

A bromide electrolyte for the electrodeposition of platinum and platinum–iridium alloy

G. Sheela¹, M. Pushpavanam*¹ and S. Pushpavanam¹

A new electrolyte is reported for the deposition of platinum and platinum–iridium alloy. The effect of operating variables and bath composition on the cathode current efficiency and alloy composition were investigated. This bath gives 75% efficiency for platinum deposition and around 50% efficiency for the alloy deposition with 70% iridium. Alloys with varying composition could easily be produced and the deposits obtained on titanium were smooth and adherent.

Keywords: Electrodeposition, Platinum, Platinum–iridium alloy, Cathode efficiency, Micrographs, Diffraction patterns

Introduction

Platinum electroplating is used in a variety of electrochemical processes such as the preparation of organic and inorganic chemicals, electroplating, cathodic protection, fuel cells, waste disposal and water electrolysis. It is also extensively used on, for example, aviation components, turbine blades, electronic components and in jewellery to improve specific properties or appearance.^{1,2} Baumgartner and Raub³ have reviewed the common electroplating baths available for platinum and it is clear that there are still problems with the performance of many of the plating electrolytes. Even the recently reported Q bath (a proprietary formulation based on a phosphate buffer) operates at very high temperature, which not only causes operational problems but also may not suit many of the substrate metals.^{4,5}

Preparation of titanium substrates to render them suitable for the production of adherent platinum deposits without any undercoat is difficult because of the presence of the tenacious oxide layer present on titanium surfaces.^{6,7} This difficulty is all the greater when platinum layers exceeding 1 μm thickness are required. The industrial thickness requirements for many applications may be as high as 7.5 μm .

Platinum–iridium alloy containing 30% iridium is well known as an anode having a very low oxygen overpotential for electrochemical oxidative reactions particularly in view of its advantages over pure platinum.⁸ So far this surface alloy has been produced by thermal decomposition of organic solutions of platinum and iridium complexes, but electrodeposition is expected to offer several advantages including the possibility of producing alloys of varying composition. Apart from the report of Tyrell,⁸ the literature on this alloy is sparse.

In the pursuit of developing platinum–iridium alloys, for use as catalytic electrodes for oxidative reactions, the authors have developed a modified iridium plating electrolyte.^{9,10} To deposit platinum–iridium alloy from this electrolyte, platinum should also be depositable the

same electrolyte from. The work described in this paper primarily concerns the development of a stable, reproducible and relatively cheap electrolyte for depositing coatings of a consistent composition on titanium, which is an economical versatile substrate for platinum metal coated electrodes.

Experimental

The platinum bromide electrolyte was prepared by reducing chloroplatinic acid with a mild reducing agent, as reported for iridium, and precipitation of as platinum hydroxide that is then dissolved in hydrobromic acid. Iridium bromide was prepared as described previously.⁹ Both the solutions were mixed together in the appropriate ratio before starting the experiments. Deposition was carried out on titanium panels of 4 \times 1 cm size with an effective plating area of 2 \times 1 cm², pretreated in conc. Hydrochloric acid based etchant as given in an earlier report.⁷ The effects of bath composition and operating variables on the cathode current efficiencies, thickness and rate of deposition, etc., of metal as well as the alloy were recorded. Cathode current efficiency was determined by the increase in the mass of the deposit after passing a known charge. The thickness of the deposits and composition of the alloy were determined using X-ray fluorescence spectroscopy (CMI, XRX Series, USA). Structural characterisation of the deposits was made using a scanning electron microscope (SEM) (Hitachi, model No. S-3000H, Japan) and X-ray diffraction (XRD) (JEOL-JDX 8030, X-ray diffractometer, Cu-K₂ radiation).

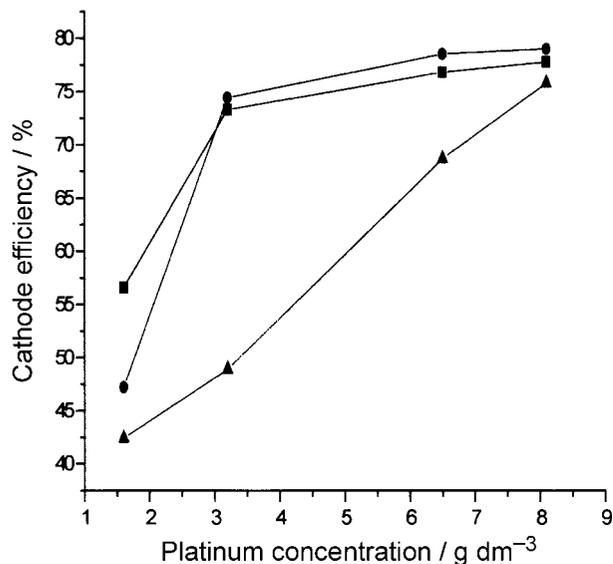
Results and discussion

Platinum deposition

Figure 1 depicts the effect of platinum concentration in the solution on the cathode efficiency at different operating current densities. Deposition at 1 A dm⁻² showed a linear increase of current efficiency with the platinum content in the bath. It rose from 42.5% at 1.6 g dm⁻³ platinum to 78% at 6.5 g dm⁻³ of platinum in solution. Operating at 0.5 and 0.25 A dm⁻² gave 47 and 57% efficiencies at 1.6 g dm⁻³ and showed a sudden increase to around 78%, which remained almost

¹Central Electrochemical Research Institute, Karaikudi 630006, TN, India

*Correspondence, email malathypush@yahoo.com

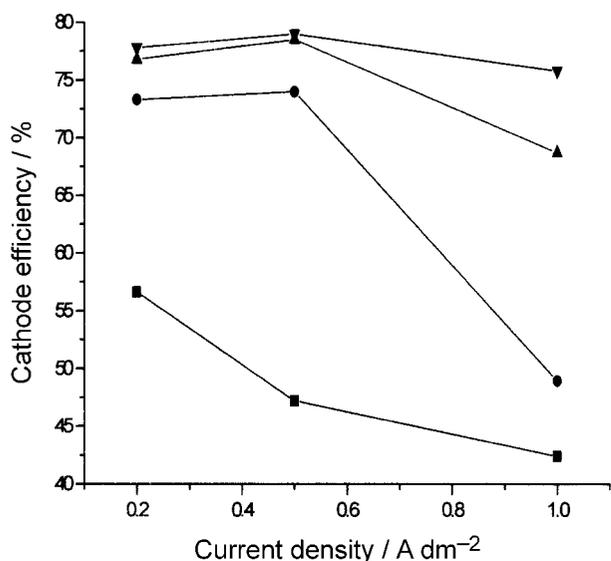


Current density (A dm⁻²): ■, 0.2; ●, 0.5; ▲, 1.0. Temperature=75°C

1 Effect of metal ion concentration on the cathode current efficiency of platinum deposition

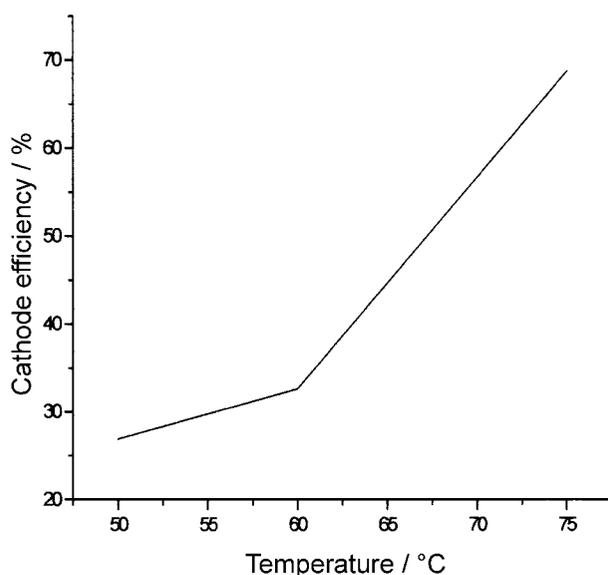
constant with increase in platinum concentration in solution. This implies that the maximum efficiency that can be obtained from this electrolyte for a platinum deposition above 3 g dm⁻³ at 75°C is around 75% irrespective of the increase in metal content. High current density can only be tolerated when the metal ion content in the solution is high. It could be concluded that 3 g dm⁻³ is the threshold metal concentration for obtaining the highest efficiency, up to 0.5 A dm⁻². High concentration baths help in producing white, smooth, compact deposits with a marginal increase in current efficiency.

Figure 2 shows the effect of current densities on the cathode current efficiency (CCE) at different metal ion concentrations in solution. A solution containing 1.6 g dm⁻³ platinum gives 57% current efficiency at



Platinum concentration (g dm⁻³): ■, 1.6; ●, 3.2; ▲, 6.5; ▼, 8.1

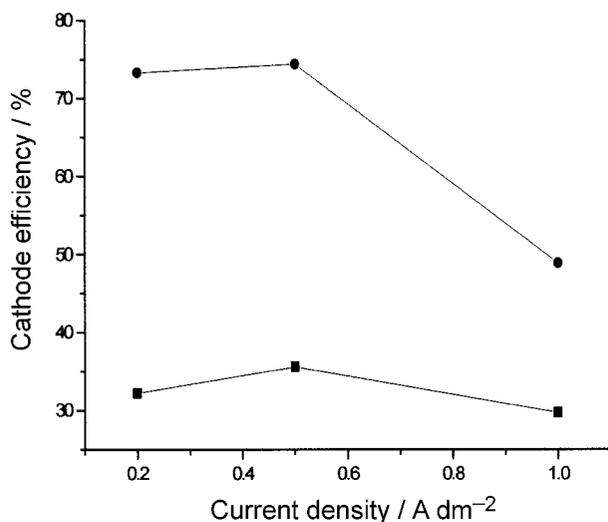
2 Effect of current density on cathode current efficiency at different Pt ion concentrations



3 Effect of bath temperature on the cathode current efficiency of platinum deposition

0.2 A dm⁻² but thereafter shows a decrease. Baths having platinum concentrations above 3.2 g dm⁻³ show a maximum in current efficiency at 0.5 A dm⁻² and thereafter show a decrease. This is similar to the performance of the conventional dinitrito sulphato platinum acid (DNS) plating solutions, but with an efficiency five times higher. Therefore, while the DNS solution can produce deposits at the rate of about 1.5 μm h⁻¹, this solution allows plating at the rate of almost 7.5 μm h⁻¹.

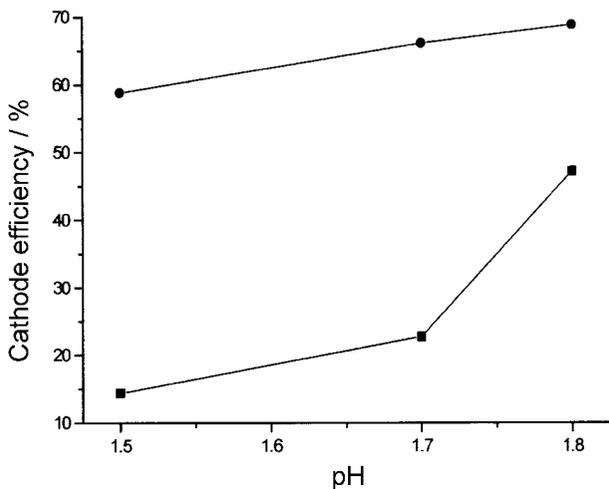
As shown in Fig. 3, the current efficiency starts increasing from 60°C and the useful maximum current efficiency is produced at 75°C. Although further increase in operating bath temperature resulted in still higher efficiencies, i.e. 92% at 95°C, and a deposition rate of 9–10 μm h⁻¹, because of operational problems and evaporation of the electrolyte, 75°C was taken as the optimum temperature. Further, because previous work showed the optimum operating temperature to be 75°C for iridium deposition, operating the platinum bath



Temperature: ■, 32°C; ●, 75°C

4 Effect of current density on cathode current efficiency of platinum deposition at different temperatures

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Platinum concentration: ■, 1.6 g dm⁻³ (0.5 A dm⁻²); ●, 6.5 g dm⁻³ (1.0 A dm⁻²)

5 Effect of pH on the cathode current efficiency of platinum deposition

at the same temperature would be preferable in the production of an alloy of the above metals.

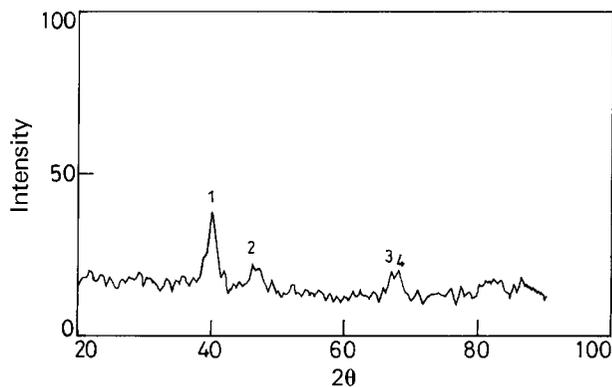
Figure 4 shows the performance of the platinum bromide electrolyte at 32°C for comparison with the conventional DNS solution. It is clear that bromide bath can yield deposits of around 35% efficiency compared with 15–20% efficiency for the latter. Therefore, the bromide bath is suitable for operation from 30 to 95°C, unlike the Q baths, which can yield good efficiency only above 90°C.

The bath is found to give a current efficiency ranging from 60 to 70% when the bath pH was increased from 1.5 to 1.8 in a solution containing 6.5 g dm⁻³ platinum at 1.0 A dm⁻². A low concentration bath shows a high dependence of the current efficiency on the pH of the solution (Fig. 5)

The SEM micrographs (Fig. 6a and b) of platinum deposits of 1 and 3 μm thickness on a titanium substrate show a globular, compact, uniform structure that resembles those produced from a DNS bath. The XRD pattern of platinum (Fig. 7) indicates that the deposits have a preferred orientation in the (111) plane and have fcc structure.

Platinum-iridium alloy deposition

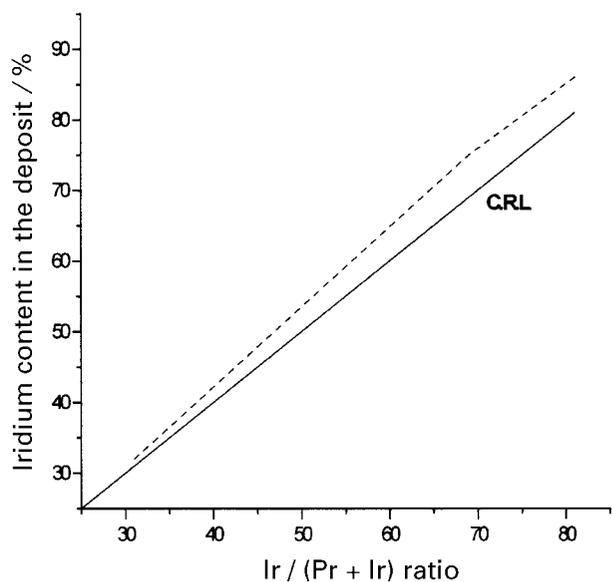
The relationship between the mole ratio Ir:(Pt+Ir) in the electrolyte and the iridium content in the deposit was



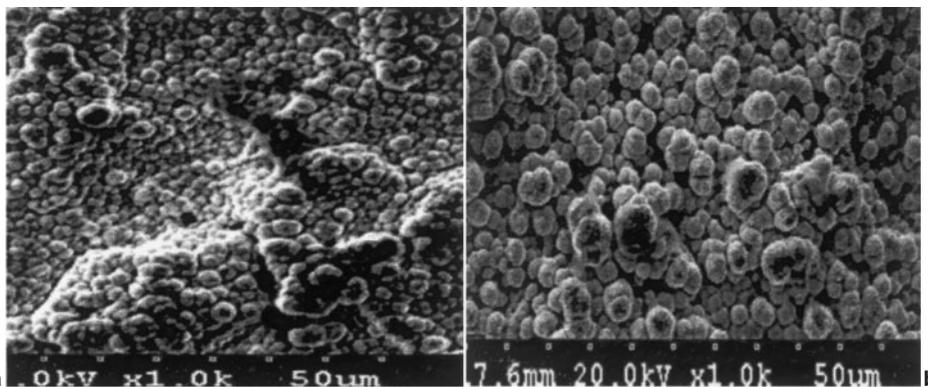
1, (111) plane; 2, (200) plane; 3, (200) plane; 4, (200) plane

7 X-ray diffractograms of platinum

explored. The iridium content in the deposit was always higher than that in the electrolyte indicating the preferential deposition of iridium compared to platinum. Because the standard electrode potential of platinum is lower than that of iridium (Pt = -1.188, Ir = -1.156), the latter should deposit faster than the former. The results in Fig. 8 show that the iridium content in the deposit is



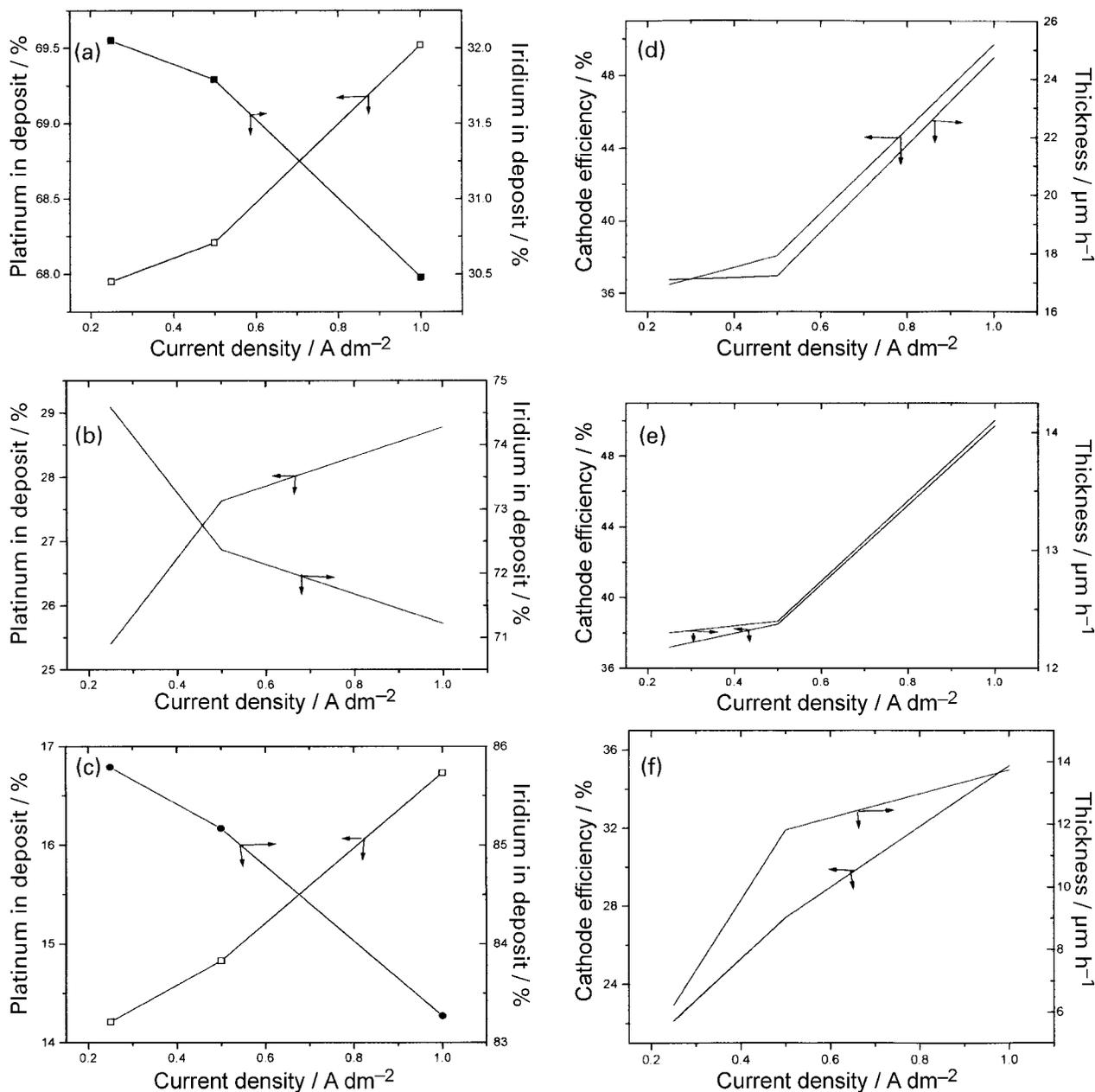
8 Effect of Pt:(Pt+Ir) ratio on the iridium content of the deposit



a, platinum (1 μm); b, platinum (3 μm)

6 SEM micrographs of deposits

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Ir:(Pt+Ir) ratio: a, 0.31; b, 0.70; c, 0.82; d, 0.31; e, 0.70; f, 0.82

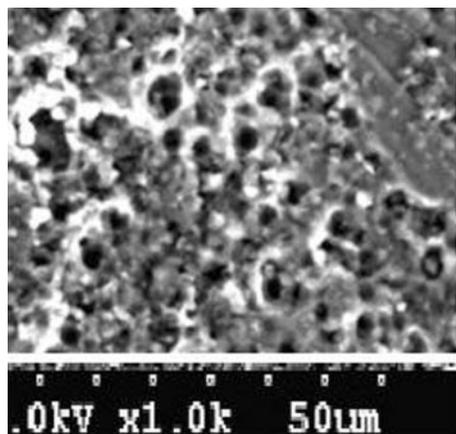
9 a-c, effect of current density on the iridium content of the alloy deposits; d-f, effect of current density on the thickness and rate of deposition of alloy deposition

always higher than its ratio in the bath as shown by the centre line average (CRL). Therefore, this system follows to a normal type deposition process. A higher iridium to platinum ratio results in iridium rich alloys and vice versa. Deposits with 30–85% iridium could easily be produced in a compact, adherent, white form.

Figure 9a-f shows the effect of plating variables on the Ir content of the deposit, cathode current efficiency and the rate of deposition. Deposits obtained at 1 A dm⁻² showed higher efficiency than at low current densities. However, operation at 0.5 A dm⁻² was preferred when considering the quality of deposits. The cathode efficiency ranged from 30 to 40% depending upon the iridium content of the alloy and concentration of the electrolyte. The rate of deposition was found to increase with increase in platinum content in the alloy.

The deposit composition was independent of the pH of the electrolyte in the pH range 0.5–2.0 and the iridium content of the alloy increased with increasing temperature. Below 60°C, the deposits were powdery and non-adherent with very poor current efficiency. Above 75°C the deposits obtained were dense, compact, smooth with a silvery appearance and had good adhesion to the titanium substrate as shown by the quenching test.⁶ Agitation by mechanical means was detrimental, producing deposits of low iridium content and of poor quality.

The SEM micrograph in Fig. 10 shows the structure of the alloy at a thickness of 3 μm to be finer grained than pure platinum or iridium¹⁰ deposited from the bromide electrolyte. The XRD pattern given for the alloy in Fig. 11 indicates that the peaks had an intermediate position with respect to those of platinum and iridium.¹⁰ It was found that with increase in iridium content, the peaks shifted



10 SEM micrograph of platinum-iridium deposit with thickness of 3 μm

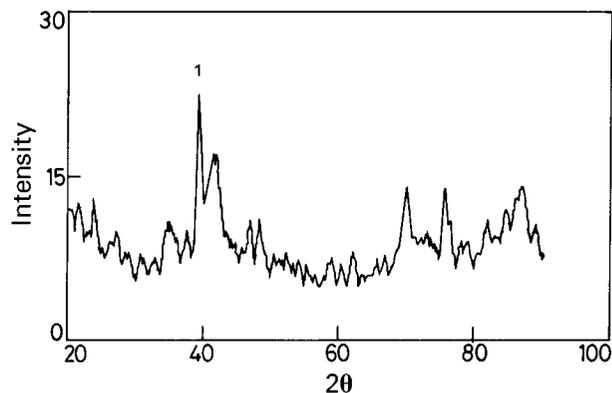
towards higher angles. The results confirmed that the alloy is a homogenous solid solution with an fcc structure with a preferred orientation in the (111) plane. This is in agreement with data shown in the literature.¹¹

Conclusion

A bromide electrolyte is suitable to produce, adherent, compact white deposits of platinum with a 75% current efficiency and good stability on titanium. The above can be used to produce platinum-iridium alloys of various compositions. The process is simple, cheap and reproducible compared to the other commercially used formulations.

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11 XRD spectra of platinum-iridium alloy

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