Malaysian Journal of Science **21A**: 191-196 (2002)

Electrochemical and SEM studies of tetra-ammine platinum (II) $[Pt(NH_3)_4](OH)_2$ solution

Wan Jeffrey Basirun

Department of Chemistry, University Malaya, Kuala Lumpur 50603, Malaysia.

ABSTRACT Electrochemical studies include cyclic voltammetry with microelectrodes were done on a solution of tetra-ammine platinum (II) $[Pt(NH_3)_4](OH)_2$ at pH 13 and showed that the electrochemical reduction of this compound was no different from the tetra-ammine platinum (II) $[Pt(NH_3)_4](HPO_4)$ at pH 10.4. The solution was instable to high temperatures and results have shown that electroplating can be done at a limited temperature range for longer periods of time or at higher temperatures for short periods of time. Scanning Electron Microscopy was done on some of the constant current electrodeposited samples at high temperatures and result obtained was satisfactory.

(Voltammetry, Microelectrodes, Tetra-ammine platinum II, Electroplating, SEM)

INTRODUCTION

More recently, Johnson Matthey PLC UK, has introduced a new electroplating bath, the Pt 5Q bath, or tetra-ammine platinum (II) in a phosphate buffer at pH 10.0 -10.4, 25.6 x 10^{-3} M $[Pt(NH_3)_4]HPO_4$, (or 5 g l^{-1} of platinum). The bath gives high quality deposits but must be operated at an inconveniently high temperature of around 368 K [2].

A new solution of tetra-aquo platinum (II) complex $[Pt(H_2O)_4](ClO_4)_2$ in 1 M perchloric acid $HClO_4$ with pH 0 showed mass transport controlled deposition even at room temperatures. But because this solution is corrosive to most metals, electroplating can only be done on substrate metals that are able to withstand high concentrations of acids. Nevertheless at intermediate current densities like 50 A m^{-2} electroplating was successful from a macroscopic view, but SEM micrographs revealed that there are some imperfections at the microscopic level [3].

EXPERIMENTAL

Instruments

The potentiostat and waveform generator are both Hi-Tek Models, DT 2101 and the PPR1 models respectively. In the microelectrode experiments, only the function generator was used and the currents were amplified. Current voltage curves were displayed on a X-Y recorder (Gould 6000 series or Yokogawa 3022, A4X-Y model). The oil bath used in the temperature variation experiments was manufactured by Memmert, model M0200. Liquid paraffin was used as the oil. All potentials were quoted versus a reference electrode, which was Ag /AgCl, in saturated KCl from Radiometer, model K801, which has a reference potential of +0.204 V with respect to the Standard Hydrogen Electrode at 293 K. The Ag /AgCl reference electrode was preferred to, for example, the SCE (Hg / HgCl), because it has better tolerence towards temperature variation.

Platinum NMR

Nuclear Magnetic Resonance spectra of the ^{195}Pt isotope were recorded on a Bruker Am 360 spectrometer at 77.4 MHz using a 10 mm borosillicate glass tube. An aqueous solution of $[PtCl_6]^{2-}$ anion was used as the reference compound [4].

With the advantages of Fourier Transform (FT) NMR spectroscopy in the early 1970s, measurement for ^{13}C as well as ^{195}Pt nuclei were possible. Several hours of accumulation is needed to produce an acceptable signal to noise ratio and this can be achieved by spectrometers operating using superconducting magnets [5].

^{195}Pt NMR shift is greatly affected by solvent and temperature with the former having several hundreds parts per million. It has been suggested that these effects are primarly due to the differences of basicity, polarizability, dielectric constant and ion pairing. The temperature effect dependence of the chemical shift is less significant than the solvent effect, but can be considerable when there is a temperature variation of 100 K [6-8].

Reagents

The reagents are shown in Table 2.

Microelectrode experiments

A pear shaped cell was used with a volume of 70 cm^3. 25 cm^3 of electrolyte was placed in the cell which contained the microelectrode, reference electrode and gas inlet. Microelectrodes were manufactured using platinum wire, from Goodfellows Metals Limited, of various diameter: 1 µm, 5 µm, 10 µm, 25 µm and 50 µm, soldered to a thicker nichrome wire and sealed in a glass tube [4]. The microelectrode tip was polished before each cyclic voltammogram with 1µm, 0.3 µm and finally 0.05 µm alumina, on a moist polishing cloth, Microcloth (Buehler). Before each polish, the tip was cleaned with deionised water and after the final polish it was cleaned by ultrasound in deionised water for 1 minute.

The solution of platinum (II) salt under study was heated to the appropriate temperature and preheated N_2 was passed to deoxygenate the solution. The temperatures were kept in the range of ± 1K of the desired value. Because of the small currents, the reference electrode also acts as the secondary electrode. Cyclic voltammograms were commonly recorded at 25 mV s^{-1}, using a freshly polished microelectrode, although for different solutions, potential limits and scan rates were varied.

Macroelectrode experiments-Electroplating

Copper panels were used as the substrate for some platinum electrodeposition experiments. Their dimensions were 25 mm x 12.5 mm x 0.5 mm. They were degreased with dichloromethane (GPR) in the ultrasonic bath, cleaned in H_2SO_4 (GPR 1 M), rinsed in deionised water (Millipore system) and dried by using an air dryer.

The panels were weighted and attached to the circuit with a wire electrical contact. It was placed in the cell with a platinum gauze anode on either side. N_2 was passed through the solution before the circuit was connected and over the solution after it was connected. After deposition, the panel was removed, rinsed in deionised water, dried and weighted. By using Faraday's law of electrolysis, the increase in mass of the copper panels after deposition and the charge passed, the current efficiency can be estimated. The electrodepositions were done in an enclosed cell to avoid evaporation. The cell has a volume of 140 cm^3, although only 100 cm^3 of solutions were used. Solutions were used for several experiments until there were black deposits in the bottom of the cell. The quality of electroplates were judged by using a magnifying glass, an optical microscope or by SEM.

Table 1: The new tetraammineplatinum electroplating bath.

Composition	Conc./ g l^{-1}	Temp./ °C	Current density/ mA cm^{-2}	Current efficiency (%)	Ref.
$[Pt(NH_3)_4](HCO_3)_2$ H_3PO_4 NaOH	9.86 2.51 pH 10.4	90-95	5-10	90-95	2

Table 2: The reagents and chemicals used throughout the experiments.

Reagents	Physical condition.	Supplier	Purity
$K_3[Fe(CN)_6]$	Solid	BDH	99 %.
Liquid parafin	Liquid	JM. Loveridge	NA.
Copper panels	Solid	Goodfellow Cambridge Ltd.	99.9 %.
Pt 5Q bath	Solution	Johnson Matthey	5 g l^{-1} Pt.
$Na_2HPO_4.12H_2O$	Solid	BDH	GPR
$NaH_2PO_4.2H_2O$	Solid	Fisons	Analytical Reagent.
Polishing Cloth	Solid	Buehler	Not Applicable.
Micropolish, 1 µm, 0.3 µm, 0.05 µm.	Solid	Buehler	Not Applicable.

canning Electron Microscopy (SEM)

canning Electron Microscopy were carried out sing JEOL 6400 analytical SEM equipped with racor Series II X-ray and Image analysis system DAX) with an accelerating voltage of 20 kV. amples were mounted with conducting cement n to metal studs.

RESULTS AND DISCUSSION

he study of $[Pt(NH_3)_4](OH)_2$ solution at pH 13. ^{5}Pt NMR of $[Pt(NH_3)_4](OH)_2$

solution of $[Pt(NH_3)_4](OH)_2$ at pH 13 (0.467 M · 91.1 g l^{-1} of platinum) was supplied by Johnson atthey. The solution was slightly green in colour nd this Pt source is available in a high ncentration. The objective was to identify the fferences from the Pt 5Q bath also containing $t(NH_3)_4]^{2+}$ but in phosphate buffer at pH 10.4.

he ^{195}Pt NMR low resolution spectra was taken pH 12 and 13 at 298 K, with $[PtCl_6]^{2-}$ as the ference compound. The spectra obtained at 7.2 MHz were compared to the Pt 5Q salt, own in Table 3

here is no significant variation between the sults at pH 12 and 13. From the ^{195}Pt NMR ectra, it can be seen that the Pt (II) is always esent in solution as $[Pt(NH_3)_4]^{2+}$.

ability studies of $[Pt(NH_3)_4](OH)_2$

he $[Pt(NH_3)_4](OH)_2$ at pH 13, 91.1 g l^{-1} was left anding at 363 K for 4 days and the solution anged from: colourless → light yellow → dark llow → light brown → dark brown → black lution with black solids. In the same experiment, NH_3 was evolved and red litmus paper turned into blue after it was placed over the solution. The change of colour commenced after only few minutes. The pH of the solution dropped to 11.6 and black solids were formed. Decomposition occured and this led to NH_3 loss. The $[Pt(NH_3)_4](OH)_2$ at pH 12, 9.11 g l^{-1} was left standing at 363 K for 7 days and the solution changed from: colourless → light yellow → light brown solution with black solids. Over the first couple of hours, the change was very small. From these experiments, the complex was found to be unstable at high temperatures.

Voltammetry on microelectrode with $[Pt(NH_3)_4](OH)_2$ at pH 13

Voltammetry experiments were carried out with 0.467 M $[Pt(NH_3)_4](OH)_2$ at pH 13 (Pt concentration 91.1 g l^{-1}) at a 10 μm diameter microelectrode with scan rate of 25 mV s^{-1}. The voltammograms were quite similiar to those of $[Pt(NH_3)_4](HPO_4)$ at pH 10.4. In particular, it was found that:

a) in the higher pH solution, H_2 evolution is shifted to more negative potentials.

b) at around > 350 K, a small wave is observed at ≈ -0.900 V, just positive to the hydrogen evolution. As the temperature is increased, the wave grows. At 363 K, this has become a well formed peak, (j_p = -1676 A m^{-2}).

Because of the instability of this platinum complex at high temperature, cyclic voltammetry experiments at temperatures more than 363 K could not be carried out.

ble 3: Data of ^{195}Pt NMR for platinum solutions [1].

Solution.	Concentrations / M.	pH.	Chemical shift δ / ppm relative to $[PtCl_6]^{2-}$.
$Pt(NH_3)_4](HPO_4)$	0.026	10.4	-2576
$Pt(NH_3)_4](OH)_2$	0.047	12	-2575
$Pt(NH_3)_4](OH)_2$	0.467	13	-2583

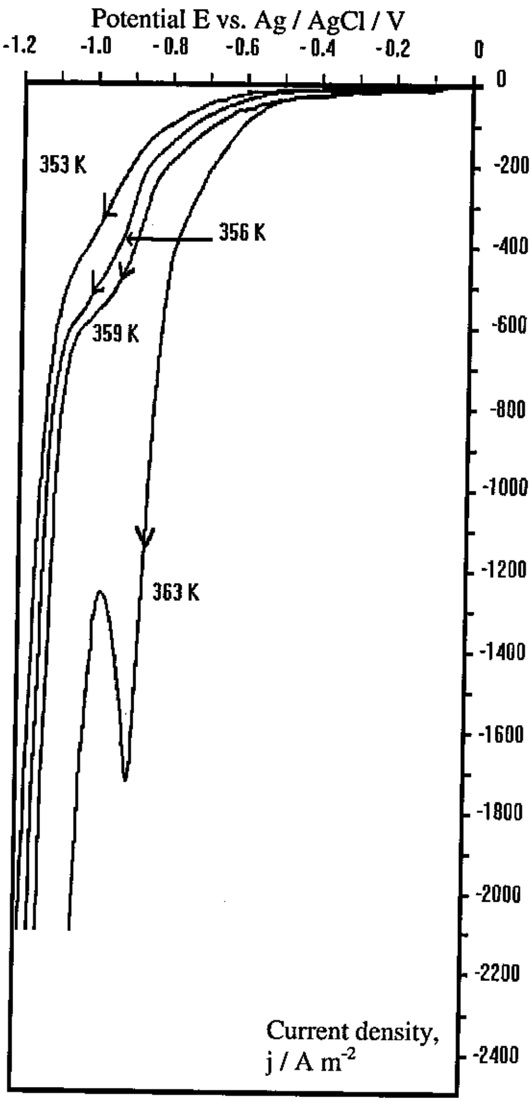

Figure 1. Voltammograms from 0.467 M $[Pt(NH_3)_4](OH)_2$, pH 13, scan rate 25 mV s^{-1}, at a 10 μm Pt microelectrode, at various temperatures.

From the results of the temperature variation experiments above, it was suggested that the 0.467 M $[Pt(NH_3)_4](OH)_2$ at pH 13 have a similar electrochemical reduction as the $[Pt(NH_3)_4](HPO_4)$ at pH 10.4 [2].

The bond breaking between the NH_3 ligand and the platinum centre requires high temperatures [2]:

$[Pt(NH_3)_4](OH)_2$ (aq) + xH_2O (aq) → $[Pt(NH_3)_{4-x}(H_2O)_x](OH)_2$ (aq) + xNH_3 (aq) (chemical step) (1)

$[Pt(NH_3)_{4-x}(H_2O)_x](OH)_2$ (aq) + $2e^-$ → Pt (s) + $(4-x)NH_3$ (aq) + xH_2O (aq) (electrochemical step) (2)

Thus at increased temperature, the electroreduction of platinum will be greatly enhanced. Also with the weakening of the Pt-N bond at high temperatures, the high hydroxide concentration will adversely attack the platinum (II) centre and produce insoluble hydroxide or oxides of platinum.

Macroelectrode experiments: The electroplating of platinum.

The current efficiency for the electrodeposition of platinum from solutions of 0.047 M $[Pt(NH_3)_4](OH)_2$ (Pt concentration 9.1 g l^{-1}) at pH 12.0 was studied as a function of temperature. 100 cm^3 of solutions were used and the pH was adjusted to the original value at room temperature. Platinum was electrodeposited on a freshly cleaned copper surface (area 25 mm x 12.5 mm x 1 mm) and the currents were typically around 31 x 10^{-3} A (current density 50 A m^{-2}). During each experiment, the current, the deposition time and the increase in the mass of the cathode were recorded. The temperatures were allowed to vary between ±1 K. The current efficiencies were calculated from equations 1 and 2. Occasional anomalous results were obtained, probably because the surface preparations were insufficient.

$$m_t = \left(\frac{ItM}{nF} \right) \tag{3}$$

$$C.E. = 100\left(\frac{m_e}{m_t} \right) \tag{4}$$

where:
m_t = theoretical mass increase / kg.
I = current / A.
t = deposition time / s.
M = molar mass of platinum / kg mol^{-1}.
n = number of electrons transferred in electron transfer step.
F = Faraday's constant (96500 C mol^{-1}).
C.E.= current efficiency / %.
m_e = experimental mass increase / kg.

The results are reported in Table 4. It can be seen that:

Table 4: Relation between current efficiency and temperature for 0.0467 M $[Pt(NH_3)_4](OH)_2$ at pH 12.0. Deposition time was 600 s. Copper cathode area was 25 mm x 12.5 mm x 1 mm.

Temperature, T/ K.	**Current efficiency / %.**	**Appearence**
354	5,6	grey.
356	7,14	grey.
358	81,12,16,8,8,9	grey.
363	82,86	slight grey edges, reflecting
366	88,90	slight grey edges, reflecting.
370	89,90	excellently reflecting.

a) there was a sudden increase in the current efficiency from 358 K to 363 K.
b) lower temperatures gave lower current efficiencies, the deposits were grey and had poor reflectivity. Higher temperatures gave higher current efficiencies and good reflectivity.
c) adhesion judged by a simple bending test were good at all temperatures.
d) the relation between current efficiency and temperature for both $[Pt(NH_3)_4](OH)_2$ and $[Pt(NH_3)_4](HPO_4)$ [2] showed the same trend.

As for $[Pt(NH_3)_4](HPO_4)$ lower temperatures (< 358 K) gave lower current efficiencies, there was no immediate formation of a platinum layer on the copper cathode and gas bubbles were seen forming at the surface. At higher temperatures, immediate formation of the platinum layer was observed as soon as the circuit was connected.

After series of electroplating experiments at high temperatures, there were formation of black solids at the base of the cell and the current efficiencies decreased. The decrease in the current efficiencies could have resulted from the depletion of the platinum concentration in solution.

The 46.7 x 10^{-3} M $[Pt(NH_3)_4](OH)_2$ at pH 12 showed far less stability than the 25.6 x 10^{-3} M $[Pt(NH_3)_4](HPO_4)$ at pH 10-10.4. The high concentration of hydroxide anions can interfere with the electroactive species and cause disproportionation reaction taking place. The black precipitates could be finely divided platinum or oxides of platinum (Pt (II) or Pt (IV)).

Scanning Electrochemical Microscopy SEM results

Scanning Electron Microscopy (SEM) was done on the three best quality deposits at 363 K, 366 K and 370 K. Figure 2, 3 and 4 shows the micrograph taken from deposits electrodeposited at 50 A m^{-2} at 363 K, 366 K and 370 K respectively from a solution of 0.0467 M $[Pt(NH_3)_4](OH)_2$ at pH 12.0. Deposition time was 600 s and copper cathode area was 25 mm x 12.5 mm x 1 mm

From Figure 2, the SEM taken at high temperature of 370 K, there are small holes on the surface of the deposit, due to hydrogen adsorption prior to hydrogen evolution reaction that can take place on the surface of the platinum deposits. In Figure 3 the SEM shows the appearance of holes and dislocations. Figure 4 also shows dislocations on the surface of the platinum.

Hydrogen adsorption can be clearly seen from the voltammogram in Figure 1 at 363 K when the current decreases beyond – 0.9 V vs. Ag / AgCl reference electrode. From the voltammograms in Figure 1 and the electroplating experiments, it can be also predicted that at higher temperatures beyond 363 K, the electrodeposition of platinum will be much enhanced because of reactions 1 and 2. Figure 1 also shows that the hydrogen evolution occurs at more positive potentials with the increase in temperature and the hydrogen evolution currents at higher temperatures are generally greater than at lower temperatures at all potentials. Hydrogen adsorption will also increase with temperature as the hydrogen adsorption occurs prior to hydrogen evolution reaction as below:

$$Pt\,(s) + H_2O\,(aq) + e^- \rightarrow Pt - H\,(s) + OH^-\,(aq) \qquad (5)$$

$$Pt - H\,(s) + H_2O\,(aq) + e^- \rightarrow Pt\,(s) + H_2\,(g) + OH^-\,(aq) \qquad (6)$$

Where Pt-H is the adsorbed hydrogen on to the platinum metal. The reaction 5 can be attributed for the decrease in the current in the voltammogram at 363 K in Figure 1.

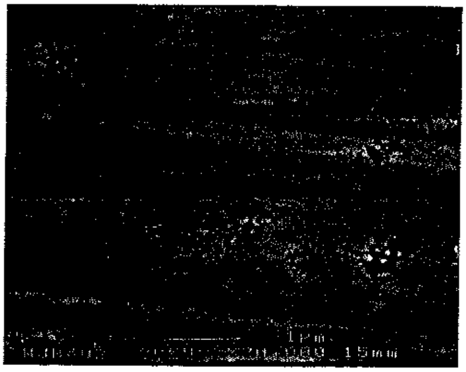

Figure 2. SEM micrograph for electrodeposit of platinum on to a copper substrate from a solution of 0.0467 M $[Pt(NH_3)_4](OH)_2$ at pH 12.0 at 370 K. Deposition time was 600 s. Copper cathode area was 25 mm x 12.5 mm x 1 mm. Scale 1 cm : 0.5 µm.

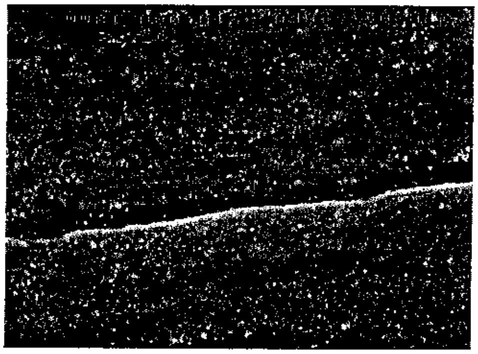

Figure 3. SEM micrograph for electrodeposit of platinum on to a copper substrate from a solution of 0.0467 M $[Pt(NH_3)_4](OH)_2$ at pH 12.0 at 366 K. Deposition time was 600 s. Copper cathode area was 25 mm x 12.5 mm x 1 mm. Scale 1 cm : 1 µm

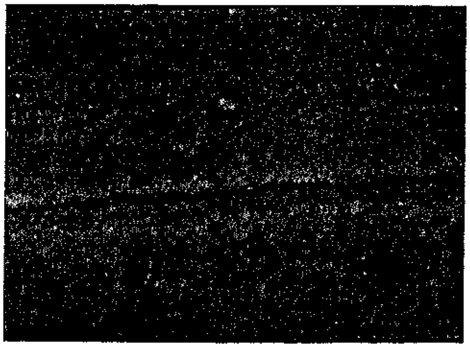

Figure 4. SEM micrograph for electrodeposit of platinum on to a copper substrate from a solution of 0.0467 M $[Pt(NH_3)_4](OH)_2$ at pH 12.0 at 363 K. Deposition time was 600 s. Copper cathode area was 25 mm x 12.5 mm x 1 mm. Scale 1 cm : 1 µm

CONCLUSION

The $[Pt(NH_3)_4](OH)_2$ solution at pH 13 is far less stable than the $[Pt(NH_3)_4](HPO_4)$ at pH 10-10.4 where it produces black solids after prolonged heating. Therefore voltammetric and electrodeposition experiments could only be performed within a limited temperature range. Even so, in general, the electrochemistry of the two solutions are similar. Electroplating experiments gave highly reflecting deposits at high temperatures beyond 363 K. The voltammograms show that at high temperatures close to boiling point, the hydrogen adsorption and hydrogen evolution is enhanced like the platinum electrodeposition reaction. This combined effect produced high current efficiencies at higher temperatures and excellently reflecting deposits, but at the microscopic level, the SEM revealed that there are some holes and dislocations, probably due to the hydrogen adsorption reaction.

REFERENCES

1. Basirun, W.J. Ph.D thesis, University of Southampton, 1997.
2. Basirun, W.J. , Pletcher, D. , Saraby Reintjes, A. *J. Appl. Electrochem.* **26** (1996) 873-880.
3. Denuault, G. in "Microelectrodes" in "Chemistry and Industry" Number **18**, 678-680 (16 September 1996).
4. Kerrison, S.J., Saddler, P.J. *J. Magnetic Resonance,* **31** (1978) 321.
5. Levason, W., Pletcher, D. *Platinum Metals Review,* (1993), **37** (1) 17-23.
6. Appleton, T.G., Hall, J.R., Ralph, S.F., Thompson, C.S.M. *Inorg. Chem.* **28** (1989) 1989-1993.
7. Appleton, T.G., Berry, R.D., Davies, C.A., Hall, J.R., Kimlin, H.A. *Inorg. Chem.* **23** (1983) 3514-3521.
8. Appleton, T.G., Hall, J.R., Ralph, S.F., Thompson, C.S.M. *Inorg. Chem.* **23** (1984) 3521.