JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 18–26

Studies of platinum electroplating baths Part V: Solutions derived from $Pt(NO_2)_4^{2-}$ in aqueous acid

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Received 7 November 1996

When $Pt(NO_2)_4^{2-}$ is dissolved in methanesulphonic acid, it is shown that nitrite ions are displaced by water ligands and the extent of ligand substitution depends on temperature, length of the thermal treatment and the concentration of acid. Although the final nitrite ligand is difficult to displace, a solution containing $Pt(NO_2)(H_2O)_3^+$ as the dominant species may be formed, and this solution (Pt concentration $6\,g\,dm^{-3}$) provides the basis of a reasonable Pt plating bath. At a temperature of 343 K, good quality coatings can be obtained with current densities in the range $1–15\,mA\,cm^{-2}$ although the current efficiencies are low (10–15%) because reduction of the nitrite ion competes with Pt deposition on the freshly formed Pt surface.

1. Introduction

Platinum electroplating is usually carried out using baths based on P-salt [1, 2] or the more recent Q-salt [2–5]; these solutions are prepared from $Pt(NH_3)_2(NO_2)_2$ and $Pt(NH_3)_4^{2+}$, respectively, dissolved in an aqueous buffer, pH ~ 10. Such baths must be operated at low current density and elevated temperature in order to give an acceptable current efficiency and deposit properties, particularly if thick plates are required. These limitations led to the development of an alternative bath based on a solution of $Pt(H_2O)_4^{2+}$ in 1 M acid which allows a high rate of deposition at room temperature [6, 7]. The difficulty in the preparation of $Pt(H_2O)_4^{2+}$ was, however, recognized as a major drawback; on all scales, preparations based on the addition of a Ag(I) salt to $PtCl_4^{2-}$ [7–9] are both expensive and difficult to control.

This has led us to consider alternative preparations of $Pt(H_2O)_4^{2+}$. Any practical route must start from the metal or a commercially available platinum compound, with K_2PtCl_4 a highly preferred material. One possibility was considered to be

$$PtCl_4^{2-} \longrightarrow Pt(NO_2)_4^{2-} \longrightarrow Pt(H_2O)_4^{2+}$$

The first stage is straightforward [10, 11] and there is also evidence that the nitrite ligands may be displaced by water either by reaction of the nitrite with stoichiometric quantities of sulphamic acid [12, 13] or simply by heating a solution of the Pt(II) complex in aqueous acid [14–17]. Methanesulphonic acid was selected as the electrolyte because it is a relatively nontoxic and noncorrosive acid and already has some applications in the electroplating industry.

Products reported from the thermal treatment of solutions of $Pt(NO_2)_4^{2-}$ in aqueous acid include the blue nitrosyl-platinum(IV) complex $K[Pt(NO)_2)_4(NO)(H_2O)].H_2O$ [14] and the bridged dimers $K_2[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]$ [15], $K_2[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]$ [16] or $K_2[Pt_2(NO_2)_4(\mu\text{-}OH)_2]$ [17] as well as the complexes $[Pt(NO_2)_{4-x}(H_2O)_x]^{(2-x)-}$ [18]. This final paper [18] appeared after our experimental programme was complete and describes in some detail the chemistry of $K_2Pt(NO_2)_4$ in several aqueous acids (although not methanesulphonic acid). In heated aqueous $HClO_4$ and CF_3SO_3H, $[Pt(NO_2)_{4-x}(H_2O)_x]^{(2-x)-}$ complexes were the major products and ^{195}Pt NMR and ^{15}N NMR were used for the definitive determination of their identity.

Platinum P-bath contains nitrite complexes and an electroplating bath based on $K_2Pt(NO_2)_2(SO_4)$ in sulphuric acid has also been described [19]. Hence, it should be recognized that complete conversion of $Pt(NO_2)_4^{2-}$ to $Pt(H_2O)_4^{2+}$ may not be essential to the production of an acceptable electroplating bath. Therefore, the voltammetry of several solutions derived from $K_2Pt(NO_2)_4$ in aqueous methanesulphonic acid was defined. Some promising solutions were also selected for electroplating trials.

2. Experimental detail

In cyclic voltammetric experiments, platinum, copper, or vitreous carbon discs were used as working

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electrodes. In addition to the electrochemical instrumentation used, the cell design and procedures employed in the pre-treatment of these electrodes have been described previously [5, 9]. All the potentials quoted were measured relative to a Ag/AgCl reference electrode (Radiometer model K801). Each of the solutions studied was thoroughly degassed using oxygen free nitrogen (BOC Ltd). When the voltammetric studies required elevated temperatures, the cell was placed in a Grant W14 water bath with temperature controller.

Copper panels (area 6.25 cm^2) were treated prior to plating by firstly degreasing in acetone, and then cleaning in 1 M H_2SO_4 (5 min, with ultrasound). Finally, the panels were washed thoroughly with water and dried. The depositions were carried out with constant currents using a two electrode system in an undivided, beaker cell. Two Pt gauze electrodes were placed on each side of the Cu plates to act as anodes. Each solution was thoroughly degassed with nitrogen prior to electroplating. The Pt electroplates prepared for structural analysis were examined using a Jeol JSM 6400 analytical scanning electron microscope. ^{195}Pt NMR spectra were recorded using a Bruker AM360 spectrometer operating at 77.4 MHz ($PtCl_6^{2-}$ in H_2O was used as the external zero reference).

Samples of $K_2Pt(NO_2)_4$ were supplied by Johnson Matthey, while all of the other chemicals used were the purest grade available from Aldrich Chemicals. Solutions were prepared with water from a MilliQ–Millirho purification system.

The Pt electrolytes were prepared by dissolving 0.6 g of $K_2Pt(NO_2)_4$ (1.3 mmol Pt) in 50 ml of acid solution (room temperature). Prior to increasing the temperature, each system was degassed thoroughly using a fast stream of nitrogen. Nitrogen was passed over the surface of the solutions for the complete duration of the selected heat treatment.

Table 1. Chemical shifts in ppm from ^{195}Pt NMR spectra for Pt species relevant to this work

Platinum species	δ^*	*Reference*
$Pt(NO_2)_4^{2-}$	−2166	[13]
$Pt(NO_2)_3(H_2O)^-$	−1797	[13], [18]
cis-$Pt(NO_2)_2(H_2O)_2$	−1365	[13], [18], [20]
$Pt(NO_2)(H_2O)_3^+$	−829	[18]
$Pt(H_2O)_4^{2+}$	+30	[21], [22]
$[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]^{2-}$	−1756	[16]
$[Pt_2(\mu\text{-}SO_4)_4(NO_2)_2]^{4-}$	−1665	[16]

[*] The shifts are quoted against $PtCl_6^{2-}$.

3. Results and discussion

3.1. *Chemistry of $K_2Pt(NO_2)_4$ in aqueous methanesulphonic acid*

Samples of $K_2Pt(NO_2)_4$ were dissolved in CH_3SO_3H, and the solutions were heated under various conditions. During such experiments, strong colour changes were observed and, in general, these were similar to those reported by Appleton *et al.* [18]. The speciation of the Pt(II) was followed using ^{195}Pt NMR; data from the literature defining the ^{195}Pt NMR shifts for the Pt species liable to occur in these systems are reported in Table 1. In addition, voltammetry was used to monitor changes in the solution; particularly the presence of electroactive species derived from NO_2^- and Pt(II) species which may be reduced to Pt metal.

Figure 1(a) shows a typical voltammogram recorded at a small Pt disc electrode (area 0.10 cm^2) for a solution containing 42 mM KNO_2 in 1.5 M aqueous CH_3SO_3H at 343 K. Also shown is a comparable voltammogram, Fig. 1(b) for the acid solution in the absence of nitrite. In the presence of nitrite there is a well formed reduction peak at +0.45 V vs Ag/AgCl, and an oxidation peak at +0.96 V. By restricting the potential limits, it may be confirmed that these peaks are not coupled, and both peaks result from direct

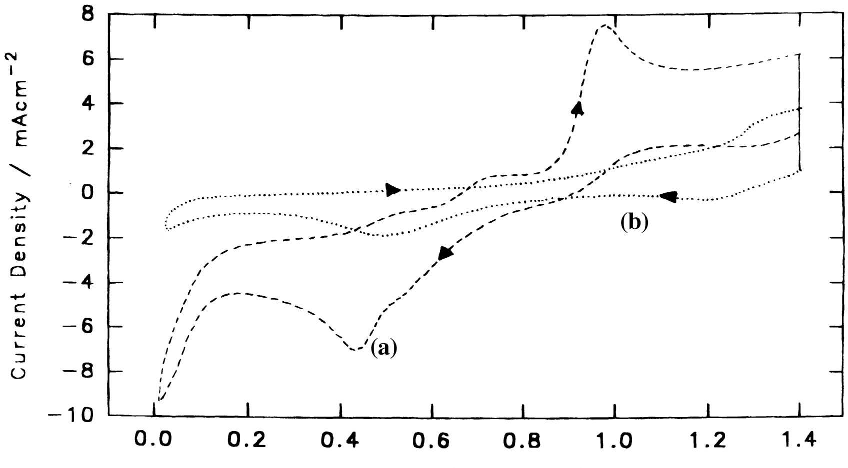

Fig. 1. Cyclic voltammogram for a solution of 1.5 M CH_3SO_3H (a) with and (b) without 42 mM KNO_2. Polished Pt disc electrode (area 0.10 cm^2). Temperature 343 K. Potential scan rate 80 mV s^{-1}.

electrode reactions of a species in solution. Moreover, both the anodic and cathodic peak current densities are proportional to the square root of the potential scan rate, indicating that the reactions become mass transport controlled beyond the peaks. The peak current densities are ~7 $mA\,cm^{-2}$ which demonstrates that, although it is unclear whether it is nitrite itself which may be oxidised and reduced, most of the NO_2^- is present as the electroactive species. On analysis of the voltammogram for nitrite, the cathodic peak appears to show a prewave, but comparison with the voltammogram for 1.5 M CH_3SO_3H illustrates that this is, in fact, a surface oxide reduction peak. The potentials of the anodic and cathodic NO_2^- peaks vary with the electrode material (carbon, platinum, and freshly plated platinum), as well as the temperature and the concentration of CH_3SO_3H. It should also be recognized that nitrite is not completely stable in the medium, and as a result, the size of the voltammetric peaks decrease with time. The rate of decrease is accelerated by heating and/or by purging the solution with nitrogen or argon. The chemistry of nitrite in these acid media is complex, but its further investigation is not essential to the objectives of this study. The observation of a reduction peak(s) in the range +0.60 to +0.40 V vs Ag/AgCl in voltammograms for solutions containing $K_2Pt(NO_2)_4$ is a clear indication that unbound NO_2^- has been formed from the Pt(II) complex. The magnitude of the cathodic peak also allows a facile estimate of the concentration of free nitrite. Peaks resulting from the reduction of Pt(II) were identified by holding the potential of a carbon disc electrode negative to the peak, and observing the formation of a Pt coating; experience showed that such peaks occurred negative to ~0.0 V vs Ag/AgCl (see later).

When a solution of 30 mM $K_2Pt(NO_2)_4$ is prepared in 1.5 M CH_3SO_3H at room temperature, there is no visible evidence for chemical reaction. No gas is evolved, and the solution remains colourless for a period of several days. In contrast, voltammetric results at a polished Pt disc electrode reveals that a small amount of free nitrite (< 1 mM) has been formed. No cathodic peaks were observed for the reaction Pt(II) → Pt(0), even when a slow potential sweep rate is used to scan into the potential region for hydrogen evolution. When this solution was examined using ^{195}Pt NMR, it was shown to contain largely $Pt(NO_2)_4^{2-}$ along with some $Pt(NO_2)_3(H_2O)^-$. On heating to 343 K, this solution became slightly blue in colour (see below), and cyclic voltammograms recorded within 5 min showed a significantly increased peak for nitrite reduction, Fig. 2(a). However, when the negative potential limit is extended to –0.25 V, there is a poorly defined cathodic peak visible at a potential slightly positive to hydrogen evolution, Fig. 2(b). The reverse scan shows a nucleation loop at about −0.1 V vs Ag/AgCl, providing convincing evidence that the cathodic current corresponds to Pt deposition. On heating the solution at 343 K for a period of several hours, the cathodic peak for the reduction of uncomplexed nitrite becomes substantially smaller, while the peak corresponding to Pt deposition shifts to slightly more positive potentials. Thereafter, on heating the solution to 343 K for up to 10 days, no further changes occur to the appearance or voltammetry of the solution.

The voltammetry of the solution containing 10 mM $K_2Pt(NO_2)_4$ in 1.5 M aqueous CH_3SO_3H was also studied at a vitreous carbon electrode, and a similar series of general trends was observed. Figure 3 shows two voltammograms recorded immediately after increasing the temperature to 323 K. On the first scan to negative potentials, with a freshly polished electrode, see Fig. 3(a), no reduction peak is observed positive to hydrogen evolution which occurs at −0.28 V vs Ag/AgCl. On the reverse scan, however, cathodic current is observed at all negative potentials, and there is a reduction wave, $E_{1/2} \approx -0.1$ V. A second forward scan recorded without cleaning the carbon disc shows a well formed cathodic peak at −0.15 V, see Fig. 3(b). Such voltammetry is typical of a cathodic reaction which involves the nucleation of a new phase on the electrode surface. Hence, it can be concluded that this peak is due to the reaction Pt(II) → Pt, but even with a slow scan rate of 10 $mV\,s^{-1}$, it is necessary to take the potential well into the region of hydrogen evolution to initiate nucleation of metallic platinum on the carbon surface. The deposition of platinum was confirmed by observing a shiny metallic layer on the carbon surface when the potential was held negative to −0.10 V. Pt deposition certainly occurred more readily at elevated temperatures. In fact, even at room temperature prior to heating the solution, it was found that Pt could be deposited on the carbon surface, but deposition was very slow, even when the potential of the carbon disc was held as negative as −0.40 V for several minutes.

The current densities for the cathodic peaks associated with Pt deposition are in fact rather large when compared to the expected diffusion controlled current density for all the Pt(II) in solution, i.e. 43 $mA\,cm^{-2}$ for 26 mM Pt(II) on Pt at 343 K (Fig. 2(b)), and 13 $mA\,cm^{-2}$ for 10 mM Pt(II) on carbon at 323 K (Fig. 3(b)). This suggests that another reaction competes with Pt deposition on the freshly formed Pt surface (again see below). It may also be concluded that even a short period of gentle heating is sufficient to create conditions where Pt deposition occurs more readily. Since there is no Pt deposition peak visible at room temperature, it seems that $Pt(NO_2)_4^{2-}$ itself is not electroactive at potentials more positive to hydrogen evolution, and some substitution of NO_2^- or chemical change to the Pt complex is essential in order to produce a species which is electroactive within the potential range for voltammetry. This situation is familiar in Pt electroplating systems [4, 9]. Also it is just possible that the need for the slightly elevated temperatures arises from very slow kinetics of formation of Pt nuclei to initiate the formation of the coating. This, however, is unlikely.

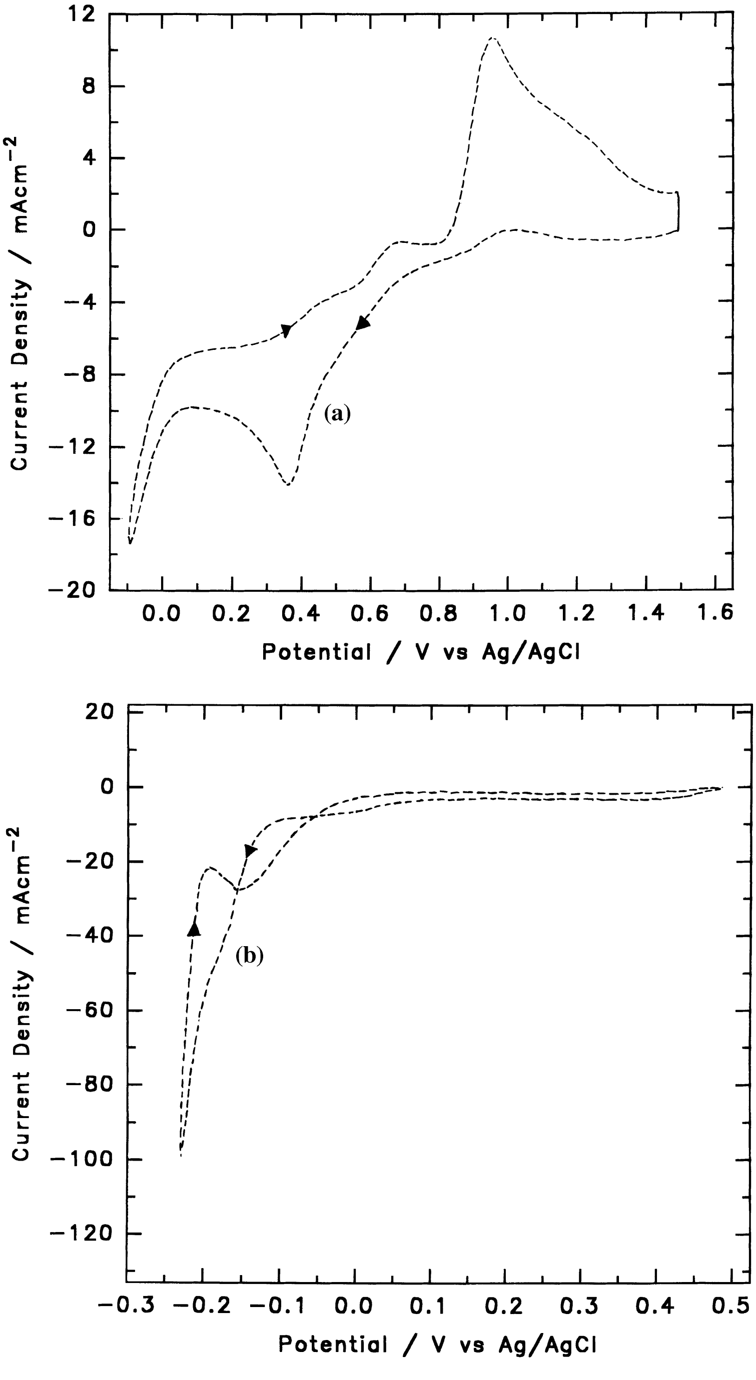

Fig. 2. Cyclic voltammograms for a freshly prepared solution of 30 mM $Pt(NO_2)_4^{2-}$ in 1.5 M CH_3SO_3H after a few minutes at 343 K. Pt disc electrode (area 0.10 cm^2). The negative potential limits are (a) 0.00 V and (b) −0.25 V vs Ag/AgCl. Potential scan rate 80 mV s^{-1} for (a) and 20 mV s^{-1} for (b).

When a solution of 30 mM $K_2Pt(NO_2)_4$ in 1.5 M aqueous CH_3SO_3H is heated at 363 K, the evidence for rapid chemical change is compelling. Over a period of several days, the solution undergoes a series of colour changes. Initially the solution is colourless, however, within several minutes it appears blue. This may be due to the presence of the $K_2[Pt(NO_2)_4(NO)(H_2O)].H_2O$ complex [14], although the formation of blue solutions from nitrite alone has also been reported [23]. With further heating, the solution changes colour sequentially; within several hours it becomes green, and then yellow, while after a few days, the solution darkens to orange, then brown, and finally a fine brown precipitate is created.

The rate of all these colour changes can be accelerated by using more concentrated methanesulphonic acid (7.5 M), or by purging the solution with a stream of gas, either air, O_2, N_2 or Ar (no clear trend with the gas used was noted). It is clear that similar colour changes, and the formation of brown precipitate are observed in other acids, including perchloric, sulphuric and phosphoric acids (each 1.5 M). Analysis of the brown precipitate formed in 1.5 M CH_3SO_3H showed the absence of both sulphur and nitrogen. As it was also insoluble in aqueous acids and bases, it was postulated that the precipitate was a hydrated Pt(IV) oxide. Although the timescale of the final colour changes and the formation of the brown precip-

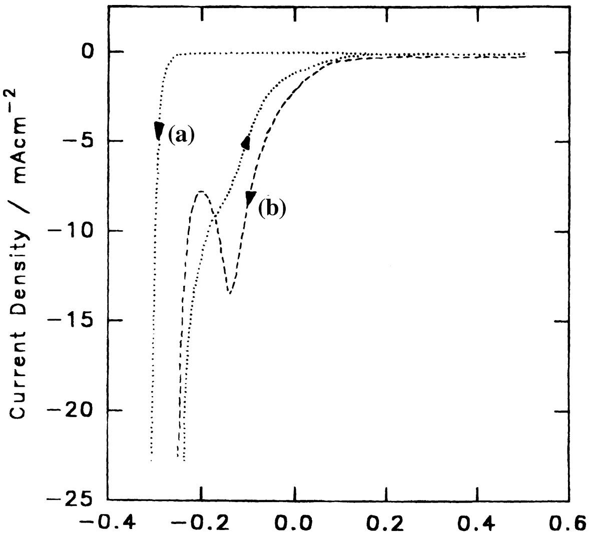

Fig. 3. Cyclic voltammograms for a freshly prepared solution of 10 mM $Pt(NO_2)_4^{2-}$ in 1.5 M CH_3SO_3H after a few minutes at 323 K. Vitreous carbon disc electrode (area 0.08 cm^2). The voltammograms labelled (a) and (b) are for the first and second scans at a polished electrode. Potential scan rate 10 mV s^{-1}.

itate is not reproducible, it is relatively simple to produce the intermediate yellow solution by heating to 363 K for 8–10 h. Once cooled to a significantly lower temperature this solution appears stable; for example, at 333 K it appears stable indefinitely. Data from ^{195}Pt NMR of the solution while heating to 363 K are reported in Table 2. On comparison of this data with chemical shifts from the literature (Table 1), the ^{195}Pt NMR peaks have been assigned as shown in Table 2. The data are compatible with the stepwise replacement of coordinated nitrite by water with time, that is,

$$Pt(NO_2)_4^{2-} \longrightarrow Pt(NO_2)_3(H_2O)^- \longrightarrow Pt(NO_2)_2(H_2O)_2 \longrightarrow Pt(NO_2)(H_2O)_3^+ \longrightarrow Pt(H_2O)_4^{2+}$$

Although it cannot be demonstrated that the observed species account for all the Pt in solution, no other peaks are present in the range +200 to −2500 ppm, confirming the absence of, for example, oxygen bridged dimeric complexes [15–17]. Several similar experiments were monitored by ^{195}Pt NMR and the same pattern of changes, that is, the stepwise substitution of nitrite ligands by water, was always found. On the other hand, the rate of these changes was less reproducible. For example, the initial solution used in the experiment described in Table 2 already shows the absence of $Pt(NO_2)_4^{2-}$, and in contrast, $Pt(NO_2)_3(H_2O)^-$ and $Pt(NO_2)_2(H_2O)_2$ are the major species. However, other solutions nominally prepared in a similar manner still contained $Pt(NO_2)_4^{2-}$ as the dominant species. It is unclear whether such differences arise from either insufficient control of the procedure for the preparation of the solutions, or storage of the solution prior to recording the ^{195}Pt NMR. However, after heating to 363–378 K for up to 24 h, the solutions always contain a mixture of $Pt(NO_2)(H_2O)_3^+$ and $Pt(H_2O)_4^{2+}$. After considering this data, it was predicted that further heating of the solution would lead to the complete conversion to $Pt(H_2O)_4^{2+}$. This proved not to be the case. Initially, with further heating, the composition of the solution remained constant but eventually the solution darkened and there was a loss in ^{195}Pt NMR signal. Finally, a brown precipitate appeared.

Table 2. Data from ^{195}Pt NMR spectra for a solution of 30 mM $K_2Pt(NO_2)_4$ in 1.5 M aqueous CH_3SO_3H is heated at 363 K (solutions were stored at 273 K for considerable periods before the spectra could be recorded)

Time at 363 K/h^{-1}	*δ from ^{195}NMR**	*Pt species in solution*
0	−1809 (60)	$Pt(NO_2)_3(H_2O)^-$
	−1380 (40)	*cis*-$Pt(NO_2)_2(H_2O)_2$
8	−1375 (45)	*cis*-$Pt(NO_2)_2(H_2O)_2$
	−846 (55)	$Pt(NO_2)(H_2O)_3^+$
24	−850 (66)	$Pt(NO_2)(H_2O)_3^+$
	+38 (33)	$Pt(H_2O)_4^{2+}$

*The shifts are quoted against $PtCl_6^{2-}$ and the numbers in brackets indicate the approximate ratio of the integrals of the signals. Note that the reference data in Table 1 refers to slightly different media and small differences in chemical shift are to be expected.

It can be concluded that, in these very acid solutions, the driving force for the stepwise substitution of the nitrite ligand is the thermal decomposition of the unbound nitrite. It also appears that the substitution of nitrite becomes more difficult for $Pt(NO_2)_{4-x}(H_2O)_x^{(2-x)-}$ as x increases, and $Pt(NO_2)(H_2O)_3^+$ strongly resists substitution of the nitrite ligand. The chemistry leading to the formation of the brown deposit was investigated further. A solution of $Pt(H_2O)_4^{2+}$ in 1 M CH_3SO_3H was heated to 363 K for several days, and it appeared to be stable; certainly a brown precipitate was never formed. Hence, it can be concluded that NO_2^- has a crucial role in the formation of the precipitate, perhaps acting as an oxidising agent for the conversion of Pt(II) to Pt(IV). In attempting to complete the conversion of $Pt(NO_2)(H_2O)_3^+$ to $Pt(H_2O)_4^{2+}$, alternative methods of heat treatment were considered, for example, heating to 343 K for 10 days, but these were unsuccessful. Likewise, the addition of sulphamic acid to react chemically with the uncoordinated nitrite ligand [13] was also unsuccessful. Although sulphamic acid reacted rapidly with free nitrite in 1.5 M CH_3SO_3H it did not react with $Pt(NO_2)(H_2O)_3^+$. There was also evidence from both voltammetry and ^{195}Pt NMR that sulphamic acid acted as a ligand for Pt(II), and prevented its reduction prior to hydrogen evolution. ^{195}Pt NMR suggested that the sulphamate displaced water ligands rather than substituting the coordinated nitrite groups.

3.2. *Electroplating from the heat treated solution*

Solutions containing $Pt(NO_2)(H_2O)_3^+$ as the dominant species were prepared by heating solutions of $Pt(NO_2)_4^{2-}$ (20–30 mM or 4–6 g dm^{-3} of Pt) in 1.5 M

CH_3SO_3H for a period of 10 h at 373 K. Preliminary electroplating experiments were carried out using both vitreous carbon and copper discs (areas ~0.1 cm^2) as working electrodes. With a vitreous carbon disc, adherent and highly reflecting Pt coatings can be obtained at room temperature either by applying a constant potential, −0.20 V vs Ag/AgCl, or a constant current density in the range 1–5 mA cm^{-2}. Copper has the tendency to corrode on open circuit in 1.5 M CH_3SO_3H, and therefore a controlled potential or current has to be imposed before the copper disc can be placed in solution. Deposits can be formed at room temperature by applying a potential of −0.20 V or a constant current density in the range 1–5 mA cm^{-2} but although they are adherent, they are not highly reflecting. Rather, the coatings are shiny and dark grey in appearance. The quality of the coatings on copper can be improved markedly by increasing the temperature to 318 K; the electroplates at this temperature are a lighter grey colour and are more reflecting. They remain very adherent and require forceful mechanical treatment to remove them.

The experiments were extended to Cu panels with an area of 6.25 cm^2. The increase in the weight of the Cu panel was used to estimate the current efficiency for Pt deposition and also the average thickness of the coating (assuming the density of the Pt layers were 21.45 g cm^{-3}). Table 3 summarizes data from a series of electrodepositions carried out at 343 K. All the deposits appear shiny and adherent but a feature of the data is the low current efficiencies which is effectively independent of the current density; it must be concluded that there is a competing electrode reaction and the importance of this reaction is independent of current density. This implies that the rate of the competing reaction in some way reflects the rate of Pt deposition and is also not a function of potential. This would not be the case, for example, if the competing reaction was hydrogen evolution. Moreover, the gas evolution seen was minor compared to that expected to account for the charge not associated with Pt deposition. The reduction of the nitrite ligand parallel to the reaction Pt(II) → Pt would be compatible with the data. The reduction of nitrite to ammonium ion is a $6e^-$ process, and the overall cathodic reaction would then be

Table 3. Electrodeposition of Pt onto Cu panels from the solution prepared by heating $Pt(NO_2)_4^{2-}$ (24 mM or 5 g dm^{-3} of Pt) in 1.5 M CH_3SO_3H at 373 K for 10 h. Temperature 343 K

Current density /mA cm^{-2}	*Deposition time* /s	*Current efficiency* /%	*Deposit thickness* /μm
2.5	3600	15	0.6
	32 900	15	5.6
5	1800	14	0.6
	3600	15	1.3
10	1800	13	1.1
	3600	12	1.9
20	1200	15	1.7

$$Pt(NO_2)(H_2O)_3^+ + 8\ H^+ + 8\ e^- \rightarrow Pt + NH_4^+ + 5\ H_2O$$

In these circumstances, the maximum current efficiency for Pt deposition would be 25%. The presence of additional nitrite ligands or unbound nitrite would reduce the current efficiency further.

Further evidence for the parallel reduction of the nitrite ligand came from the observations that the current efficiency for Pt deposition was almost independent of:

(a) the temperature. Current efficiencies were 13% and 11% at 313 K and room temperature respectively;

(b) the concentration of the CH_3SO_3H. For example, in 0.1 M CH_3SO_3H and at 343 K, the current efficiencies were all in the range 12–15% for current densities between 2.5 mA cm^{-2} and 20 mA cm^{-2}.

(c) the concentration of Pt(II) at least over the range 2–6 g $dm^{-3}$of Pt.

It should also be emphasised that with this bath, good quality Pt deposits could be electroplated at temperatures as low as 313 K.

Scanning electron microscopy (SEM) of the deposits onto the Cu panels (see Fig. 4), show that the Pt layers are uniform except for some small pinholes, and on a higher magnification, some hemispherical structures can be observed. The 2 μm thick deposit show some cracks, revealing stress within the deposits.

3.3. *Electrochemistry of the heat treated solution*

Figure 5 reports cyclic voltammograms recorded with a Pt disc electrode at four temperatures. The solution contained mainly $Pt(NO_2)(H_2O)_3^+$ and was prepared by heating $Pt(NO_2)_4^{2-}$ (24 mM) in 1.5 M CH_3SO_3H at 373 K for 10 h. At all temperatures, only small cathodic currents are observed at positive potentials (hence the concentration of unbound nitrite is low), but significant differences can be noted in the potential range just prior to hydrogen evolution where the reaction Pt(II) → Pt is to be expected. At room temperature, Fig. 5(a), it can be seen that the reduction of Pt(II) appears only as a wave merging with hydrogen evolution. At 319 K, Fig. 5(b), a well formed cathodic peak is observed at −0.17 V vs Ag/AgCl, and with further increase in temperature, there is a continued positive shift in the peak; at 344 K, Fig. 5(c), the peak potential is −0.07 V. It is also clear that, by this temperature, peak broadening is occurring and these trends continue to 364 K, Fig. 5(d). The reduction peak is seen at −0.03 V and the response can easily be deconvoluted into two processes, the first commencing positive to +0.10 V. At elevated temperatures, therefore, there is clear evidence for two reducible species in equilibrium, and these may be $Pt(NO_2)(H_2O)_3^+$ and $Pt(H_2O)_4^{2+}$. The positive shift in the peak potential for the Pt(II) → Pt reaction which accompanies an increase in temperature demonstrates a role for kinetics when determining the voltammetric

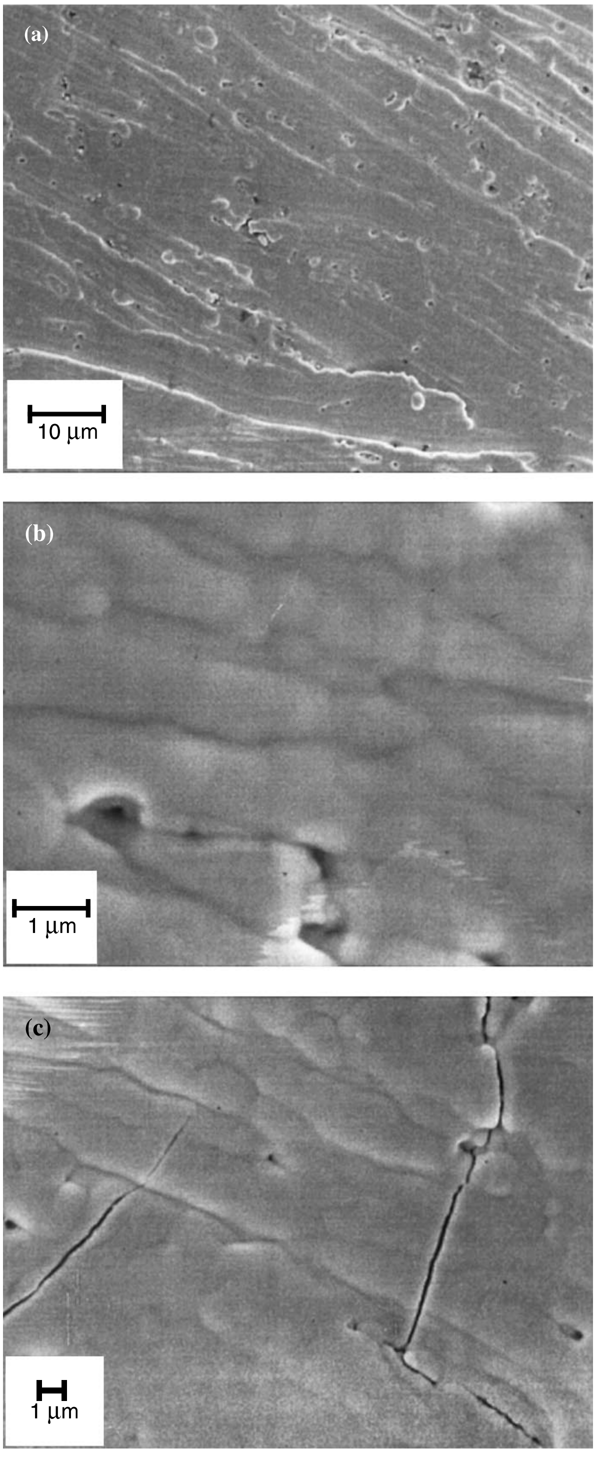

Fig. 4. Scanning electron micrographs of Pt deposits on Cu panels. The bath was prepared by heating $Pt(NO_2)_4^{2-}$ (24 mM or 5 g dm^{-3} of Pt) in 1.5 M CH_3SO_3H at 373 K for 10 h. Bath temperature 343 K. Current density 5 mA cm^{-2}. Plating times (a) and (b) 1800 s and (c) 3600 s.

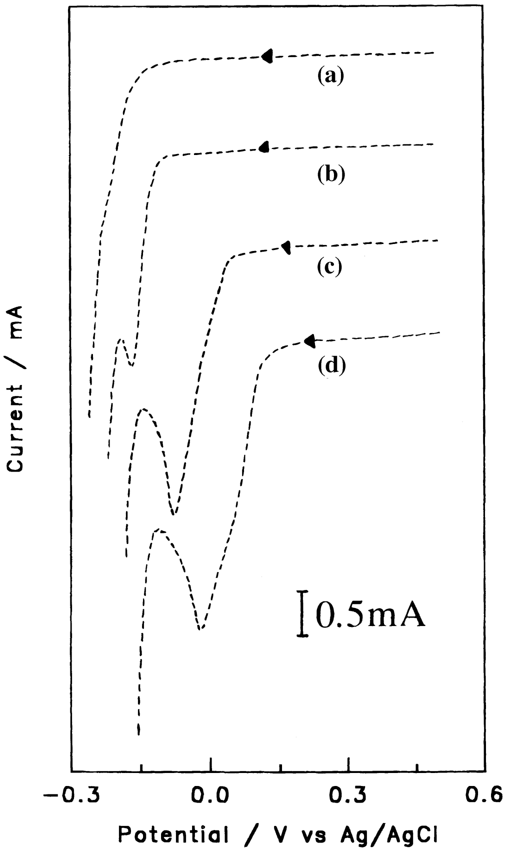

Fig. 5. Linear potential sweep voltammograms for a solution prepared by heating 24 mM $Pt(NO_2)_4^{2-}$ in 1.5 M CH_3SO_3H at 373 K for 10 h and containing $Pt(NO_2)(H_2O)_3^+$ as the major Pt(II) species at (a) room temperature (b) 319 K (c) 344 K and (d) 364 K. Pt disc electrode (area 0.10 cm^2). Potential scan rate 20 m V s^{-1}.

responses but it cannot be ascertained whether the slow step is a chemical step or the electron transfer process.

At all temperatures, peak current densities are proportional to the square root of the potential scan rate. It should also be noted that the increase in peak current density when raising the temperature from 319 to 364 K is only ~25%, a change which may be accounted for only by the expected change in diffusion coefficient for the species in solution. On the other hand, the peak current densities all appear large for the amount of Pt(II) in solution; for example, the peak current density for a 24 mM Pt(II) solution, a potential scan rate of 20 mV s^{-1} and at 319 K is 23.5 mA cm^{-2}. This, together with the consistently low current efficiency for plating from this solution, led to a further investigation of the electroactivity of nitrite. Figure 6 compares voltammograms at 343 K for the Pt electroplating solution before and after the addition of an equimolar amount of nitrite. Accompanying the addition of nitrite, colour change from yellow to green is observed and, once again, reduction waves could be seen at about +0.40 V. More importantly, it leads to a substantial enhancement of the peak current density for the process associated with Pt deposition (from 40 to 53 mA cm^{-2}).

Figure 7 reports another interesting experiment; Fig. 7(a) illustrates a voltammogram from 70 mM NO_2^- in 1.5 M CH_3SO_3H at 345 K using a polished Pt disc, while Fig. 7(b) presents the voltammogram for the same solution but with a Pt disc electrode which was freshly coated with a further layer of electroplated Pt. It can be seen that while the peaks at more positive potentials are similar, the electroplated layer causes the peak at 0.0 V vs Ag/AgCl to increase in height and also to shift to more positive potentials. We believe that this peak corresponds to the direct reduction of

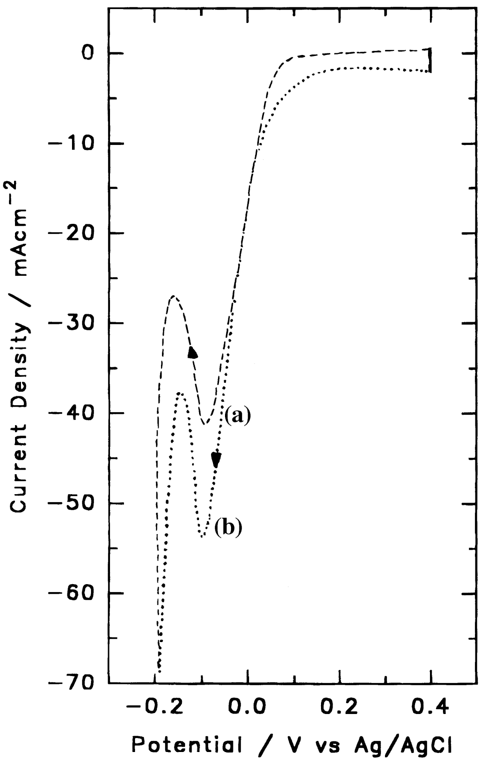

Fig. 6. Linear potential sweep voltammograms for a solution prepared by heating 24 mM $Pt(NO_2)_4^{2-}$ in 1.5 M CH_3SO_3H at 373 K for 10 h and containing $Pt(NO_2)(H_2O)_3^+$ as the major Pt(II) species (a) before and (b) after the addition of 24 mM KNO_2. Temperature 343 K. Pt disc electrode (area 0.10 cm^2). Potential scan rate 20 mV s^{-1}.

nitrite (the peaks at more positive potentials are thought to arise from species formed from the reactions of nitrite and strong acid) and, if this is correct, clearly the clean surface of the electroplated layer is a superior catalyst for nitrite reduction. It appears from the voltammogram for nitrite reduction on the freshly plated Pt that the reduction potential for nitrite in these conditions is positive to those where Pt deposition occurs. Therefore, during the electrodeposition of Pt onto another substrate such as vitreous carbon, the extent of nitrite reduction will reflect the coverage of the carbon by platinum and, as in fact observed, nitrite reduction will have the effect of increasing the current density for the Pt deposition peak.

4. Conclusions

Although it proved impossible to prepare a solution of $Pt(H_2O)_4^{2+}$ by thermal treatment of $Pt(NO_2)_4^{2-}$ in 1.5 M CH_3SO_3H, it is possible to create an electroplating bath where the major Pt(II) species is $Pt(NO_2)(H_2O)_3^+$. Pt coatings may be electroplated at room temperature; adhesive and reflective deposits may be formed at very moderate temperatures, around 318 K, compared to both P-bath and Q-bath which must be operated at >363 K [1–5]. It has, however, been shown that the current efficiency for Pt deposition is always $< 15\%$ and this results from the catalytic reduction of NO_2^- on the freshly plated Pt surface. Even so, this solution has some attractive properties as a Pt electroplating bath which will be investigated further.

Acknowledgement

The authors would like to thank Johnson Matthey Materials Technology Division for financial support of this programme and permission to publish this paper.

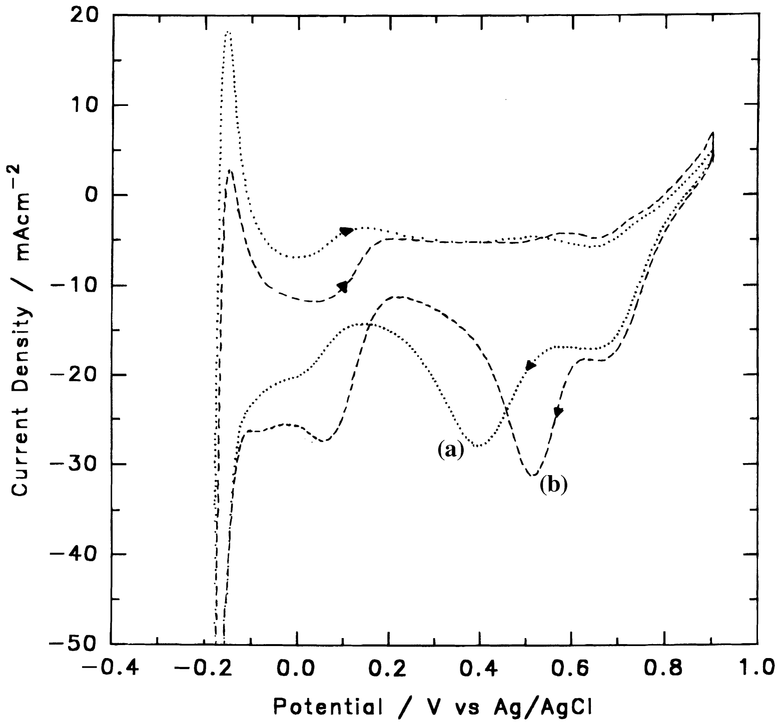

Fig. 7. Cyclic voltammogram for a solution of 70 mM KNO_2 in 1.5 M CH_3SO_3H at (a) a polished Pt disc electrode (area 0.10 cm^2) (b) a freshly plated Pt coating on a polished Pt disc electrode (area 0.10 cm^2). Temperature 345 K. Potential scan rate 80 mV s^{-1}.

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