Electrodeposition of Platinum From an Alkaline Electrolyte

By Stojan S. Djokić

Electrodeposition of platinum from an alkaline electrolyte at 65 °C was investigated. The results showed that the current efficiency did not depend on the current density. Smooth, crack-free deposits were obtained when the thickness of the platinum layer was less than 5 μm. According to XRD analysis, electrodeposited platinum coatings are polycrystalline, with crystallite size ranging from 6 to 15 nm.

Electrodeposited platinum coatings have been used for various industrial applications, such as chemical processes, aerospace devices, electronics etc. Interest in electrodeposition of platinum dates from the 1840s.[1] There were considerable difficulties in the early stages, where electrodeposition of platinum was mainly investigated for batteries and decorative purposes. In recent years, the emphasis has shifted markedly to industrial applications.

Research on electrodeposition of platinum and its alloys was recently reviewed.[2] Various types of solutions have been used. For a review of these solutions, see Ref. 2.

Alkaline solutions for electrodeposition of platinum were used in early developments.[3] These electrolytes were based on $Pt(OH)_6^{-2}$ as a source of platinum, with electrodeposition carried out at 65 to 80 °C. At a current density of 0.8 A/dm^2, and with insoluble Pt anodes, current efficiency was estimated at 80 percent. A similar electrolyte for electrodeposition of platinum was reported by Cramer and Schalin.[4] Above pH 10, current efficiencies ranged from 32 to 45 percent. The originally pale-yellow solution turned brown, however, after seven hr at 80 °C.

Solutions based on chloroplatinic acid were also reported.[5] Because of hydrolysis of chloroplatinic acid, electrodeposition below pH 2 was recommended. Smooth deposits of platinum were obtained. Based on unusually high acid content in this electrolyte, electrodeposition is suitable only for deposition of platinum on noble metal substrates.

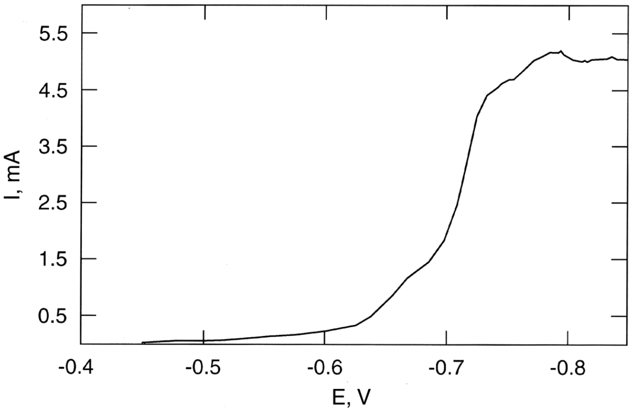


Fig. 1—Polarization curve for electrodeposition of platinum on a 304 stainless steel electrode (65 °C).

Other electrolytes used for electrodeposition of platinum include electrolytes derived from $Pt(NH_3)_2(NO_2)_2$ or $Pt(NH_3)_4^{+2}$, commonly known as solutions based on P-salts and Q-salts, respectively.[6-8]

The aim of this study was to investigate electrodeposition of platinum on stainless steel substrates from alkaline solutions.

Experimental Procedure

Electrodeposition of platinum was carried out from an alkaline solution with the following composition: H_2PtCl_6 12 g/L and KOH 40 g/L. By mixing these chemicals (analytical grade) in distilled water, a pale-yellow precipitate was obtained. To dissolve the precipitate, the solution was boiled and, as a result, a clear yellow solution was obtained. This solution was stable at room temperature for more than eight months.

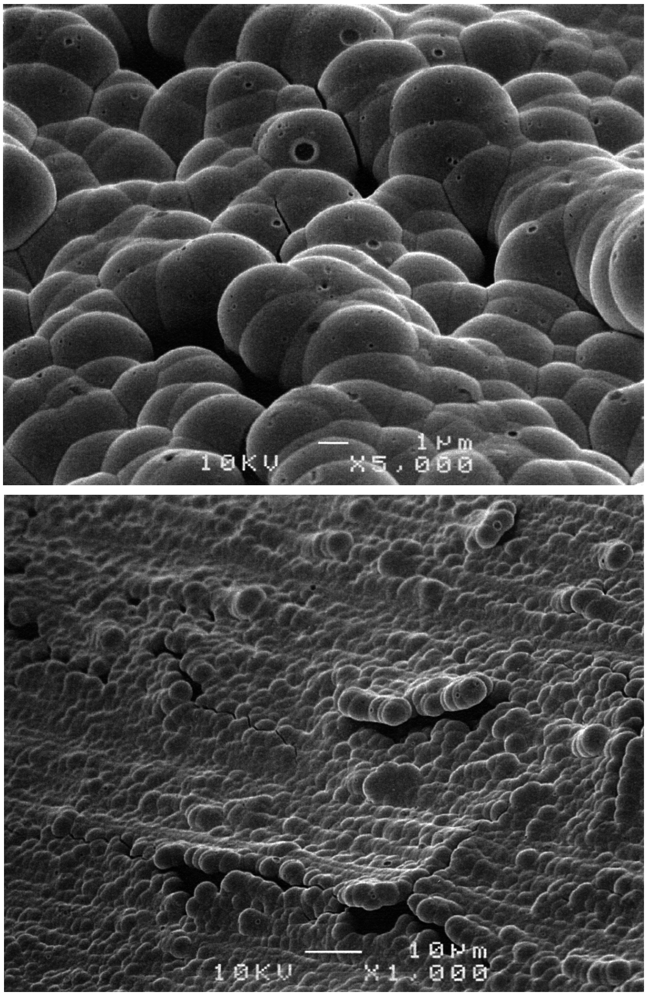


Fig. 2—SEM micrographs of electrodeposited platinum at 3.5 mA/cm^2, 65 °C (thickness about 7 μm).

Electroanalytical measurements were performed using a three-electrode cell arrangement with 250 cm^3 of electrolyte. The working electrodes were prepared from 304 stainless steel and were mechanically polished with 800-grit SiC paper and 0.25 μm diamond paste. Just prior to being placed in the cell, substrates were etched for 20 sec in one-percent H_2SO_4 solution, rinsed with water and dried in air. The apparent surface area of the working electrode was 1 cm^2. Platinum foil served as a counter-electrode. All potentials were measured against a saturated calomel electrode (SCE). Electroanalytical measurements were performed at 60 to 70 °C. Galvanostatic electrodeposition was performed on substrates made of 304 stainless steel, with an apparent surface area of 1 cm^2. In these experiments, a platinum foil served as an anode. Electrodeposition was carried out at 65 °C. Electrodeposited platinum coatings were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and electron dispersive spectroscopy (EDS).

Results & Discussion

Mixing H_2PtCl_6 and KOH in distilled water created an alkaline complex solution of Pt(IV). As soon as H_2PtCl_6 and KOH were mixed, a pale-yellow precipitate was obtained. This is described by the reaction:

$$PtCl_6^{-2} + 4OH^- \rightarrow PtO_2 + 2H_2O + 6Cl^- \qquad (1)$$

The yellow precipitate of PtO_2 is further dissolved by heating the alkaline solution to boiling;[9] a complex ion of $Pt(OH)_6^{-2}$ is produced according to the following reaction:

$$PtO_2 + 2H_2O + 2OH^- \rightarrow Pt(OH)_6^{-2} \qquad (2)$$

According to the literature, the complex $Pt(OH)_2^{-2}$ is stable in solutions with pH above 8.[10]

Calculated pK for the reaction

$$Pt^{+4} + 6OH^- \rightarrow Pt(OH)_6^{-2} \qquad (3)$$

is 20.97.[10] Based on literature data,[10,11] the Gibbs free energy for the above reaction is $G^0_{Reaction}$ = -119.644 kJ/mol. The Gibbs free energy of formation of $Pt(OH)_6^{-2}$ is $G^0(Pt(OH)_6^{-2})$ = -619.502 kJ/mol. The clear solution obtained in this way was stable at room temperature more than eight months.

Polarization curves for the electrodeposition of platinum at 65 °C are shown in Fig. 1. This figure shows that electrodeposition of platinum takes place at potentials more negative than -0.6 V vs. SCE. Electrodeposition of platinum can be described by the reaction:

$$Pt(OH)_6^{-2} + 4e^- \rightarrow Pt + 6OH^- \qquad (4)$$

According to the thermodynamic data given above, standard Gibbs free energy for this reaction is -324.256 kJ/mol and, consequently, its standard potential is E^0 = 0.84 V at 25 °C. Current efficiency of platinum electrodeposition is estimated at greater than 87 percent and does not depend on current density within its range (0.5 to 5.5 mA/cm^2).

Simultaneous with electrodeposition of platinum from the system investigated is hydrogen evolution, which is described by

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (5)$$

with E^0 = -0.828 V.

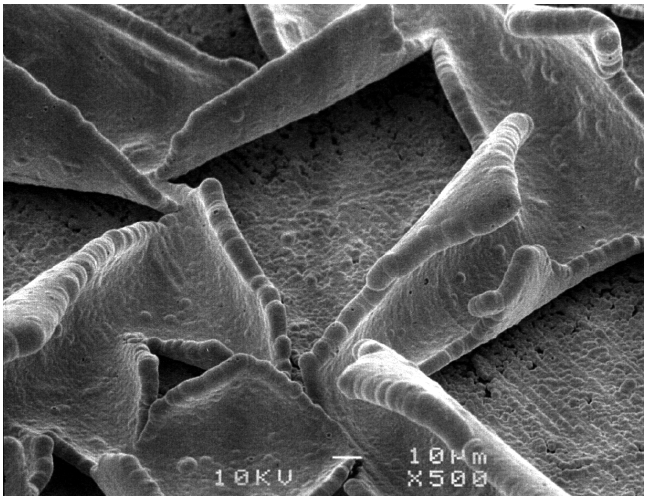


Fig. 3—SEM micrograph of electrodeposited platinum showing appearance of cracks on the electrodeposited platinum coating (Note: deposition of platinum continues on the naked 304 SS substrate after appearance of cracks) (65 °C, 3.5 mA/cm², thickness 5 µm).

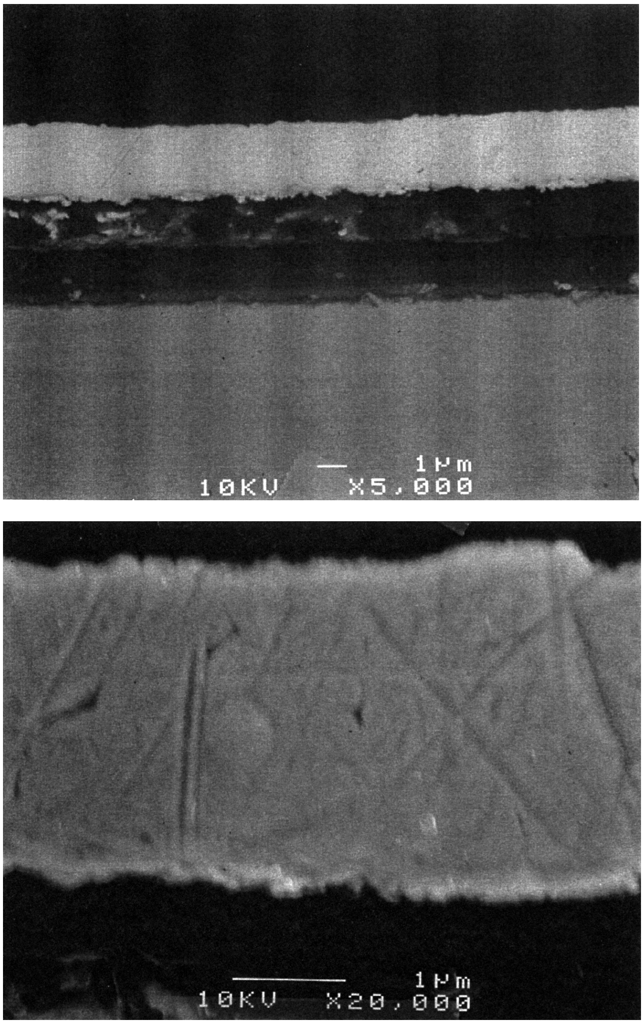


Fig. 4—Cross section of electrodeposited platinum coatings (current density 3.5 mA/cm², 65 °C).

Surface Morphology & Structure of Electrodeposited Platinum

Electrodeposited platinum coatings were bright and metallic in appearance. EDS analysis found that the electrodeposited platinum contained about 99.83 percent pure platinum. Impurities included potassium (0.06%) and chlorine (0.11%). Surface morphology of platinum deposits depended on current density and time. Figures 2a and b show SEM micrographs of electrodeposited platinum. These micrographs reveal that the electrodeposited platinum exhibited a cauliflower surface morphology. For coatings thicker than 5 µm, cracks appeared, as shown in Fig. 2b. A formation of cracks is clearly shown in Fig. 3. Crack formation is attributed to high internal stress of electrodeposited platinum, or to poor adhesion to the stainless steel substrate. Hydrogen is probably a source of high internal stress. As stated above, during platinum electrodeposition, hydrogen is simultaneously evolved. Simultaneous hydrogen evolution during electrodeposition leads to its partial incorporation into metal deposit. Uniform, crack-free deposits of platinum were obtained when the thickness was less than 5 µm. The cross section of platinum deposits is shown in Fig. 4. This figure shows uniform deposits of platinum with a thickness of about 3 µm.

Figure 5 shows the XRD pattern of electrodeposited platinum films from the solution investigated. This XRD pattern shows that polycrystalline film of platinum with orientations (111), (200), (220), (311), and (222) were deposited. Crystallite sizes were estimated from the half-width peak and ranged from 6.2 to 15 nm (see Fig. 5).

Conclusions

Electrodeposited platinum from an alkaline electrolyte leads to the production of smooth coatings with a cauliflower surface morphology. The uniform, crack-free coatings of platinum, under the conditions investigated, were obtained when the thickness is less than 5 µm. Current efficiency, about 87 percent, did not depend on the current density within its range (0.5 to 5.5 mA/cm^2). Impurities in the platinum coatings included K and Cl, and were estimated at about 0.2 percent. Based on the XRD analysis, electrodeposited platinum films are polycrystalline with crystallite size ranging from 6 to 15 nm.

Editor's note: *Manuscript received, July 1999.*

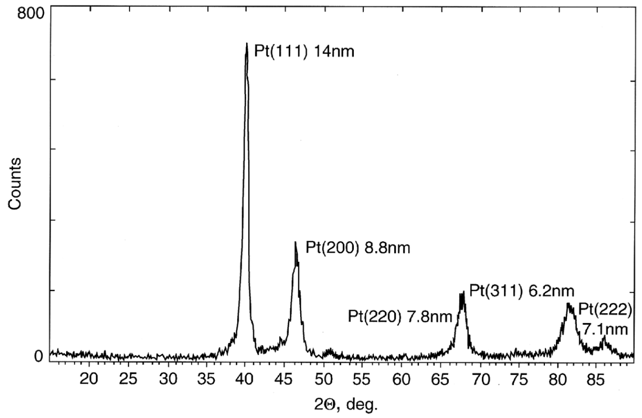
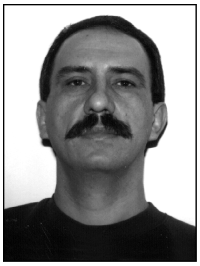


Fig. 5—XRD pattern of electrodeposited platinum coating (65 °C, 3.5 mA/cm^2, thickness 5 µm).

References

1. P.D. Buchanan, *Platinum Metals*, **25**(1), 32 (1981).
2. M.E. Baumgärtner & Ch.J. Raub, *Platinum Metals*, **32**(4), 188 (1988).
3. E.C. Davies & A.R. Powell, *J. Electrodpositors Tech. Soc.*, **13,** 7 (1937).
4. S.D. Cramer & D. Schlain, *Plating*, **56,** 56 (1969).
5. R.H. Atkinson, *Trans. Inst. Met. Finish.*, **36,** 7 (1958-59).
6. S.I. Khotyanovich, *Vopr. Khim. Khim. Tekhnol.*, (46), 40 (1977).
7. R. Le Penven, W. Levason & D. Pletcher, *J. Appl. Electrochem.*, **22,** 415 (1992).
8. W. Levason, D. Pletcher, A.M. Smith, & A.R. Berzins, *J. Appl. Electrochem.*, **28,** 415 (1998).
9. S.E. Livingstone, in *Comprehensive Inorganic Chemistry*, **Vol. III**, J.C. Bailer, H.J. Embeléus, R. Nylholm & A.F. Trotman-Dickenson, Eds., Pergamon Press, Oxford, 1973; p. 1330.
10. V.A. Nazarenko, V.P. Antonovich & E.M. Nevskaya, *Metal Ions Hydrolysis in Dilute Solutions*, Moscow, Atomizdat, 1977; p. 147.
11. A.J. Arvia & D. Posadas, in *Standard Potentials in Aqueous Solutions*, A.J. Bard, R. Parsons & J. Jordan, Eds., Marcel Dekker, New York, 1985; p. 294.



About the Author

Dr. Stojan S. Djokić is a senior scientist with Westaim Biomedical Corporation, 10102 114th St., Fort Saskatchewan, Alberta T8L 3W4, Canada. He holds a BSc in chemical engineering, an MSc in electrochemical energy conversion and a PhD in electrochemistry/materials science from the University of Belgrade, Yugoslavia. At the University of Ottawa, as a postdoctoral research associate, he has worked in the field of molten salt electrochemistry. Dr. Djokić has published more than 40 papers, including three chapters in Modern Aspects of Electrochemistry *and holds two U.S. patents. His professional experience covers both industrial and academic environments in the fields of electrochemistry, polymeric composite materials, biomaterials, materials science and analytical chemistry. His current interests include electroless and electrodeposition, kinetics, corrosion and biomaterials used in immunodiagnostics and as antimicrobial agents.*