11] in the ^{15}N labelled analogue, ie. $^1J(^{195}Pt\text{-}^{15}N) = 287$ Hz; using the ratio of the magnetogyric ratio $\gamma_N 14/\gamma_N 15$, the coupling constant is calculated as 204 Hz. Although the recording of such spectra involves prohibitively long accumulation times for routine studies, they do suggest that, when necessary, confirmation of the major species in solution may be obtained via the coupling patterns, without recourse to ^{15}N labelling.

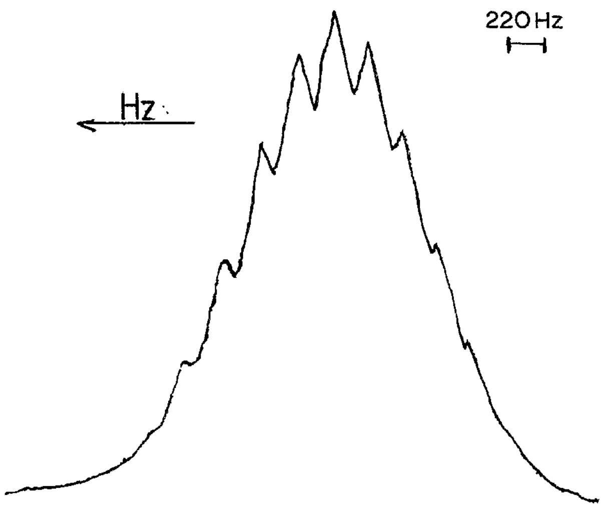

Fig. 1. High resolution $^{195}Pt\{^1H\}$ NMR spectrum of $Pt(NH_3)_4^{2+}$ at pH 7 in H_2O/D_2O at 300 K. Spectrum obtained at 77.3 MHz, 80 000 transients, relaxation delay of 1 s, exponential line broadening factor -1. The $^1J(^{195}Pt\text{-}^{14}N) = 200 \pm 6$ Hz.

3.2. *Electroplating experiments*

A series of copper panels (5 cm × 2.5 cm) were electroplated with platinum in the solution, 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5, at a series of temperatures. In line with electroplating practice, the solutions were not deoxygenated. The current density was 6.4 mA cm^{-2} and the current efficiencies, see Fig. 2, were determined by weighing the panel before and after the deposition. With the exception of the highest temperature, shiny and adherent deposits were obtained; at 372 K the deposit was grey and uneven but local boiling of the solution was clearly occurring. It can be seen that the influence of temperature reported by Skinner [3] is fully confirmed. The current efficiency for platinum deposition is only 12% at 363 K but rises very steeply to reach 74% at 366 K. Such a change in the dominant electrode reaction over such a narrow temperature range is most unusual although a similar result was

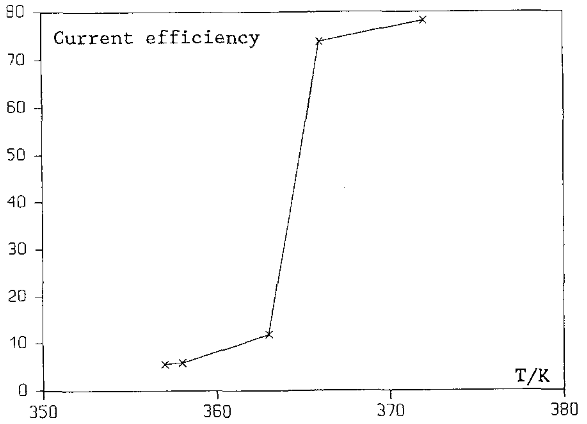

Fig. 2. The influence of temperature on the current efficiency for platinum deposition onto a 25 cm^2 copper panel from an air equilibrated, aqueous solution of 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5. Current density 6.4 mA cm^{-2} and plating time 900 s.

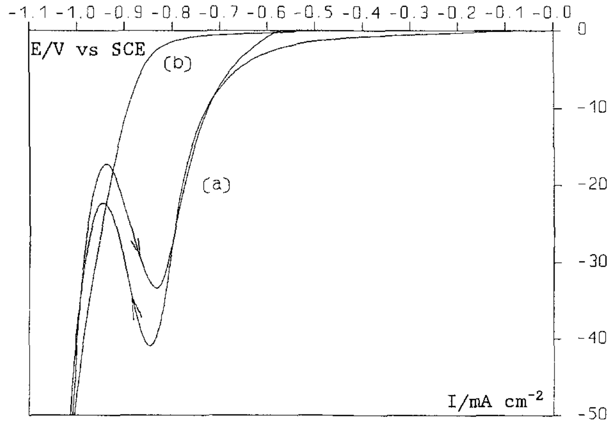

Fig. 3. *I–E* curves for deoxygenated 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 (a) with and (b) without the addition of 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$. 2.5 μm radius platinum microdisc electrode. Temperature 368 K. Potential scan rate 100 mV s^{-1}.

reported [1] for earlier platinum plating baths based on $Pt(NH_3)_2(NO_2)_2$.

3.3. *Microelectrode studies of platinum deposition*

Figure 3 shows a cyclic voltammogram recorded with platinum microdisc electrode (radius, $r = 2.5\,\mu m$) at 100 mV s^{-1} and at 368 K for a deoxygenated aqueous solution of 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5; also shown is the forward scan for the phosphate buffer without the addition of the platinum salt. The latter curve shows that H_2 evolution occurs negative to -0.85 Vs/SCE while in the presence of the Pt(II), a well formed reduction peak is observed. On the forward scan, the peak occurs at $E_p = -0.84$ V. The current density at this peak is, however, only 42 mA cm^{-2}, low compared to the diffusion limited current density for the reduction of all the Pt(II) in solution at this microelectrode (estimated from

$$I_D = 4nFDc/\pi r \qquad (1)$$

as 400 mA cm^{-2} at this temperature). The back scan also shows a very similar cathodic peak with $E_p = -0.82$ V. It should also be emphasised that the response differs from that expected for a simple electrode reaction at a microelectrode in another important respect; the reduction, Pt(II) $\longrightarrow$ Pt, would be expected to give an S-shaped wave, not a peaked response [7–10].

The potential sweep experiments were repeated at a series of temperatures and a typical set of responses are reported in Fig. 4. At 293 K, there is no reduction peak at -0.84 V; indeed, the only electrode reaction seen with this deoxygenated solution is hydrogen evolution. By 344 K, a small cathodic wave is discernable and, with further increase in the temperature, it transposes into the reduction peak which becomes rapidly larger. Figure 5 shows the variation of the peak current density with temperature, presented as a plot of log I_p against $1/T$. This Arrhenius plot is reasonably linear and the slope leads to an energy of activation of 78 kJ mol^{-1}, a high value. Also shown on this figure is the estimated diffusion controlled current density at each temperature. These have been calculated using Equation 1 and assuming values for the diffusion coefficient for $Pt(NH_3)_4^{2+}$ at 293 K (6×10^{-6} cm^2 s^{-1}) and an energy of activation for diffusion (8 kJ mol^{-1}). It is clearly confirmed that the reduction of platinum (II) in this solution is never diffusion controlled.

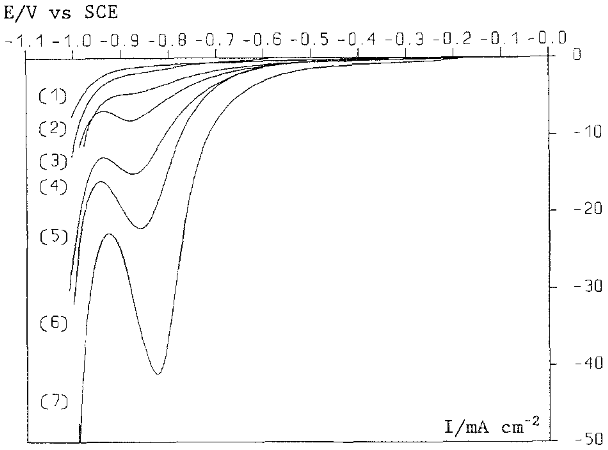

Fig. 4. *I–E* curves for deoxygenated 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 at a 2.5 μm radius platinum microdisc electrode. Potential scan rate 100 mV s^{-1}. Temperatures (1) 293 K (2) 330 K (3) 344 K (4) 352 K (5) 359 K (6) 364 K (7) 368 K.

The variation of the cathodic peak current density with temperature is, however, consistent with an electrode reaction where there is one or more chemical steps preceding the electron transfer step. Clearly, the electroactive species cannot be $Pt(NH_3)_4^{2+}$ itself and with such a metal complex, ligand substitution seems the most likely chemistry. In this platinum plating solution containing only phosphates, sodium ions and water in addition to the $Pt(NH_3)_4^{2+}$, there is little choice in possible chemistry. The most likely mechanism for platinum deposition is

$$Pt(NH_3)_4^{2+} + xH_2O \longrightarrow Pt(NH_3)_{4-x}(H_2O)_x^{2+} + xNH_3 \qquad (2)$$

$$Pt(NH_3)_{4-x}(H_2O)_x^{2+} + 2e^- \longrightarrow Pt + (4-x)NH_3 + xH_2O \qquad (3)$$

Certainly ammonia ligands on platinum (II) are not labile and their substitution is slow [12, 13]. In order to obtain evidence for the key role of Reaction 2, the potential sweep experiments were repeated in deuterium oxide. The *I–E* curves obtained were similar to those reported above but the peak at -0.84 V is, at each temperature, some 6 to 7 time smaller than when the experiments were carried out in H_2O (see Fig. 5). This primary isotope effect is to be expected if Reaction 2 determines the rate of platinum deposition. The *I–E* curves were also recorded for a series of pH in the range 9–11, (experiments were carried out at both 353 K and 366 K, either side of the temperature for the step in current efficiency for platinum plating) and although the Pt(II) reduction peaks shift positive as the pH is decreased, the peak current densities do not change.

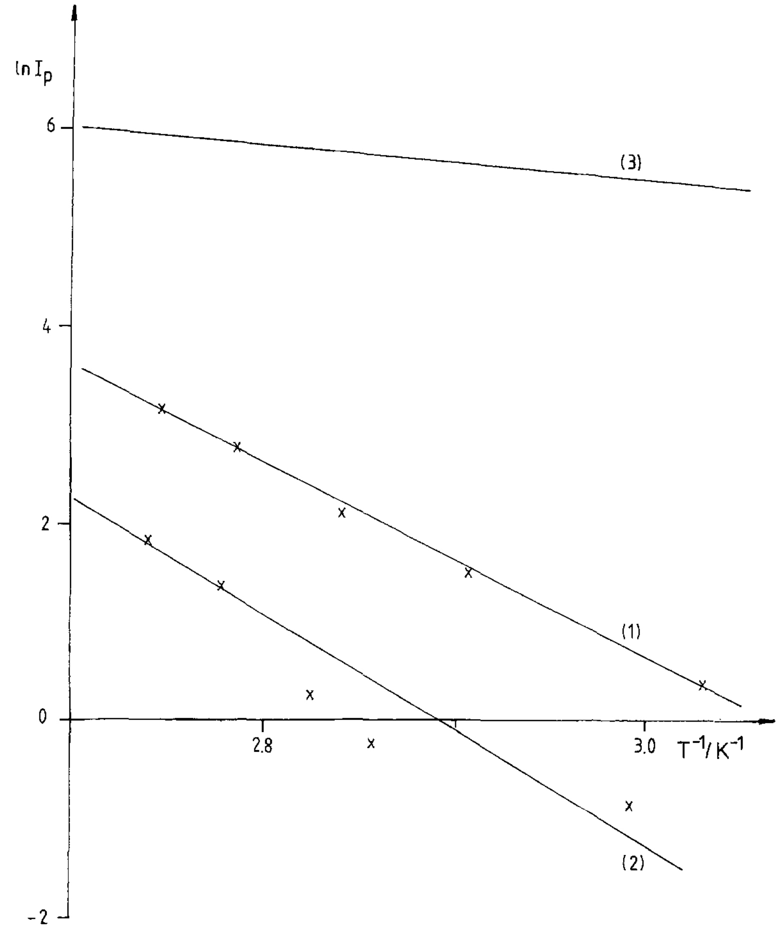

Fig. 5. Plots of log I_p against $1/T$ for (1) a solution of 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 in H_2O (2) a solution of 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 in H_2O and (3) a plot of log I_D against $1/T$ where I_D is the diffusion controlled current density for platinum deposition in the above solutions, estimated using Equation 1 and assuming $D = 6 \times 10^{-6}$ cm^2 s^{-1} at 293 K and an energy of activation for diffusion of 8 kJ mol^{-1}.

3.4. *Oxygen reduction in the plating solution*

Figure 6 shows linear potential scans for the platinum plating bath, recorded at 366 K, both saturated with oxygen and thoroughly deoxygenated. It can be seen that oxygen reduction gives a single, rather drawn out, reduction wave, $E_{1/2} = -0.33$ V on the platinum microdisc. The literature [14, 15] would indicate that, at Pt, the response consists of two overlapping reduction waves. In the plateau region, a $4e^-$ reduction takes place and this reaction is mass transport controlled. From the viewpoint of platinum electroplating, the important feature is that oxygen reduction occurs at a much less negative potential than platinum deposition and will, therefore, always be the preferred reaction. These experiments were repeated over a wide temperature range and Fig. 7 compares, as a function of temperature, the peak current density for platinum deposition with (i) the limiting current density for the reduction of an oxygen saturated solution and (ii) the limiting current density for the reduction of oxygen for a solution in equilibrium with air (estimated as 0.21 of the limiting current for the oxygen saturated solution). This comparison will be discussed further later in the paper but it should be noted that, in the case of oxygen, the limiting current density passes through a maximum close to 333 K. This arises because the diffusion coefficient for oxygen increases with temperature but its solubility decreases.

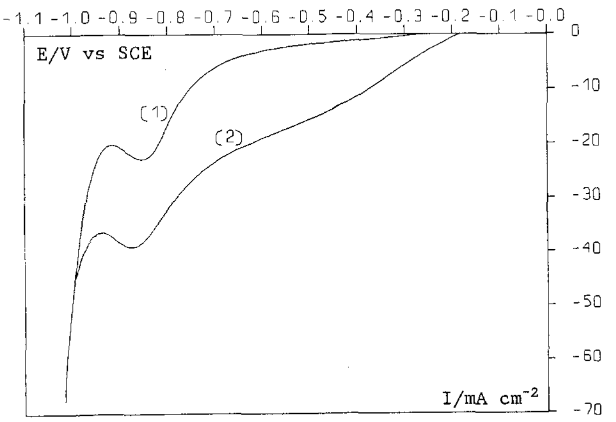

Fig. 6. I–E curves for (1) deoxygenated and (2) oxygen saturated 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 at a 2.5 μm radius platinum microdisc electrode. Potential scan rate 100 mV s^{-1}. Temperature 366 K.

4. Discussion

It was noted above that, at the higher temperatures, the deposition of platinum always leads to a cathodic peak despite the use of a microdisc electrode where the

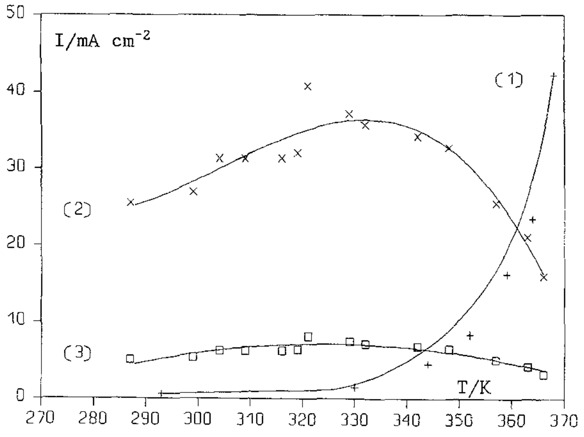

Fig. 7. Variation with temperature of (1) the peak current density for platinum deposition from 26 mmol dm^{-3} $Pt(NH_3)_4HPO_4$ + 28 mmol dm^{-3} Na_2HPO_4, pH 10.5 (2) the limiting current density for oxygen reduction in the oxygen in the oxygen saturated plating solution and (3) the estimated limiting current density for oxygen reduction in the air equilibriated plating bath. 2.5 μm radius platinum microdisc electrode. Potential scan rate 100 mV s^{-1}.

normal response for most electrode reactions is a wave (in fact, peaked curves are also obtained at a rotating disc electrode although the responses can be somewhat distorted by *IR* drop). The decrease in current density negative to the peak must result from inhibition of platinum deposition by some species adsorbed on the surface of the cathode in this potential range. The most probable species is the hydrogen atom; cyclic voltammograms, recorded at much higher sensitivity, for the platinum microdisc in the phosphate buffer without Pt(II) and oxygen show both adsorption and desorption peaks for hydrogen negative to −0.85 V and prior to hydrogen gas evolution. Moreover, the reversibility of the inhibition (*i.e.* the cathodic peak on the reverse scan) is also consistent with adsorbed hydrogen atoms as the inhibiting species. Such inhibition by adsorbed hydrogen has also been postulated in Pt–P–salt baths [1].

The source of platinum in an electroplating bath must have three key properties: (i) it must be stable, for example, to hydrolysis, (ii) the reaction $Pt(II) \longrightarrow Pt$ must occur readily, *i.e.* at potentials less negative than hydrogen evolution even on the freshly plated platinum surface, and (iii) the chemistry of the deposition reaction should not lead to an irreversible change in the composition of the bath. The first two requirements are, in some respects, not compatible. The stability is enhanced by strong interaction with ligands but complexation will also cause a negative shift in the reduction potential for $Pt(II) \longrightarrow Pt$. Hence, it is essential to select systems where the Pt(II) is complexed sufficiently but not too strongly. Moreover, the maximum rate deposition of the metal will be found when the rate of Pt(II) reduction is determined only by its mass transport to the electrode surface. In fact, in the system under study, there can be no doubt that the rate of a chemical step preceding electron transfer determines the rate of platinum deposition. The choice of such a system, however, may itself be a compromise since stability may arise from kinetic as well as thermodynamic factors. Hence, the chemical stability of the platinum plating bath may result from the inertness to substitution of $Pt(NH_3)_4^{2+}$ while the deposition of platinum depends on its conversion to a more readily reduced Pt(II) species (which might be less stable in solution). The nature of the preceding chemistry has been proposed above, see Equations 2 and 3. On the evidence available, it is not possible to ascertain x and, thus, the structure of the electroactive species. This is the target of further studies. Another objective of our programme is to define other PtL_4 complexes which are stable in solution but which undergo ligand substitution at a more rapid rate. This would allow faster platinum electroplating and/or the use of a lower and more user friendly temperature.

The results also suggest an explanation of the strong dependence of the current efficiency on temperature around 363 K. In general, it can be seen by comparison of curves (a) and (c) in Fig. 7 that for the plating bath in open contact with air, (i) at low temperatures, oxygen will by the predominant reaction, and (ii) above 333 K, the maximum current density for platinum deposition increases rapidly while oxygen reduction becomes less important. Platinum plating using a solution with a platinum (II) concentration of 5 g dm^{-3} (26 mmoles dm^{-3}) is always carried with a current density of a few mA cm^{-2}. As noted in the introduction, comparing such current densities with those at the microelectrode is difficult, particularly when the current densities show various degrees of mass transport control. Even so, it is clear that at temperatures below 350 K, the rate of platinum deposition will be insufficient and hydrogen evolution and oxygen reduction will consume most of the charge. Moreover, it is possible to envisage a higher temperature range where the change from mainly oxygen reduction to mainly platinum deposition is rapid. Deoxygenating the solution should therefore lead to a more gradual change in current efficiency with temperature.

Acknowledgement

The authors would like to thank Johnson Matthey Materials Technology Division for financial support and Mr P.E. Skinner for his advice and encouragement throughout the programme.

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