

# Electrochemical deposition of iridium and iridium-nickel-alloys

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**Abstract.** To develop durable and reliable electronic contacts, precious metals are still very important for finish plating of contact surfaces. The lesser-known iridium might be an interesting alternative to substitute gold alloys, platinum or rhodium for applications with highest demands to wear and corrosion resistance such as sliding and plug contacts. As matters stand there is no commercial electrolyte for iridium plating. Initial investigation screened the parameter range for different iridium compounds when an iridium layer occurred on the substrates. This approach showed that the oxidation state of iridium is crucial to reach contenting deposits. Best results came from Ir(IV) electrolyte with high bromine concentration coming from the starting compound, while electrolytes made from Ir(III) compounds gave very poor deposits. In subsequent experiments different organic compounds were added to the electrolytes to improve plating efficiency and stability of the solutions. So found electrolytes gave crack-free deposits up to two microns with a micro-hardness of 600 HV. To reduce the iridium content in the layer, iridium-nickel-alloys were investigated, finding that a nickel-content of 10 wt% raised the layer hardness to more than 900 HV.

## 1. Introduction

Despite iridium having some remarkable physical and chemical properties regarding the needs of electronic or chemical industries, the platinum metal is only used for niche applications. Insoluble anodes made by thermal oxidation of iridium compounds are used for electrolysis or electroplating processes. [1] Furthermore there is a wide field of scientific uses in sensory applications. Iridium oxide is known to be pH-sensitive, so it became a preferred material for measurements in biological media. Thin iridium layers can be used as planar micro sensors for pH-measurement or as stimulating electrode for medical purposes. Such iridium layers are commonly made by physical vapour deposition or thermal oxidation of iridium compounds.[2] Vacuum-metallized iridium-platinum-layers are used as wear protection for hardware with direct contact to molten glass.[3]

There are some uses as alloying constituent in platinum alloys to improve hardness and corrosion resistance. Such materials can be found in jewellery or premium pen tips as well as electronic contacts and spark plug tips. Electronic contacts are implemented by tight fittings or welding contacts. There is a much wider field of application for iridium as a contact material, due to its good electrical conductivity, the high hardness and the outstanding corrosion resistance. The galvanic deposition of iridium layers could unlock these potentials, if an efficient electrochemical process can be developed.



Incipient investigations concerning iridium plating were carried out by Tyrell and Conn. [4-5] The present research project pursues the improvement of the electrodeposition process for iridium and the identification of coating characteristics. The project aims to utilize iridium as an option for finish plating of contact surfaces and to search for new alloying elements to improve the properties of such surfaces.

## 2. State of the art

To date there is no commercial electrolyte for the deposition of iridium. There were some investigation to reduce iridium from fused salt electrolytes, which gave good adherent and ductile deposits up to 100  $\mu\text{m}$ . The plating bath was based on a mixture of sodium- and potassium cyanide, but the process required high operating temperatures combined with water and oxygen free conditions, which were ensured by an argon atmosphere. The high expenditure for equipment and process control as well as the high failure proneness caused by smaller contamination made the process not very beneficial for contact plating. [6]

First investigations of aqueous iridium electrolytes were realised in the 1960s. Comprehensive studies of different electrolytes were carried out by Tyrell. These electrolytes were made by dissolving hydrated  $\text{IrO}_2$  in various acids. He found that an electrolyte based on hydrobromic acid gave best results. [4] Conn used an electrolyte based on iridium(III)chloride and sulphamic acid, but he needed unusual high anodic current densities to sustain the deposition [5]. MacNanmara investigated different iridium-halogen complexes and concluded, that the tetravalent state is crucial for the deposition [7]. All found electrolytes had low cathode efficiencies, which decreased further when the solution was worked. A more recent paper by Sheela verified Tyrells experiments, but used another preparation route for the iridium bromine solution [8]. All mentioned works were concerned with the deposition of pure iridium layers and focussed on the behaviour of the electrolyte itself. There is no detailed information about the characteristics of the iridium layers.

Very few publications dealt with the co-deposition of other metals to create an alloyed iridium layer. Tyrell and Sheela investigated the deposition from iridium-platinum solutions. [9,10] Sheela implemented iridium-platinum alloys with amounts of 30 % to 70 % iridium depending on the used current densities and the iridium contents of the solutions.

## 3. Experimental

The iridium salts used in the present work are outlined in table 1. To allow a big amount of experiments, the electrolyte volumes were limited to 30 ml in beakers of 50 ml. The iridium concentration was set to 5 g/l iridium for the experiments. To reduce the evaporation loss and to get a constant distance between anode and cathode, the electrodes were mounted in a lid. The substrates were made from printed circuit board material with 30 $\mu\text{m}$  copper and etched to samples with a size of 1  $\text{cm}^2$ . To ensure that the strong acidic electrolyte with  $\text{pH}=2$  won't attack the substrates a coating system of 15  $\mu\text{m}$  nickel and 1 $\mu\text{m}$  gold was applied before the iridium plating to protect the copper. The pure nickel layer was applied by galvanic deposition from the electrolyte Nicorsit EPG supplied by BECE. The gold layer was made by galvanic deposition from the Dodurex electrolyte Puramet 202 to get pure gold layers.

**Table 1.** Iridium salts used for the experiments.

| chemical designation       | valence | chemical purity | supplier       |
|----------------------------|---------|-----------------|----------------|
| sodium hexabromoiridate    | (IV)    | 99.9%           | Metakem GER    |
| hydrogen hexachloroiridate | (IV)    | 99.9%           | Metakem GER    |
| iridium acetate            | (III)   | 99.9%           | Heraeus GER    |
| iridium chloride           | (III)   | 99.9%           | Alfa Aesar GER |

Sections of the substrates which did not dip into the electrolyte where protected by an adhesive tape, to avoid any contamination caused by the aggressive vapour. Platinum sheets of 4 cm<sup>2</sup> or insoluble iridium oxide electrodes were used as anode. So the anode-cathode-ratio amounted 4:1. The convection of the electrolyte was ensured by a magnetic mixer in combination with a controlled heating. The temperature varied from room temperature up to 80 °C with constant steps of 20 K. Since very low but constant currents where required – especially for long term experiments – a potentiostat was used as source of electricity.

First of all some screening experiments were made to get an overview of the electrochemical properties of the dissolved iridium salts and their behaviour in different conditions. The main parameters were temperature, pH-level und current densities. The plating time was set to 15 min. The parameter range is summarised in table 2.

**Table 2.** Parameter range for screening experiments.

| parameter       | lowest value        | highest value        | intervals           |
|-----------------|---------------------|----------------------|---------------------|
| temperature     | 20°C                | 80°C                 | 20K                 |
| pH-value        | pH=2                | pH=8                 | pH=2                |
| current density | 3mA/cm <sup>2</sup> | 21mA/cm <sup>2</sup> | 9mA/cm <sup>2</sup> |

Next attempt was to improve the deposition characteristics by different additives. As the mode of action for these additives wasn't known in detail, a practical selection was made from compounds used in similar platinum metal electrolytes. The investigated additives and their concentrations are listed in table 3. To reduce the number of experiments, the temperature was set to 80°C while the pH-value was set to pH=2. Electrolytes, which gave an iridium layer within the first 15 min were determined for longer periods to study the efficiency behaviour during the process. Therefore the layer thickness was determined after 15min of plating, bevor the process continued on the same substrate.

**Table 3.** Additives used during experiments.

| chemical designation | chemical formula                             | investigated concetrations [mmol] |     |     |
|----------------------|----------------------------------------------|-----------------------------------|-----|-----|
| sulphamic acid       | H <sub>2</sub> NSO <sub>3</sub> H            | 52                                | 206 | 412 |
| oxalic acid          | C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> | 5.5                               | 28  | 55  |
| ascorbic acid        | C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> | 5.6                               | 28  | 56  |
| nitrite acid         | HNO <sub>3</sub>                             | 3.2                               | 16  | 32  |
| phosphonic acid      | H <sub>3</sub> PO <sub>3</sub>               | 2.4                               | 12  | 24  |
| sulphuric acid       | H <sub>2</sub> SO <sub>4</sub>               | 2                                 | 10  | 20  |

The layer thickness was determined by x-ray fluorescence (Oxford X-Met 7500, acceleration voltage 45 kV, 30 s measurement time). The reference thickness for the calibration was ascertained by measuring the polish cross section. Due to the small cathode area there were no quantifiable weight differences. So the cathodic efficiencies were calculated from the layer thickness determined by x-ray fluorescence. The measured layer thickness divided by the theoretical thickness calculated from Faraday's law gave a good approximation of the efficiency. All efficiencies given in this paper were calculated from a minimum of three experiments. The quality of the layers was rated by visual impression. For layers of more than 1µm thickness the micro hardness was measured by nanoindentation with the Fischerscope H100c (Fischer, Germany) The test force was adjusted to 3 mN for a period of 10 s until the force was retracted. An optical analysis of the formed layers by microscopy gave information about cracks and pores.

Latest experiments were concerned with the development of iridium-alloy deposits. Different elements were considered to give an alloy with iridium to reduce the noble metal consumption and these were phosphor, silver, copper and nickel. To determine the contents of the alloys x-ray fluorescence analysis and energy dispersive x-ray analysis (Bruker Quantax 200, energy 25 keV, 2 min measurement time, area 2.5 x 1.8 mm<sup>2</sup>) were used. To avoid the distortion of the results by measuring the nickel signal coming from the substrate, the substrates were directly coated with 2 µm gold from the Puramet electrolyte, without any nickel interlayer.

#### 4. Results

##### *Iridium chloride*

The aqueous solution showed an orange colour and pH 1,8 after dissolving the salt. It was not possible to get any deposit from this solution by itself. According to reference 6, there was a very thin iridescent film when sulphamic acid was added with concentrations of more than 200 mmol/l and high temperatures of 80 °C occurred. In the investigated range of current densities, no further deposit was observed. All other additives did not tend to result in any advance. Raising the pH-value led to black precipitate formed on the anode. This effect was increasing for higher current densities.

##### *Iridium acetat*

The dissolved salt had a very low electrolytic conductivity, so inorganic acids were added to reduce the electrolytic resistance. The cyan coloured solution did not give any deposit. The addition of oxalic and sulphamic acid led to very thin layers in conditions of 80 °C and pH=2, similar to the layers formed in the iridium chloride electrolyte. The precipitate formation for higher pH-values was although very similar to that observed in the iridium chloride electrolyte.

##### *Iridium hexachloroiridate*

This solution gave black-brown powdery deposits for current densities of more than 10 mA/cm<sup>2</sup> and temperatures higher than 60 °C, while there was not any layer formation for lower current densities. The addition of nitrite acid as well as sulphuric acid led onto metallic depositions, with very low cathode efficiencies of less than 10 %. After 30 min the deposition ceased. There were no possibilities found to restart the process.

##### *Sodium hexabromoiridate*

The bromoiridate gives the best results of all investigated iridium compounds. Adherent bright layers are formed from 3 to 12 mA/cm<sup>2</sup> in conditions of pH=2 and temperature range from 60 °C to 80 °C. The cathode efficiency averages 40% at the beginning of the plating process for 3 mA/cm<sup>2</sup> and 80 °C, but decreases with increasing current densities. Plating with 60 °C gives poor efficiencies of less than 5%. During the first 15min the electrolyte changes colour from green to dark blue. If the electrolyte is worked with current densities between 3 and 12 mA/cm<sup>2</sup> the efficiency slowly decreases. For current densities of more than 30 mA/cm<sup>2</sup> the deposition stops after 45 min. If the anodic current density exceeds 20 mA/cm<sup>2</sup> a black powder covers the anode. After filtering off this precipitate, the iridium concentration halved.

The most interesting additives are nitrite and oxalic acid. The nitrite acid raises the cathodic efficiency to 50 % while a current density of 3 mA/cm<sup>2</sup> is applied. The improved efficiency is stable for 3 h. Because of the low pH-level, the substrates are attacked through some defects in the gold layer, caused by delamination. For that reason this electrolyte was no longer regarded. The oxalic acid has a comparable positive effect on the deposition rate with 3 mA/cm<sup>2</sup> and raised the cathodic efficiency to more than 60 %. The colour change from green to blue is inhibited during the first 30 min of the process. Similar to the behaviour of the pure bromoiridate solution, the efficiency is not stable for longer terms and relapses to 30 % after 3 h. Thereafter the efficiency decreases over process time. This behaviour is depicted in figure 1. After 6 h the experiments were stopped, while the efficiency

was reduced to less than 15%. Refreshing the electrolyte by adding oxalic acid during the process did not show any positive effect.

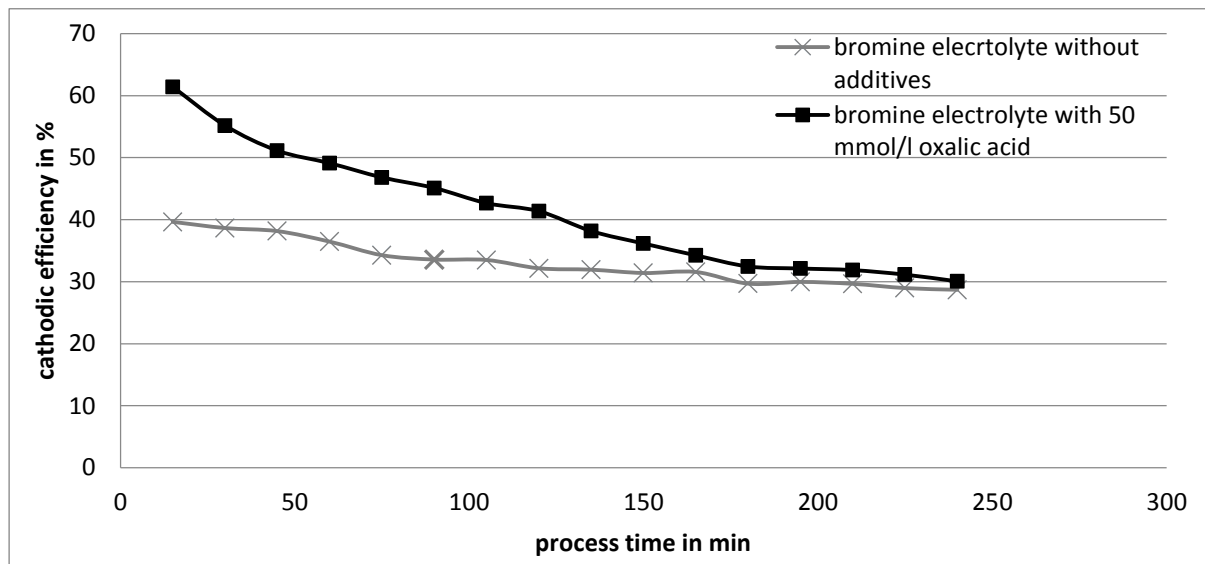


**Figure 1.** Electrolytes worked with 3 mA/cm<sup>2</sup> and 80 °C.

The layer thickness is limited to 2 µm. Higher thicknesses caused cracked deposits and delamination due to internal stress. A clear correlation between current density and propensity for cracked layers was found. The cracking occurred much earlier when the electrolyte was worked with high current densities (see also figure 2 and figure 3). The maximum thickness of 2 µm was reached with 3 mA/cm<sup>2</sup> starting from fresh electrolyte. Worked electrolytes tend to give cracked deposits with increasing age. Furthermore the electrolytes with oxalic acid tend to crack earlier, but there was no quantified limit for layer thicknesses from oxalic electrolytes. The hardness was measured to 600 HV for pure iridium deposits with small quantities of bromine and oxygen incorporated. There is no sign, that oxalic acid had any impact to the layer hardness.

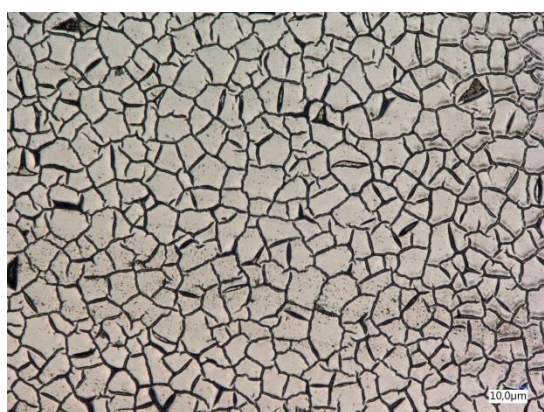


**Figure 2.** Cracked layer, 21mA/cm<sup>2</sup>, 1 µm.



**Figure 3.** Crackfree layer, 3mA/cm<sup>2</sup>, 1 µm.

#### *Iridium alloys*

As the best results came from the hexabromoiridate solution, this electrolyte should be used for the alloying experiments. For that reason silver could not be investigated. Free bromine would react with silver ions to form the low-soluble silver bromide. Phosphor added as phosphonic or phosphoric acid

did not have any impact to the deposition, but there was never any incorporated phosphor measured. The addition of sodium hypophosphite resulted in a colour change to orange when the solution was heated. No deposition is possible from this electrolyte. The copper solved as copper sulphate hindered the deposition, so that the efficiency decreased very fast until the reduction stopped. This effect was already observed, when the copper on the substrates was attacked by bromine vapour. Very low concentrations reduced the efficiency to less than 5 %.

From the suggested elements, only nickel could be co-deposited by dissolving nickel sulphate in the bromine electrolyte reaching a nickel concentration of 1 g/l. The temperature behaviour followed the base electrolyte made from hexabromoiridate. Thin deposits are obtained from 60 °C to 90 °C with an efficiency optimum at 80 °C. The nickel content raises the efficiency for low current densities to more than 80 % for initial deposition, but working this electrolyte decreased the efficiency over time to 30 %, which conforms to the values of the pure iridium electrolytes. For higher current densities the efficiency never exceeded 40 % while a fast decline to 30 % was observed after 1 h.

The current density has the strongest impact to the nickel content of the obtained layers. The relation for an electrolyte with 1g/l nickel is shown in figure 4. Low current densities gave also low nickel contents in the coating, while raising the current density to more than 10mA/cm<sup>2</sup> leads to nickel contents of 16%. This content is very stable when higher current densities up to 20 mA/cm<sup>2</sup> are applied. Nickel concentrations from 0.1 g/l also give incorporations of 10 % for plating with 6 mA/cm<sup>2</sup>.

To date of this publication there are no indications that higher nickel concentration would lead to higher incorporation rates than the maximum of 17 % that was already reached with 1 g/l nickel.

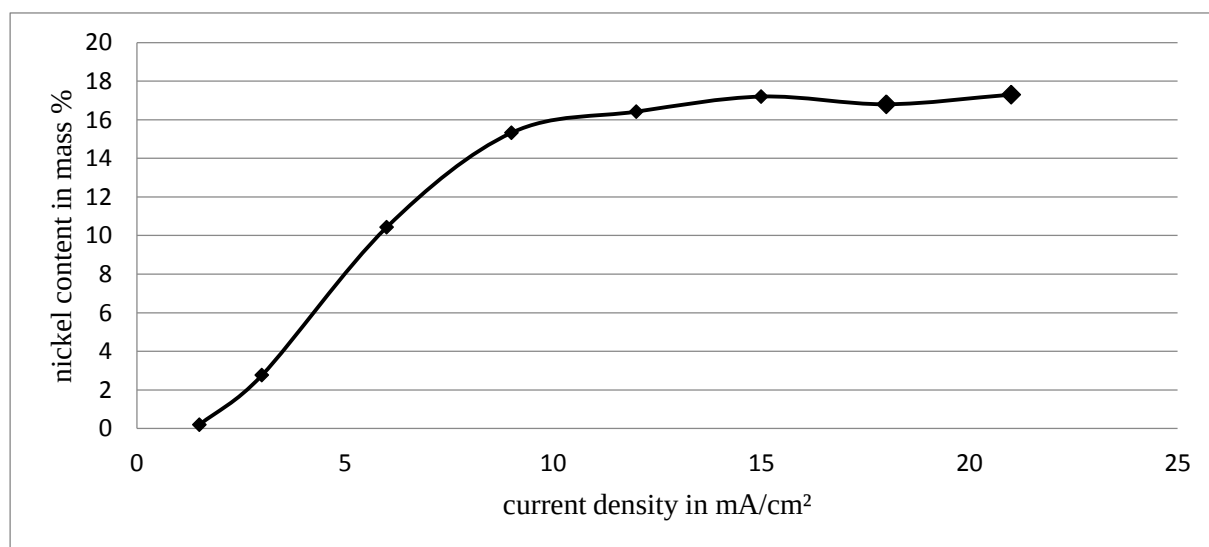


**Figure 4.** Nickel content as a function of cathodic current density (with 1g/l nickel).

The characterisation of the iridium-nickel-deposits showed crack-free layers for thicknesses smaller than 2 µm made from fresh solution with 3 mA/cm<sup>2</sup>. Deposits from worked electrolytes or higher current densities resulted in cracked layers and delamination as already observed for the pure iridium electrolyte. Crack-free iridium-nickel-layers of 1.5µm thickness possessed a hardness of 900HV measured by nanoindentation.

## 5. Conclusion

The experiments confirm the assumption made by Macnamara and Tyrell [4,7], that the tetravalent state is crucial for the reduction of iridium from aqueous solutions, due to the fact that there was no adequate deposition from trivalent iridium salts. However, there should be additional studies to explain the mechanism of the reduction process for iridium.

The only working electrolyte is still based on bromine solutions. High temperatures are identified as primary parameter to form an appropriate complex to reduce iridium from aqueous solutions. This formation starts at 60 °C and has an optimum at 80 °C. Second to temperature a low pH-level is vital for the deposition. The current efficiency raises with decreasing pH-level. For practical aspects a pH-level lower than pH 1.5 is not useful, due to massive substrate attack.

The current efficiencies that were obtained in previous experiments by Tyrell and Sheela [4,8] can be improved by the addition of oxalic acid to a maximum of 60 %. Further investigations should be concerned with the maintenance of this efficiency level.

The electrolyte made from hexabromoiodate gives bright, adherent and crack-free deposits up to 2µm thickness with a plating rate of 0,8µm/h for optimum parameter values, which is an adequate form for practical applications. The layer hardness of 600HV is very encouraging to force the development of iridium plating for electronic contacts with abrasive strain. Furthermore the co-deposition of nickel in crack-free layers with 2µm thickness heightened the hardness to 900HV. This is a promising result to develop contact plating with excellent wear resistance compared to other platinum metals or hard-gold. For coming experiments contact and corrosion resistance of such layers should be determined to get a more detailed characterisation.

## Acknowledgment

The present work is a co-operation between the “University of Applied Sciences Mittweida” and the “Institute for precious metal chemistry FEM” in Schwäbisch Gmünd. The research project “Development and characterisation of iridium- and iridium-alloy-deposition for electrical contact applications” is publicly sponsored by budgets of German Federation of Industrial Research Associations (AiF) with the identification number 18543BG.

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