

# The Electrodeposition of Platinum and Iridium from Fused Salts

## AN ELECTROANALYTICAL STUDY OF THE REACTIONS

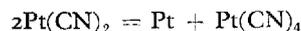
The electrodeposition of platinum from fused salt electrolytes has been successfully developed in the past few years and is being used increasingly, particularly because the deposits show better ductility and a freedom from porosity compared with those from aqueous solutions. A recent paper by the present writer (1) gave an account of the process developed in the Johnson Matthey Research Centre and described a number of its applications.

A further study of the process by William B. Harding of the Bendix Corporation, Kansas City, (2), carries our knowledge of electrodeposition from fused salts a little deeper as it is the first work on these systems in which electroanalytical methods have been applied to elucidate the chemical reactions involved. The work used specially purified melts, generally kept under glove box conditions to control closely melt oxidation.

Initial experiments with lithium chloride-potassium chloride eutectic melts at 450°C gave deposits which were always dendritic and non-adherent. Platinum and iridium could be added to this melt either as the salts  $K_2PtCl_4$  and  $K_3IrCl_6$  or by electrolytic dissolution of a metal anode. The deposit from melts with both metals added was always pure platinum. Voltammetry showed that iridium was about 100mV less noble than platinum and would not be expected to co-deposit.

Greater success was obtained with experiments in the cyanide system. Three melt compositions were chosen, pure sodium cyanide, equal weights of sodium and potassium cyanides and equal weights of sodium cyanide and potassium cyanate. These enabled operation between 450 and 600°C.

Platinum was introduced into these melts using soluble anodes or by adding  $Pt(CN)_2$  or  $Na_2Pt(CN)_4$ . The electroplating performance was unaffected by the melt used, cathode efficiencies from 60 to 80 per cent being obtained throughout, with anode efficiencies ranging from 100 to 275 per cent according to the melt oxidation rate. At low temperatures the sublimation of the cyanide was reduced and so was the decomposition of the platinum salt in the melt. The platinum content of an unused melt fell from 1 per cent to 0.5 per cent over ten days, and then more slowly. This is taken as evidence for the reaction:



analogous to the thermal decomposition of  $PtCl_2$ . It was therefore recommended to use the cyanide-cyanate melt for a practical process because of its greater stability.

Iridium was also added to the melts electrolytically or as  $K_3Ir(CN)_6$ . Cathode efficiency fell rapidly to zero in melts containing cyanate or in cyanide melts after exposure to air. However, an efficiency of 15 per cent could be obtained by raising the melt temperature to 650°C and the current density to 40mA/cm<sup>2</sup>. In pure cyanide melts containing 0.2 per cent iridium anode efficiencies of 100 per cent were reported and cathode efficiencies of 70 per cent, which fell after a period of use to 20 per cent. Higher current densities equated to lower cathode efficiencies and this appeared to be partly due to the formation of a passive layer of polymerised cyanogen on the anode. The fall of the cathode efficiency with time was believed to be due to the presence of an Ir(IV) complex formed by oxidation of Ir(III) at the anode. It was proposed that future work should

include the use of porous diaphragms to separate the anode and cathode in an attempt to eliminate these side reactions.

For alloy deposition, melts containing mixtures of the metals were prepared by the methods described. Although platinum is again more noble the metals will now co-deposit. Deposit composition was not constant in its thickness nor did it bear any relation to the melt composition except at high current density ( $20\text{mA/cm}^2$ ) when deposition was diffusion limited. Alloy deposition was not seen as a practical process unless the side reactions outlined for the individual metals could be controlled.

The deposits were described as being sound and coherent and with mechanical properties comparable to the wrought metal, but no

details of the deposit thicknesses obtained are given except in the case of platinum. Platinum formed columnar deposits with a visibly crystalline surface at 75 microns. Nodular deposits formed at greater thickness.

The carefully controlled experimental conditions used by the author of this work were previously recommended by him in his review paper (3) and the results obtained have done much to resolve apparent differences in the results of previous workers.

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### References

- 1 J. H. F. Notton, *Platinum Metals Rev.*, 1977, **21**, (4), 122-128
- 2 W. B. Harding, *Plating Surface Finish.*, 1978, **65**, (2), 30-35
- 3 W. B. Harding, *ibid.*, 1977, **64**, (9), 48-55

## Recent Patent Literature on Emission Control

**Automotive Pollution Control Catalysts and Devices** BY MARSHALL SITTING,  
Noyes Data Corporation, Park Ridge, New Jersey, 1977, 323 pages, \$39

With catalyst systems now firmly established as the means for controlling exhaust emissions from motor vehicles sold in America, it is opportune for the technology associated with this major new development to be summarised and made available to future researchers in this and related fields.

In their series of Pollution Technology Reviews, the Noyes Data Corporation have followed their previous practice in publishing a book based upon a digest of United States patents in this instance granted in the years 1970 to mid 1977. This period is particularly relevant as it spans the interval in which the major developments in catalyst and related technology were made leading to full commercial exploitation which started in 1974.

In an introductory chapter, the background to the problem of exhaust emissions from motor vehicles is described together with the legislation which has largely determined the systems which have been employed by the car industry for the control of exhaust emissions. These and other possible technical solutions are compared to complete a good summary of the subject.

The following seven chapters are concerned entirely with catalysts and the means for incorporating them into the exhaust system

of a motor vehicle. A chapter on methods for making catalyst supports in the form of pellets, ceramic and metal monoliths is followed by chapters on carbon monoxide/hydrocarbon oxidation catalysts,  $\text{NO}_x$  reduction catalysts and the advanced "Three Way" systems. Both base and noble metal catalysts that have been evaluated are in many cases described in detail. The review is completed with chapters on the overall converter systems and their components and control devices.

While, there is no detailed subject index, the combined contents and subject index are adequate to enable information on a particular aspect of the subject to be found without reading the complete book.

The book is likely to be of interest to those already working in this field as a source of reference information. To others involved in catalyst research but not familiar with this particular application the book will provide an insight into new developments in support technology, the use of promoters to achieve specific activity goals and not least, the means for achieving high temperature stability and durability in conditions previously considered beyond the reach of catalyst technology.

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