

Developments in Platinum Electroplating: P and Q Salt Solution Optimization

*S.E. Hadian and D.R. Gabe
Institute of Polymer Technology and Materials Engineering,
Loughborough University, Loughborough LE11 3TU, UK*

Processing conditions for the 'P' and 'Q' salt baths (containing platinum as diamminodinitrate) have been studied using electrochemical methods with a view to improving cathodic efficiency while maintaining an adequate current density.

The mechanism of electrodeposition is discussed in terms of the complexing behaviour and simple calculations based on potential shifts have supported this approach.

For more information contact:

Professor David Gabe

Tel: +44 1509 223335
Fax: +44 1509 223949
e-mail: D.R.Gabe@lboro.ac.uk

Introduction

The platinum group metals have extreme noble characteristics and consequently pose special problems for electrodeposition process development, notably the difficulty of establishing a good soluble form of the metal. A further preference is to avoid the use of organic solvents or fused salts although the latter is advantageous sometimes, e.g. production of platinized titanium. Any metal complex needs to be relatively cheap, appropriately stable, environmentally acceptable and easy to make and maintain. Four fit into these categories:

- ammines
- nitrito
- hydroxy
- acid chloride

Each has well-recorded formulations from the 1940-1970 period [1]. For example, chloroplatinic acid has been shown to give softer more ductile deposits which can be used to produce platinized platinum surfaces [2]. Platinum may be used in both the II and IV valent states for commercially viable processes:

- Pt(II) phosphate-based 'P' salts
- Pt(IV) hexahydroxyplatinate or tetrachloride solutions including 'Q' salts

A recent continuing study by Pletcher et al [3-8] has addressed several options especially those based on 'Q' salt or $\text{Pt}(\text{NH}_3)_4^{2+}$ in a phosphate buffer which can be considered to be a newer version of the older 'P' salt or diammino dinitrate $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$; both are supplied by the main agencies of Johnson Matthey or Engelhard.

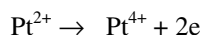
This investigation has taken the most common commercial solutions based on P and Q salts and studied the common solution composition

adjustments that can be made with phosphate and pH to maximize cathodic efficiency in the context of overlay coating for aero engine parts such as turbine blades. Preliminary work has been reported elsewhere [9-11] and has dealt with the use of phosphates in the 'P' salt formulations and the use of pulsed current. In these studies the avoidance of high temperature processes has been a consideration, it having been recognized that commercial formulations have recommended the use of temperatures $>90^\circ\text{C}$ and $\text{pH} > 10$ [12].

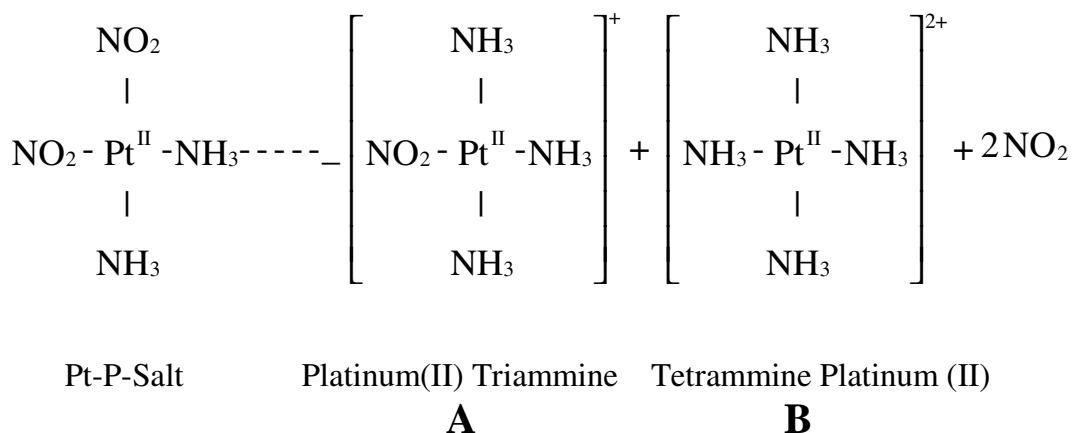
In the ideal solution it is normal for platinum metal ion additions to be the only maintenance required. For such solutions, using 'P' salt, 'Q' salt etc, the compositions used in this study are shown in Tables 1-2.

Factors affecting process performance

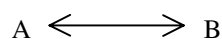
According to the usual method of formulation of platinum solution, plating efficiency of the 'P' salt solution tends to decrease with time and use. On an initial make up the efficiency should approach 15% (i.e. 1 μm deposited in 15 minutes), however this will drop depending on the bath's workload and overall age. The reason for the decline in efficiency was initially thought to be due to oxidation of the platinum, i.e.



However, recent NMR (nuclear magnetic resonance) studies have shown that the formation of an electrochemically stable species may hold the key to a steady decline in plating efficiency; this is shown below.



During the dissolution of 'P' salt in aqueous ammonia, two distinct products are formed. In a newly prepared bath the following equilibrium is formed:



As the bath is worked, the equilibrium slowly drifts towards species B. This shift is speeded by high current density plating through preferential depletion of complex A. To reduce this drift there are two important factors to consider. Firstly, a high excess of ammonia will tend to drive the equilibrium from left to right and hence the bath should be operated at the low end of pH range. Secondly, the replenisher stocks should be kept to a minimum to prevent 'long storage' decomposition.

It is well-established that deposition rates of platinum solution of 'Q' salt can be increased by consideration of a number of factors. At a platinum concentration of 5 g/l, 0.6 A/dm² was optimal. At 20 g/l Pt a current density of greater than 1 A/dm² can be maintained with current efficiency greater than 50%. At 30 g/l Pt still higher current densities are feasible. The bath will operate at a cathode density between 0.1 and 0.5 A/dm². The optimum current density, however, is 0.25 A/dm², depending upon the metal to be plated.

Agitation of the solution is required to achieve even distribution of the platinum within the bath. The current efficiency obtained depends on the temperature and current density. Results between 30 and 90% have been obtained. Optimum results of around 70% are obtained at 90°C and 0.25 A/dm², depending upon factors such as electrode geometry and the substrate. These are shown in Tables 3-6.

Optimization has been reported based on multivariable experiments and analysis by statistical diagrams [11]. In this work polarization characteristics have been explored and discussed in the context of the known process performance parameters.

Experimental

Normally platinum metal ion is the only maintenance required, using 'P' or 'Q' salt. Platinum solution compositions are given in Tables 1-2.

The following processing sequence was employed in the experiments:

1. Ultrasonic vapour degrease for 30 seconds.
2. Cathodic clean: 1 min at 60°C and 40 mA/cm².
3. Demineralised water rinse.
4. 50 v/v hydrochloric acid pickle for 5 min at 50°C.
5. Demineralised water rinse.
6. Pt 209 for 8 min at 20 mA/cm², 90°C and pH=8.0-9.0.
7. Demineralised water rinse.
8. Pt 'Q' salt deposition for 110 min at 7.5 mA/cm², 80°C and pH ~12.0 giving 10 µm thickness.
9. Demineralised water rinse, used later to replenish-top No 8.
10. Demineralised water spray rinse.
11. Dry.

Polarisation was carried out in a 2-litre culture vessel with a separate lid, which had five openings, thereby facilitating the insertion and removal of various reference and counter electrodes, thermometer and gas bubbler. The lid of the beaker was sealed in the position with a gasket and clip

Anodic and cathodic polarisation tests were carried out in various platinum solutions as follows:

- (a) Fresh 'P' salt with phosphate buffers.
- (b) Phosphate base solution (i.e. plating bath composition but without platinum).
- (c) Different ratios of platinum solutions.
- (d) Plating solutions directly from plating baths No. A (based on 'P' salt).
- (e) 'Q' salt from Johnson Matthey (bath D).
- (f) Fresh 'P' salt with sodium buffers.

The platinum solutions were made up from individual chemicals and brighteners. Table 7 shows the standard solution make up for platinum plating with phosphate buffers, A being a large tank experiment and B, C and D consecutive small tank experiments.

Polarization Results

Cathodic polarization curves for the electrodeposition of platinum are shown in Figures 1-12. These show polarization curves for the phosphate base solution without addition of 'P' salt. Maximum and minimum currents (mA/cm²) were achieved within -1.1 and -0.7 V. They also illustrate polarization curves for bath A with the same pH value which was used in phosphate base

solution. Current inflexion was more pronounced in the region of 15 mA/cm^2 to 5 mA/cm^2 and this was accounted for by the hydrogen evolution reaction. This effect was recorded within a range of -0.65 to -0.7 V . The cathodic polarization curves for phosphate base solution and bath A show that current drops were observed at -0.6 V due to the effect of hydrogen evolution for both solutions.

Figure 1 also shows polarization curves for bath A with addition of sodium hydroxide. The data for the platinum solution without addition of NaOH reveals hydrogen evolution at -0.65 V ; it includes a platinum solution with an addition of 130 ml NaOH for a 2-litre solution and the consequent hydrogen evolution effect. The polarization curve for this case was shifted towards a more negative value. Finally, in the platinum solution with a high addition of 20 g NaOH for a 2-litre solution, hydrogen evolution was noted at -0.7 V for which the polarization curve was also shifted towards a more negative value.

Figure 2 represents bath D; polarization curves for this bath may be compared with those for bath A, freshly made solution (Pt 'P' salt) and phosphate only. Although the pH and temperature values are different, allowance can be made by subtraction of $2 \times 0.059 \text{ mV}$ for pH values for comparison between bath A and D. Nevertheless, the hydrogen evolution occurred at -1.0 V and the degree of current inflexion was low from $18\text{-}12 \text{ mA/cm}^2$ when compared with bath A.

Laboratory and experimental tests resulting from bath D have shown that the rates of plating, current efficiency and plating time have shown better improvement. These results indicate that when the polarization shifted towards more negative values, operating difficulties were encountered in the use of all baths. Three electrolytes with different phosphate ratios but having constant platinum content of 3 g/l were prepared. The bath composition and operating conditions are given in Tables 1,7 and the effect of various potentials upon these electrolytes is shown in Figures 1-12. The phosphate ratios of 7:1, 4:1 and 1:1 were prepared with a high degree of accuracy; cathode efficiency measurements were made and are given in Tables 4, 6.

Cathodic polarization measurements were made and the results are shown in Figures 1-12. From the above results it can be concluded that the electrolyte with the high ratio (i.e. 7:1) had the highest cathode efficiency and hydrogen evolution did not take place until the maximum current

density was achieved; this corresponds with cathodic polarization having a more negative value and is probably due to the amount of disodium orthophosphate in solution.

Further tests were carried out with and without phosphates in platinum solutions; results are shown in Figure 1. It appears from this Figure that higher temperatures could raise the current density and lower hydrogen evolution or vice versa. These tests were also carried out using fresh platinum solutions, as shown in Figures 8-11.

Effects on cathodic polarisation of high and low pH as well as temperature were investigated and are shown in Figures 8-12. This work represents the cathodic polarisation for platinum baths with high pH and platinum content, compared with low pH and low platinum content.

Discussion

The cathodic polarization curves plotted for platinum are, in general, of a typical cathodic shape culminating in the approach to a limiting current indicating mass transport limiting deposition. Dahms and Croll [13] showed that a local pH rise near the electrode surface is favoured when H_2 evolution proceeds simultaneously with deposition and it seems that sodium hydroxide can be precipitated in the vicinity of the electrode surface. The adsorbed sodium hydroxide permits a high discharge rate of Pt^{2+} according to their postulation.

The current density-potential curves of these electrolytes show very characteristic behaviour in the alkaline pH range, in so far as the current density increases up to a maximum limiting current, it drops to a low value of current before increasing again with potential due to hydrogen production. How far this kind of 'cathodic passivation' is connected with the hydrogen co-discharge and the adsorption of hydrogen is not as yet clear; another explanation might be a sudden change in pH value in the cathodic layer caused by hydrogen evolution possibly yielding incipient precipitate films not obviously identified.

The critical current density can be increased by an increase in the concentration of the Pt 'P' salt. Temperature has a very decisive influence on the critical current density, while potentials remain nearly constant. Passivation is no longer observed at pH values below 7.0, since hydrogen evolution starts before platinum discharge begins and presumably films are unable to be nucleated. Initial investigations of 'P' salt solutions and 'Q'

salt consisted of electroplating of the most promising solutions from the bath A and D.

The pH of bath D ('Q' salt) has been kept constant at values of 9-10, whereas the pH range value for bath A ('P' salt) was 7.0-7.5; this effect generally agrees with the work of Dahms and Croll [13]. Under discharge in these circumstances, according to results shown in Figures 6-12 the hydrogen evolution was delayed or shifted towards more negatively with a local pH rise.

The main influence on the passivation characteristics of a platinum solution, except 'P' salt and 'Q' salt solutions, was the pH. In essence a very low pH value resulted in a high value for i_{crit} and consequently, a high dissolution rate for anodically formed coatings in this type of solution. All groups showed remarkably dissimilar responses at the different pHs tested: pH 7.0 'P' salt solution curve exhibited high current densities for low overpotentials, and generally did exhibit a large number of inflections; pH 9.0 solution of 'Q' salt exhibited smaller current values for given potentials and also the appearance of less marked inflection phenomena. For all pH of 9.0-10.0, 'Q' salt solution currents at given potentials were generally smaller up to -1.0 V but gradually increased to 34 mA/cm² at high overpotentials of about -1.7 V.

Surface characteristic features after cathodic polarisations were recorded and 'P' salt solutions were observed to yield dark, dull finishes, with silver matt to grey shades being prominent. 'Q' salt samples were generally reflective, bright and less heavily coloured.

Broadly categorising the inflections is difficult because of the scatter of values from individual solutions. However, there does appear to be some evidence of a trend whereby all hydrogen-evolution analogues seem to produce inflection-type features at the range of values around -700 mV vs SCE for 'P' salt and one also around -1000 mV vs SCE for 'Q' salt. However, it must be reiterated that these values should be regarded as very approximate.

As a guide to corrosion resistance the diffusion coating test was found to be useful. The results indicate that 'P' salt coatings consistently produced the best performance; 'Q' salt coatings showed larger variations between the duplicate samples tested for each processing condition. This suggests that either the diffusion coating process was producing uneven coating or that the specimens coated at a particular condition were truly variable. 'P' salt coatings were clearly

superior to 'Q' salt, producing consistently high levels of uniform coating and surface platinum corrosion product.

Due to the difficulty in observing the actual commencement of hydrogen evolution in a large bath operation, it is assumed that the actual onset occurred before these experimental potentials. This suggests the second inflection (usually strong) on the 'P' salt curve appears to be around -800 mV vs SCE reference scale. SEM investigations were carried out on 'P' salt and 'Q' salt coatings that were subjected to diffusion treatment. However, this type of processing produced a non-adherent coating from 'Q' salt solution. On examination the surface of the specimen from 'P' salt solutions generally appeared to consist of spherical crystal. The 'Q' salt coated surface was made of irregular spherical crystal (some of which exhibited internal cracks) which could possibly be as a result of post-treatment that resulted in the cracking of the initially-formed film.

Referring to three electrolytes with different phosphate ratios having a constant platinum content of 3 g/l Pt, the bath composition and operating conditions being given in Table 8 and the effect of various potentials upon these electrolytes shown in Figures 1-7. Although careful attempts were made to maintain constant experimental conditions, the weight gains obtained during a series of similar deposition runs were subject to considerable variation, indicating large variations in cathode current efficiency. The phosphate ratios of 7:1 and 1:1 were carefully prepared and cathode efficiency values are given. From these results it is apparent that a ratio of 7:1 gives the highest efficiency and that hydrogen evolution does not commence until the highest current density is achieved. Further tests, with and without phosphates, showed that higher temperatures allowed higher current densities and lower hydrogen evolution.

When the deposition potential lies below the reversible hydrogen potential there is usually some concomitant hydrogen evolution and possible reduction of other ions; these all lead to lower efficiency and electrical wastage. This statement can be related to the polarization curves. Potential shifts for non-standard conditions can be calculated from the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{a_M}{a_M^{n+}} \right) \quad \sim \quad \{1\}$$

or at 298K, 1 atm. pressure and pure metal:

$$E = E^o + \frac{RT}{nF} \log(a_M^{n+}) \sim \{2\}$$

Any potential shift can be expressed as:

$$\Delta E = (E - E^o) \sim \{3\}$$

The equilibrium constant for a complex such as $\text{PtCl}_4^{2-} = \text{Pt}^{2+} + 4\text{Cl}^-$ is:

$$\frac{\text{PtCl}_4^{2-}}{\text{Pt}^{2+} \times (\text{Cl}^-)^4} = 10^{-16} \sim \{4\}$$

Using these equations, calculation shows that the following values are found:

Overpotential (mV)	a_M^{n+}
500	$10^{-16.95}$
600	$10^{-20.34}$
650	10^{-22}
700	10^{-23}
750	$10^{-25.4}$

From the above calculation it can be concluded that as excess Cl⁻ is high, the activity of Pt²⁺ is less and therefore Pt²⁺ will be less than is being estimated so that the calculation is justifiable as a guide. Comparison now follows of the potential shift; calculation gives that for:

$$a_{\text{Pt}^{2+}} = 10^{-16}, \Delta E = 500 \text{ mV}$$

Consequently, it is reasonable to attribute the potential shift primarily to the chloride complexing effect for Pt²⁺.

Conclusions

The operating conditions for a 'P' salt based platinum plating solution have been studied and the effects of current density and current efficiency explored in particular.

Electrochemical measurements of potential have been related to the solution composition and the data discussed in terms of the complexed nature of the solution and the consequent deposition mechanism.

Acknowledgements

The authors would like to thank Mr. M. Dean, managing director of C.U.K.Ltd., for his support and encouragement.

References

1. M.E.Baumgartner and C.J.Raub, *Platinum Metals Rev.* 1988, **32**, 188.
2. R.H.Atkinson, *Trans. Inst. Met. Fin.* 1958, **36**, 7.
3. R.Le Penven, W.Levason and D.Pletcher, *J. Appl. Electrochem.* 1992, **22**, 415.
4. A.J.Gregory, W.Levason and D.Pletcher, *J. Electroanal. Chem.* 1993, **348**, 211.
5. A.J.Gregory, W.Levason, R.E.Nottle, R.Le Penven and D.Pletcher, *ibid* 1995, **399**, 105.
6. W.J.Basirun, D.Pletcher and A.Saraby-Reintjes, *J. Appl. Electrochem.* 1996, **26**, 873.
7. W.Levason, D.Pletcher, A.M.Smith and A.R.Berzins, *ibid* 1998, **28**, 18.
8. W.J.Basirun and D.Pletcher, *ibid* 1998, **28**, 167.
9. S.E.Hadian and D.R.Gabe, *Trans. Inst. Met. Fin.* 1998, **76**, 227.
10. S.E.Hadian and D.R.Gabe, *ibid* 1999, **77**, 108.
11. S.E.Hadian and D.R.Gabe, *Plating Surf. Fin.* 2000, to be published.
12. Johnson-Matthey commercial process data.
13. H.Dahms and I.M.Croll, *J. Electroanal. Chem.* 1976, **70**, 233.

Table 1. Dinitrodiammine Platinum 'P' salt solution composition.

Dinitrodiammine Platinum		
(Pt 10 g/l)	Pt (NH ₃) ₂ (NO ₂) ₂	16.5 g/l
Ammonium Nitrate	NH ₄ NO ₃	100 g/l
Sodium Nitrite	NaNO ₂	10 g/l
Ammonia(28% solution)	NH ₄ OH	50ml /l
Anodes	Platinum	

Table 2. Sodium Hexahydroxyplatinate 'Q' salt solution composition.

Sodium Hexahydroxyplatinate	
Sodium platinate	20 g/l
Sodium Hydroxide	5.6 g/l
Sodium Oxalate	5.6 g/l
Sodium Sulphate	33.7 g/l

Table 3. Cathode current efficiency and pH: Solution with 5g/l Pt at 91°C.

pH	CCE%
9.9	58
10.0	59
10.1	60
10.2	63.7
10.3	64
10.4	63
10.5	60
10.6	59
10.7	59
10.8	58.8
10.9	57

Table 4. Current density and temperature relationship at pH=10.5

CCE%	Temperature °C
2	75
5	80
6	83
8	86
10	88
60	90
60	91
60	93
60	97

Table 5. Current density and time required to deposit 1µm Pt per dm².

C.D (A/dm ²)	Time in min/dm with C.C.E 75%	Time in min/dm with C.C.E 60%	Time in min/dm with C.C.E 50%
0.9	5.7	6.8	8
0.8	6.4	7.3	9
0.7	7.3	8.5	10.4
0.6	8.5	10	12.2
0.5	10.2	12	14.4
C.D (A/dm ²)	Time in min/dm with C.C.E 70%	Time in min/dm with C.C.E 60%	Time in min/dm with C.C.E 50%
0.5	10	13	15
0.4	13	15	18
0.3	17	20	24
0.2	25	30	35
0.1	51	59	72

Table 6. Current density and current efficiency influencing deposition rates.

C.D (A/dm ²)	CCE%	Time to achieve 1.0µm thickness(min)	Thickness per hour (µm)
0.25	30	47	1.3
	50	28	2.1
	70	20	3.0
0.50	30	24	2.5
	50	14	4.2
	70	10	6.0

Table 7. Solution make-up for small (A) and large tanks (B,C,D).

Composition	Weight/ Volume	
	170 Litre Bath	335 Litre Bath
Pt as 'P' Salt, 28.0g/l	425(Pt)	837(Pt)
Disodium Hydrogen Orthophosphate	14.0 Kg	27.0 Kg
Diammonium Hydrogen Orthophosphate	2.8 Kg	5.5 Kg

Table 8. Solution compositions for various constituent ratios.

Bath Composition and Operating Conditions for Different Ratios of Plating Baths			
Composition Ratios	7:1	4:1	1:1
Pt as 'P' Salt, 28.0g/l	214	214	214
Sodium Nitrite, g/l	102	102	102
Disodium Hydrogen Orthophosphate, g/l	213	187	85.2
Diammonium Hydrogen Orthophosphate, g/l	39.6	63.4	158
pH	7.65	7.7	7.7
Temperature, °C	84-86	84-86	84-86

C.P= Cathode Potential
 C.D= Current Density
 W.G=Weight Gain
 C.C.E= Cathode Current Efficiency

Table 9. Cathode potential values and consequent process characteristics.

C.P (mV)	W.G (g)	C.D (mA/cm ²)	C.C.E (%)	C.P (mV)	W.G (g)	C.D (mA/cm ²)	C.C.E (%)	C.P (mV)	W.G (g)	C.D (mA/cm ²)	C.C.E (%)
Ratio 4:1			Ratio 7:1			Ratio 1:1					
-600	0.0	0.11	-	-600	0.0	0.083	-	-600	0.0	0.083	-
-700	0.012	9.0	6.6±1.2	-700	0.009	7.0	6.2±0.9	-700	0.0	0.7	-
-800	0.038	22.0	8.6±1.4	-800	0.04	25.6	8.0±1.2	-800	0.011	10	5.6±1.2
-900	0.064	20.5	15.8±1.5	-900	0.061	19.4	15.9±2.1	-900	0.055	24.6	11.3±2.3

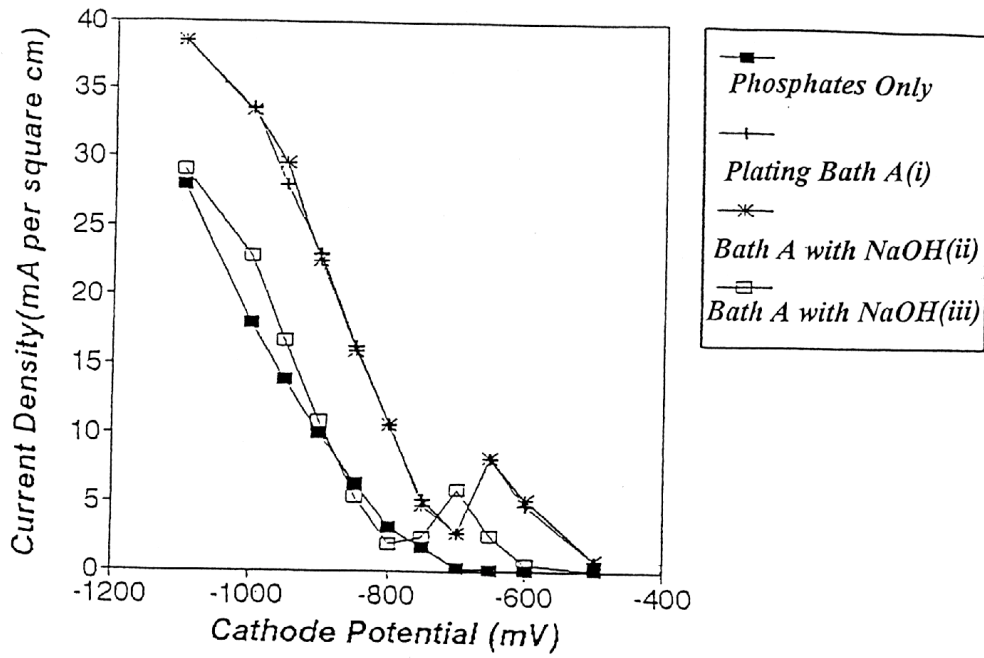


Fig. 1. Cathodic polarization for different solutions: effect of current density.

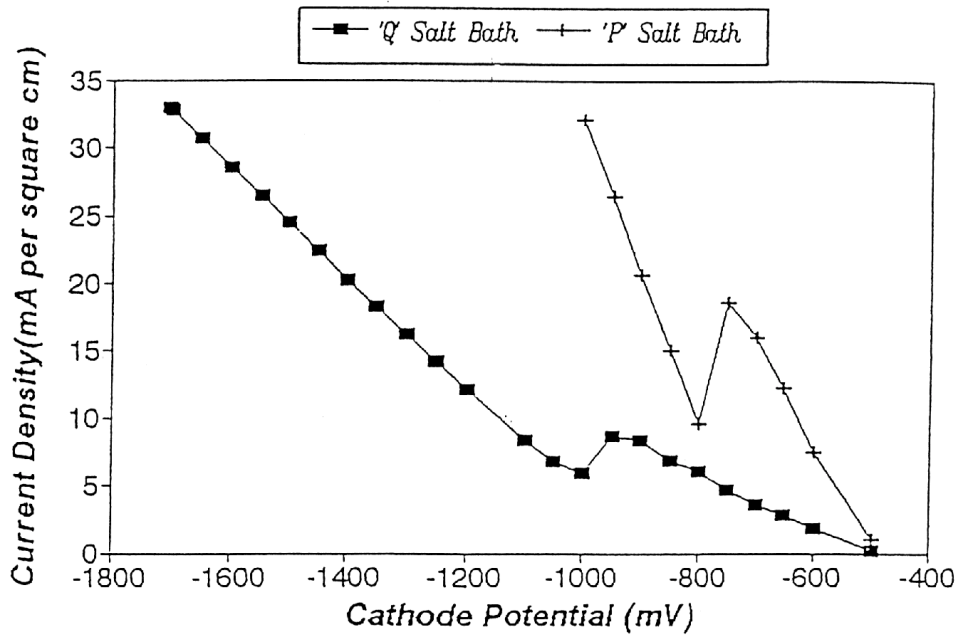


Fig. 2. Cathodic polarization for 'P' and 'Q' salt solutions: effect of current density.

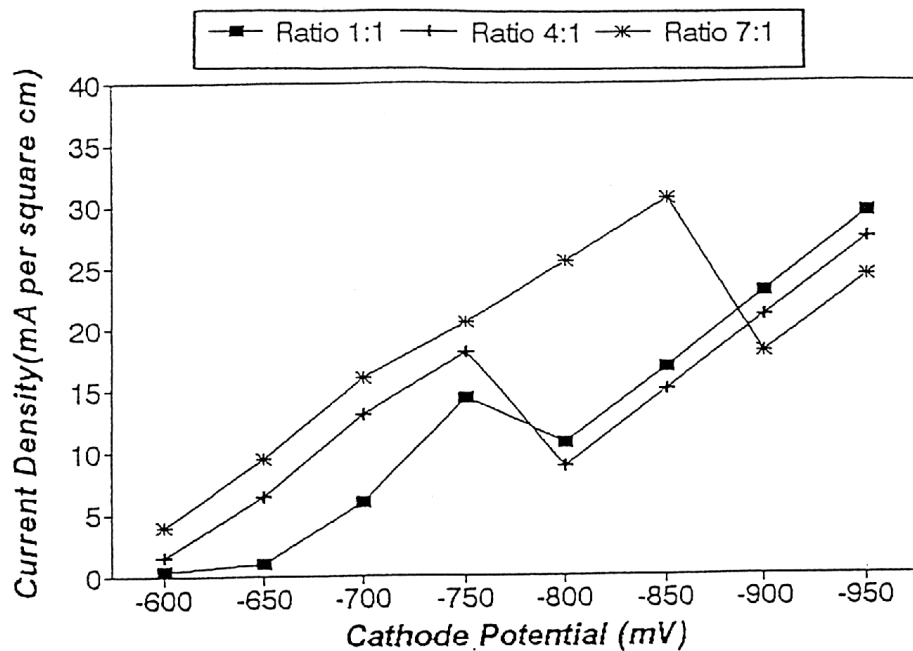


Fig. 3. Cathodic polarization for four different ratio solutions with effect of current density.

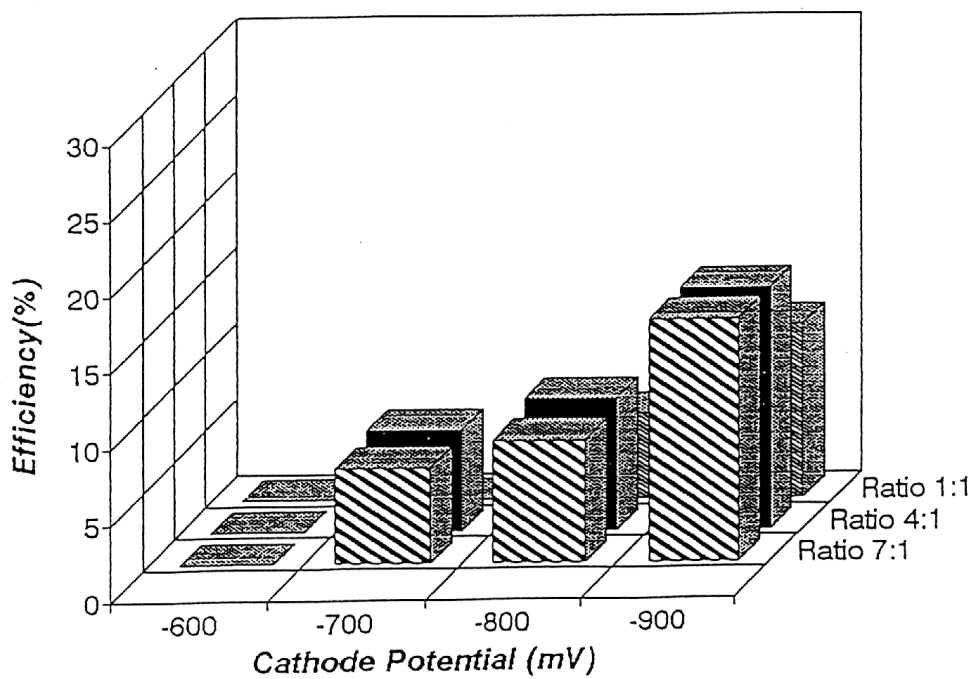


Fig. 4. Cathodic polarization for four different solutions: effects of potential upon efficiency.

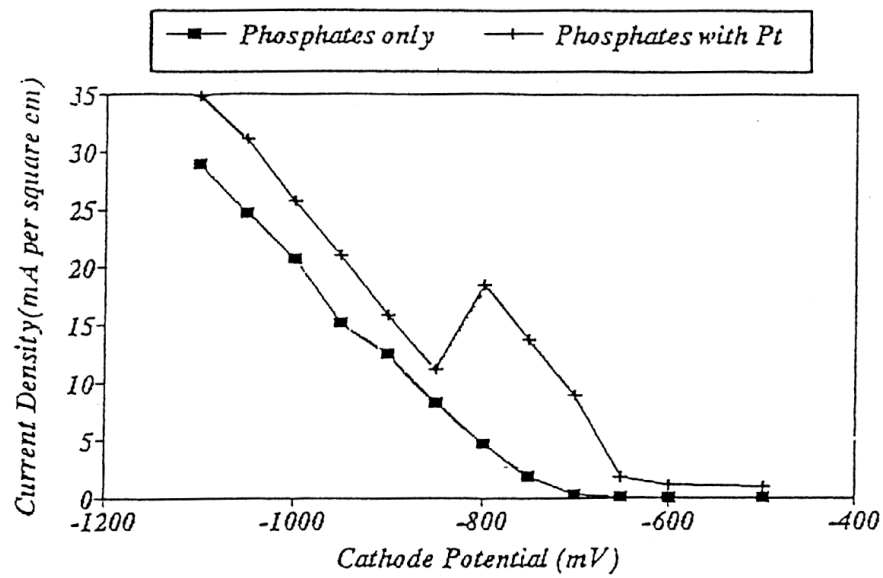


Fig. 5. Cathodic polarization for phosphates and platinum: effect of current density.

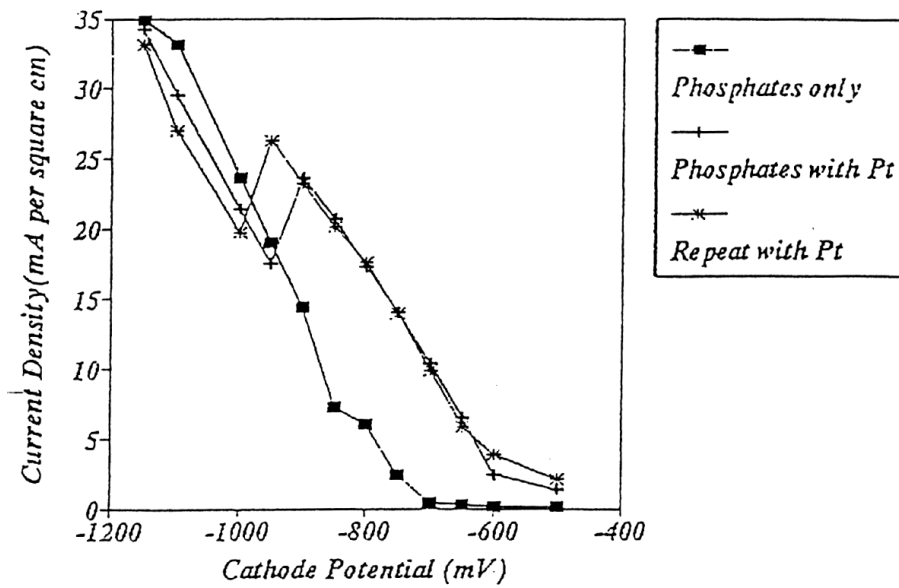


Fig. 6. Cathodic polarization for phosphates and platinum: effects of current density and repeated usage.

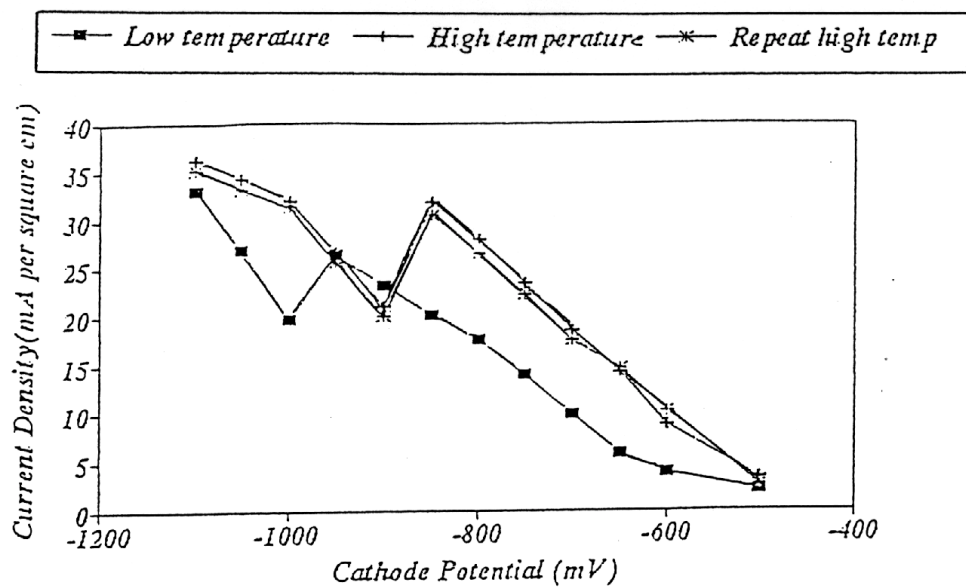


Fig. 7. Cathodic polarization for platinum solutions at high and low temperatures.

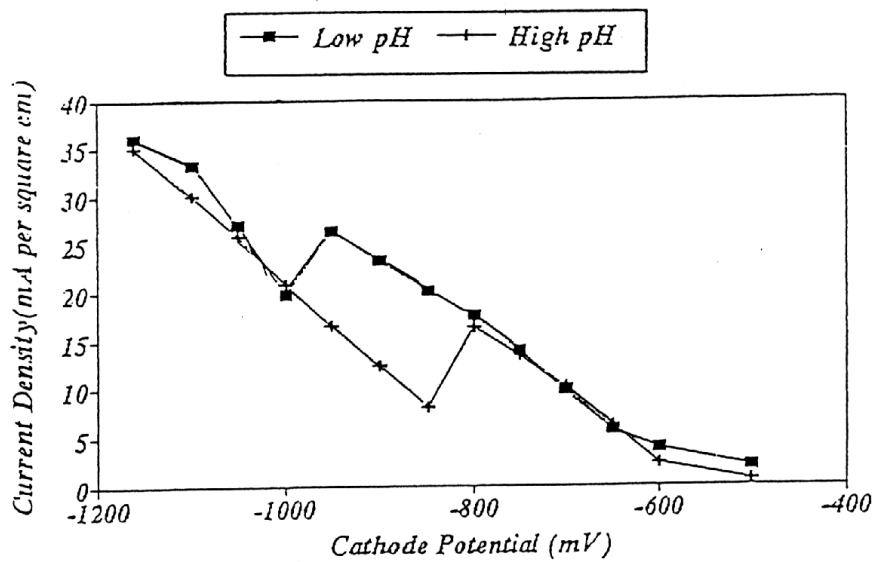


Fig. 8. Cathodic polarization for platinum solutions at high and low pH.

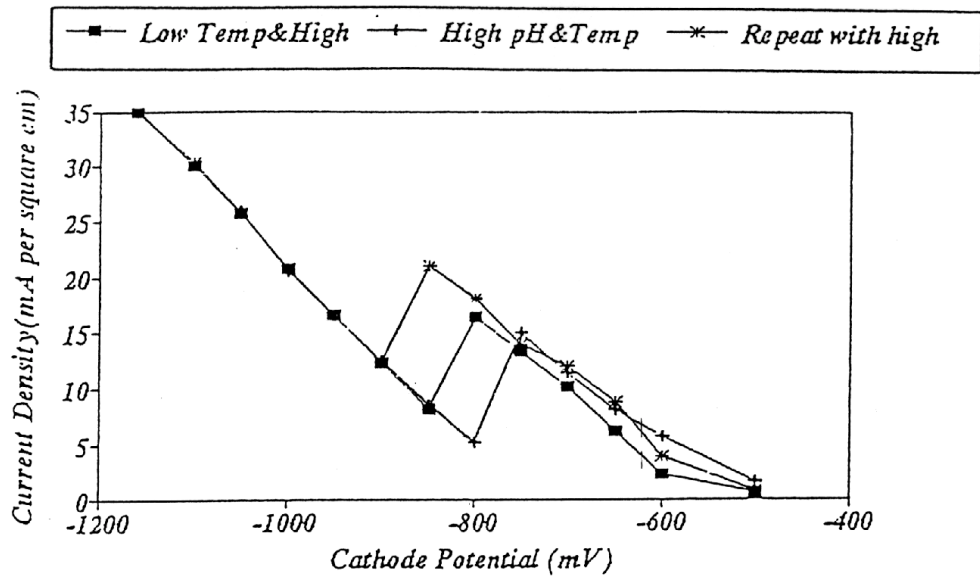


Fig. 9. Cathodic polarization for platinum solutions at high temperature and low pH compared to low temperature and high pH.

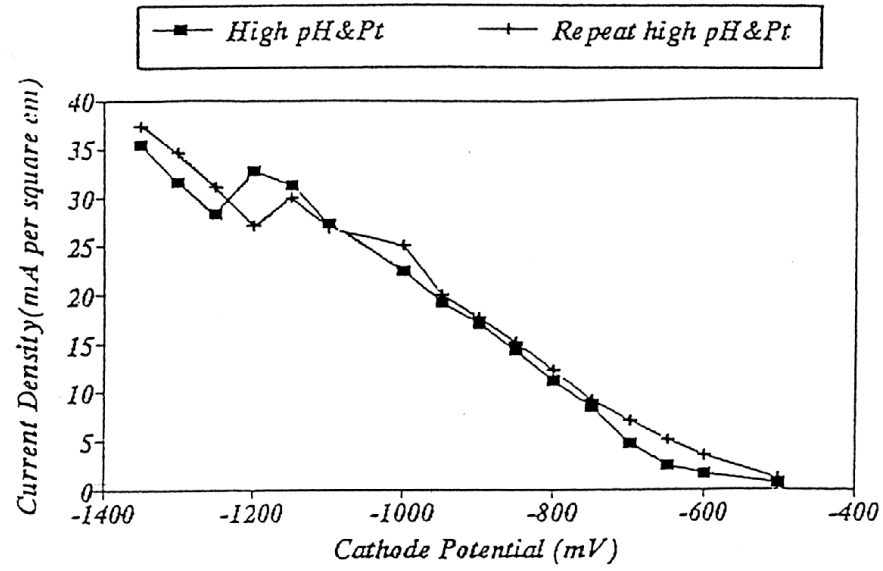


Fig. 10. Cathodic polarization for platinum solutions with high Pt and high pH compared to low Pt and low pH.

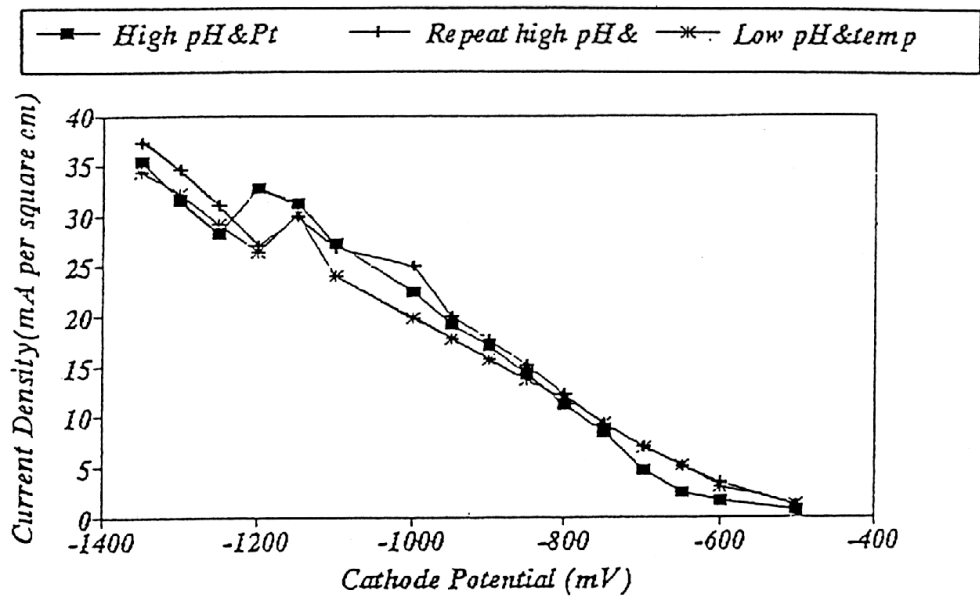


Fig. 11. Cathodic polarization for platinum solutions with high Pt and low pH and low pH with low temperature.

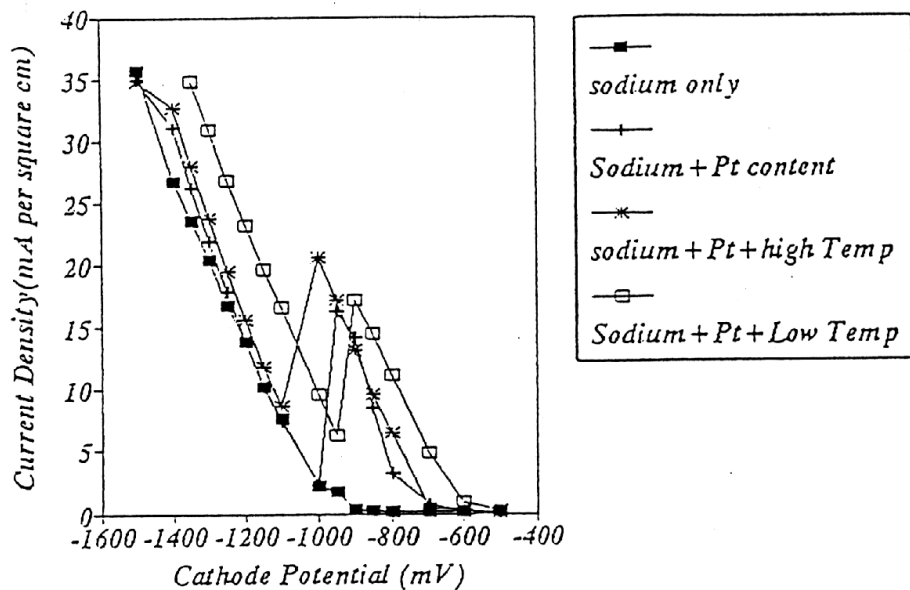


Fig. 12. Cathodic polarization for solutions containing:
 a. added sodium, b. added sodium and Pt, c. sodium with Pt at high temperature and d. sodium with Pt at low temperature.