

Development of the Noble Metal/Oxide Coated Titanium Electrode

PART II: THE MOVE FROM PLATINUM/IRIDIUM TO RUTHENIUM OXIDE ELECTROCATALYSTS

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In the first part of this paper, published in the January issue, development work resulting in the first noble metal/oxide coated titanium electrode was described and some of the teething problems encountered were discussed. Here, the story is continued with the further development of paint compositions: platinum-only and platinum/iridium, for coating the electrodes, and their utilisation in chlorate, mercury- and diaphragm-type chlor-alkali cells. Later, these coatings were replaced by ones containing ruthenium dioxide. This part begins with the early platinum paint compositions.

One commonly-used, early, resin-ate-based, platinum-only paint, Engelhard '05X', had an aromatic smell that operators at that time are unlikely to forget. Because of its original function for metallising ceramic capacitors used in the electrical industry, the paint contained small amounts of rhodium and traces of tin and bismuth, to help with wetting and coating adhesion. Even as late as 1965, '05X'-coated titanium electrodes were being evaluated in the U.K. in both mercury- and diaphragm-type chlorine cells. Performance in the former was disappointing, mainly because of the inevitable anode/amalgam shorts and the formation of 'mercury butter' (a localised thickening of the electrolyte), but the performance of the '05X' platinum coatings in diaphragm-type chlorine cells was more encouraging.

Resinate Based Paint: 70/30 Pt/Ir Coatings, 'Ir1'

By 1965, there was an increasing switch from pure platinum to a nominal 70/30 platinum/iridium, Pt/Ir, coating; the origin of the 70/30 ratio can be traced back to *ad hoc* trials at International Nickel. Once it was ascertained that this composition was superior to platinum, the 70/30 formulation became rather 'written in stone'.

The fact that platinum will dissolve in aqua regia, and also alloys with up to 30 per cent iridium is fortuitous, and apparently had no bearing on the original selection. The Hanovia Division of Engelhard made up a resin-ate-based paint to the nominal 70/30 Pt/Ir ratio, their so-called 'Ir1', but without any additives – as no-one asked for them.

The 'Ir1' paint was destined to have a long history, and still has residual commercial use today. After repeated paint/thermal decomposition cycles, see Figure 3, to build up a significant deposit, it was thought appropriate – for no good technical reason at the time – to apply a Beer-type post heat treatment. Industry would not tolerate the uncertainties of the ammonia/butane component of Beer's post heat treatment, but there were on hand various non-oxidising atmospheres, such as cracked ammonia and hydrogen-containing burnt town gas. So, completely by arbitrary selection, after the paint/thermal decomposition of the 'Ir1' paint, air was flushed out of the furnace using argon, followed by cracked ammonia for 15 minutes, then argon again and finally flowing air for 60 hours. Those chlorine and chlorate producers who tested the nominal 70/30 Pt/Ir coated electrodes in long-term trials (~ 2 years) with and without the 'full



Fig. 3 Laboratory track and tunnel furnace used in the preparation of small electrodes by the paint/thermal decomposition process. The small electrodes are suspended between large heat-conserving baffle plates

post heat treatment', invariably selected electrodes that had received the full heat treatment.

All this may seem to be laboured unimportant commercial practice, but later examination of coatings done by techniques not available in the mid 1960s revealed some interesting findings: while the as-deposited 'Ir1' coating was basically a solid solution alloy of platinum and iridium, it did contain a small quantity of iridium oxide. However, after the full post heat treatment, the composition changed almost entirely to Pt + IrO₂. Thus, the preferred composition for electrocatalysts, found by testing in chlorate and diaphragm-type chlorine cells, comprised platinum metal and iridium oxide, and not as once thought a solid solution of iridium in platinum.

It was later discovered that coatings of platinum and iridium oxide can be formed, without the need for the complex post heat treatments, if a paint is made up from chlor-platinic and chlor-iridic acids dissolved in an alcohol,

and then thermally decomposed at a higher temperature than is used for the resin-based 'Ir1' paint. This is now the favoured method of depositing the so-called 70/30 Pt/Ir coatings.

First Large Commercial Chlor-Alkali Application

In 1968, and still unaware that the true composition of the nominal 70/30 Pt/Ir was a metal/oxide mixture, 'Ir1' resin-based paint was used to coat titanium-based electrodes in two custom-built European sodium chlorate plants, belonging to Solvay et Cie. This was to be the first sizeable commercial application of titanium-based electrodes for chlor-alkali use. The loading of the applied electrocatalyst was low, under 5.0 g m⁻², because the plant was planned to operate at low current density, compared with more recently constructed chlorate plants. Details of the electrode performance remain commercially confidential, but it is understood that the original coatings were still

being used after more than 10 years. The electrodes were later recoated, not because the original coating had worn, but because it had become passivated, resulting in increased operating cell voltage and hence more costly chlorate production.

In the latter part of the 1960s, and early 1970s, the nominal 70/30 Pt/Ir coating was applied to electrodes in several chlorate plants worldwide, at the end of which time it was estimated that over half of world chlorate was being produced using this electrocatalyst. The applied loading for later plants was raised to $\sim 10 \text{ g m}^{-2}$ – to ward off ‘passivation’, often using staggered higher loadings to assist in smooth recoating programmes, which have, so far, been unnecessary.

Passivation of Platinum Electrodes

Passivation requires some explanation. Platinum exhibits an anodic passivation characteristic not unlike that of titanium, namely, an active corrosion zone, and at higher anode potentials a region of passivation – the currents involved in both active corrosion and passivation are small for all practical purposes.

Iridium oxide produced by the optimised paint/thermal decomposition method is believed to be non-stoichiometric in composition but capable of passivation to a stoichiometric, less-electrocatalytically active form.

It was initially difficult to accept that the platinum and iridium oxide components had to be in an active corrosion form for the nominal 70/30 Pt/Ir to have a low chlorine overpotential, though the rate of platinum anodic dissolution is very small even in the active corrosion region.

During operation of the electrodes the platinum selectively dissolves with respect to the iridium oxide; the latter is presumed to be the principal electrocatalyst. If 70/30 Pt/Ir is applied initially at too low a loading, or operated at too high a current density, then the platinum passivates and allows the iridium oxide to follow. The coating rarely wears away completely, but in this passivated condition the electrical energy cost for chlorate formation increases.

Irrespective of knowing the true composition,

the nominal 70/30 Pt/Ir coating has been the subject of scares. For example, if there are even a few parts per billion of soluble iridium in the brine then serious decomposition of chlorate will result. Fortunately iridium solubilisation has always been so low that it has never become a commercial problem.

Another example cropped up just when it seemed that the technology of the 70/30 Pt/Ir coating was on a sound course. Electrodes were supplied to one chlorate plant where ‘graphitic’ brine was used as the electrolyte feed, the latter being regenerated brine from the output of mercury-type chlorine cells fitted with graphite electrodes. The 70/30 Pt/Ir coating, assessed by non-destructive monitoring, dissolved unexpectedly fast. When, by chance, the feed was changed to fresh brine, the high wear rate of the Pt/Ir coating reverted to the expected very slow rate. Evidently an example of coating corrosion rate being affected by impurity in the electrolyte.

Just as the corrosion rate of platinum increases as dilution of brine increases, so a similar effect occurs in chlorate technology. The feed to a chlorate plant may begin as saturated brine, but as chlorate forms the residual brine level decreases. If the brine content falls below 100 g l^{-1} , and certainly below 80 g l^{-1} , there is an increase in the corrosion rate. With only a few g l^{-1} of residual brine, coatings which might otherwise last for 5 or 10 years, dissolve in a matter of hours. It is presumed that this is another example of the effects of conjoint chlorine and oxygen generation.

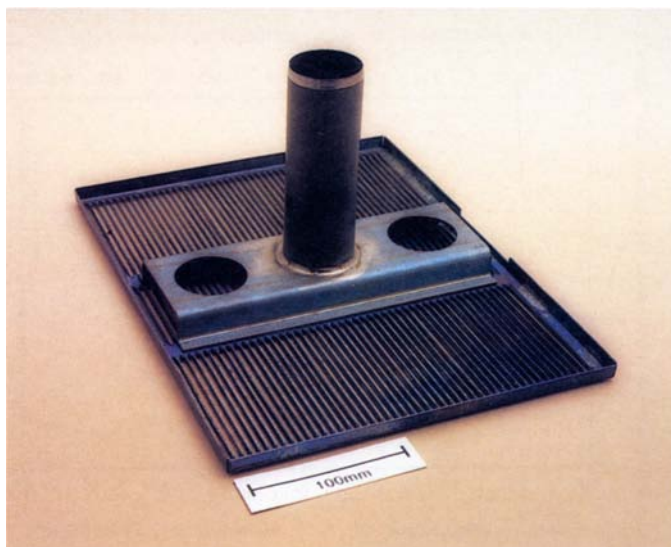
The nominal 70/30 Pt/Ir coating has now largely been replaced by ruthenium-based coatings, probably because of the lower initial cost rather than for technical reasons.

Beer’s Ruthenium Oxide-Based Coatings

By 1965, even with the improved performance from the nominal 70/30 Pt/Ir coatings compared with pure platinum, there was general frustration that more successful coated titanium electrodes for mercury-type chlorine cells, see Figures 4 and 5, had not been found.

In Europe at that time mercury-type chlorine technology predominated, whereas in North

Fig. 4 A prototype titanium anode for a mercury-type chlorine cell, consisting of a central column or post in-filled with copper for the electrical connection; a cross-piece spine connects to a grid coated on the lower part with noble metal oxide. Such anodes come in a range of designs and sizes, larger ones having two or four posts. Much development has gone into ensuring the lowest electrical resistance in the structure to the blades, for minimum usage of titanium



America diaphragm-type cells were mainly used. Beer (still linked with Magneto Chemie in the Netherlands) then proposed another change of coating – to ruthenium oxide. Now, every change of coating type required considerable retesting in the well-established, but costly-to-run, test rigs. Was ruthenium oxide to be another ‘wild

goose chase’? Ruthenium oxide electrocatalyst did seem, on initial consideration, to work, but there existed in industry an inertia to the change from the noble metal to the oxide. It was accepted, with resentment, that if a noble metal oxide did confer attractive chlorine evolution characteristics (many minerals exist in a stable



Fig. 5 The vast size and apparent inactivity of a mercury-type chlorine cell room belies the complexity of construction and continuous high current density electrochemical reactions in progress. This cell room will contain many thousands of titanium-based electrodes

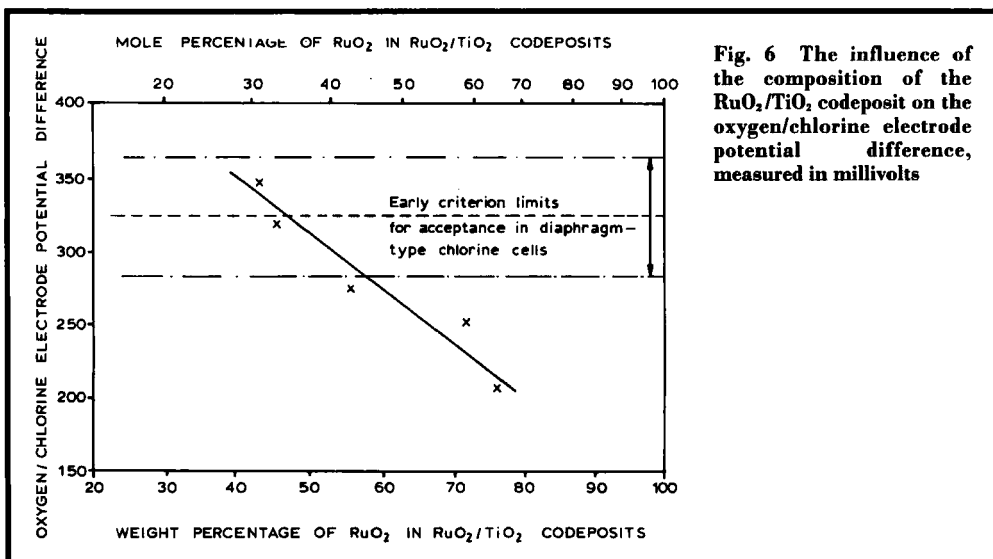


Fig. 6 The influence of the composition of the RuO₂/TiO₂ codeposit on the oxygen/chlorine electrode potential difference, measured in millivolts

oxide form) then oxides might just be suitable.

However, the grudging acceptance of Beer's work, and his desire to speed up exploitation, led him to sell his technical concepts and join forces with de Nora, an electrochemical company in Italy, and to relinquish all ties with ICI.

At about the time of the changeover, Beer filed his now celebrated first oxide patent, 'Beer 65', sometimes affectionately known as Beer 1 (17). He claimed the deposition of ruthenium oxide, and admixing a soluble titanium compound to the paint, to approximately 50 per cent. There are several key aspects to Beer 1:

- codeposition
- depositing a coating of improved adhesion, and
- producing a coating of improved durability in mercury-type chlorine cells.

In 1967, Beer filed his 'Beer 2' patent (18). It would seem routine now to accept a coating composed principally of titanium oxide, but in 1967 it seemed quite ludicrous. All the subtleties of the mixed metal oxide coating could hardly have been appreciated then, when improvements to durability under mercury-type chlorine cell conditions were important.

However, the fact that Beer recognised the advantage of lowering ruthenium oxide content below 50 per cent must be to his lasting credit. Thus, the big breakthrough in chlorine technology was achieved in the manufacture of commercially

viable anodes for mercury-type chlorine cells. To give the user confidence, (a master stroke in commerce) the electrode producer leased anodes and guaranteed performance!

During the 1970s, a method, believed to have originated from the Electrode Corporation (a joint activity between de Nora and Diamond Shamrock) of classifying the performance of coated titanium electrodes for diaphragm-type chlorine cells, was to use a single electrode potential difference as follows:

Chlorine single electrode potential w.r.t. nHE:
 310 g l⁻¹ sodium chloride
 current density 1 A inch⁻²
 temperature 70°C

Oxygen single electrode potential w.r.t. nHE:
 1 M sulfuric acid
 current density 1 A inch⁻²
 temperature 25–30°C

The required difference in potential between the above two values for efficient use in diaphragm-type chlorine cells was held to be 325 ± 40 mV.

It is of interest to compare the variation in the above electrode potential difference with those of RuO₂/TiO₂ compositions, see Figure 6. In order to achieve the required high values, it is

clear that a Beer 2 rather than a Beer 1 formulation must be chosen. The more expensive 70/30 Pt/Ir coating is characterised by potential differences of over 400 mV. The potential difference is effectively a method of stating that an electrocatalyst must have low chlorine overpotential and high oxygen overpotential for chlorine to be selectively released from brine solution (especially from dilute brines).

The potential difference of an electrode is affected by its composition. It is evident that ruthenium oxide is a more powerful chlorine electrocatalyst than oxygen electrocatalyst. By decreasing the effective area of exposed ruthenium by adding titanium oxide, the chlorine overpotential remains low while the net oxygen overpotential rises. Chlorine overpotential remains sensibly low with changing composition, while oxygen overpotential rises with decreasing ruthenium oxide content.

Beer 2 Coatings

Much emphasis has been given in the literature to the fact that codeposited $\text{RuO}_2/\text{TiO}_2$ coatings are true mixed crystals, and that this is the secret of their durability. Both RuO_2 and TiO_2 (rutile) possess the same crystal symmetry, and their lattice constants are similar. For patent reasons (rather than coating performance) there have been many high precision X-ray diffraction studies of such coatings. In general the X-ray lines of the two components are so close that they merge to give apparent single broad peaks displaced in the direction of mixed crystal formation. A complicating factor in lattice parameter considerations has been the relatively large contribution from chloride ions in the lattice (19, 20). If the deposit is heated to $\sim 100^\circ\text{C}$ or higher, above the normal paint decomposition temperature, the X-ray lines separate into ruthenium oxide and titanium oxide compounds (possibly recrystallisation or perhaps coalescence of like species).

In practice, it does not really matter whether such codeposits are true mixed crystals or exceedingly fine-scale intermixes. But, to reiterate, the importance of the Beer 2 patent is the codeposition of ruthenium and titanium oxides

to give a deposit with the required electrode potential difference.

Since the 1970s, titanium-based electrodes coated with Beer 2 type $\text{RuO}_2/\text{TiO}_2$ have totally transformed the chlorine, chlorate and hypochlorite industries and their economics. This success has resulted from an interplay between anode producer and users, which has been far too complex to describe here.

Sodium Amalgam Shorting

In mercury-type chlorine technology there have been various methods, over and above Beer 2 type coatings, of improving resistance to sodium amalgam shorting. In one anode construction a thick, electrically-conducting interlayer was deposited between the titanium and the electrocatalyst. In another, there was deliberate admixture of ceramic particles within the codeposit paint. Previously, graphite electrodes were massive and heavy, and the anode/cathode gap was adjusted by a manually operated screw mechanism. The much lighter titanium-based



Fig. 7 A box-type diaphragm-type chlorine cell anode structure consisting of noble metal oxide coated titanium mesh spot welded to a central copper cored titanium rod and plain titanium sheet gussets



Fig. 8 View of a cell room in a chlor-alkali plant in Saudi Arabia, which uses diaphragm cell technology. Diaphragm cells produce around 75 per cent of the chlorine and caustic soda in the world
 Courtesy of OxyTech Systems, Inc.

electrode structure can be electrically raised and lowered, and sensors have been used to raise anodes automatically during expected amalgam shorts. Sodium amalgam shorts in mercury cells cannot be totally eliminated, but their frequency can be minimised.

Diaphragm-Type Chlorine Cells

There have also been comprehensive changes in diaphragm-type chlorine cells, see Figures 7 and 8. To decrease the anode/cathode gap, there was a change in anode design from the 'thin' box to the 'thick' box construction, and then to expandable anodes, where the ends of the diaphragm were left open for springiness. The natural asbestos-based diaphragms have been replaced by synthetic ones, and the cathodes have also been changed; a succession of modifications now leaving little room for improvements to either current or power efficiency.

During the change-over from graphite to titanium-based electrodes in diaphragm-type chlorine technology, K. O'Leary of Eltech Corporation filed an interesting patent claim (21). He proposed that coatings would be cheaper and electrode life extended if part of the ruthenium oxide was replaced by tin oxide. For example, where a 20 g m^{-2} Beer 2 coating might have

a life of 8 years, the O'Leary composition (with half the RuO_2 content) raised life expectancy to around 12 years.

It is interesting to conjecture why the O'Leary modification is successful. Decreasing the ruthenium oxide content to below about 30 per cent raises the potential difference of the electrode in sulfuric acid and chloride solutions, see Figure 6. A restriction on decreasing the RuO_2 content too far is that the associated electrical resistance of the $\text{RuO}_2/\text{TiO}_2$ mixture progressively increases, and the voltage drop across the coating contributes significantly to the net overpotential. It would seem that the more electrically conducting SnO_2 , compared to TiO_2 , allows the RuO_2 level to be decreased without unduly raising the overall electrical resistance of the coating.

A similar explanation could explain the successful coatings patented by Solvay (22) which allow the RuO_2 content to be lowered, compared to TiO_2 , by adding RhSbO_4 . The Canadian company Chemetics would seem to have 'fine tuned' this variety of coating (23).

During the years where the Beer 2 patent owners and licensees held a monopoly, many attempts were made to compete. There were also professional patent breakers, whose aim was to damage the validity of the Beer patents, but none met with much success.

One route taken to circumvent the codeposition aspects of the Beer coatings was a two stage process. In the first part, a bed of porous titanium oxide was formed electrochemically on etched titanium from a Ti^{3+} solution (24). This

was then infilled with RuO₂ by a paint/thermal decomposition route. The resultant coating was a fine scale mixture (not mixed oxide) of RuO₂ and TiO₂ at an approximately stable ratio of ~50/50 weight per cent. When electrodes coated in this way were first introduced into diaphragm-type chlorine cells, the chlorine efficiency was claimed to be marginally lower than in cells fitted with Beer 2 codeposited coatings. The two stage method did produce slightly more oxygen in the chlorine, slightly increasing the risk of explosion during liquefaction of the gas, but it also gave rise to less chlorate in the anolyte than occurred with Beer 2 coatings. In at least one chlorine plant it was thought better to accept slightly more oxygen in the chlorine so that less chlorate in the anolyte would pass through the diaphragm, thus minimising plant corrosion in the evaporator stage.

Now that the Beer patents have expired, any adjustment to the RuO₂/TiO₂ ratio can easily be achieved by adjusting the starting composition of the paint. This two stage coating process, which in the fullness of time gave electrodes with lives comparable to those of Beer 2 coated electrodes, would seem to disprove the need to use true mixed oxides for maximum electrocatalytic activity.

The efficiency of diaphragm-type chlorine cells is acutely dependent upon the properties of the diaphragm, and one method of in situ control was to add common sugar. Some plants, it is understood, used to thrive on this. Ruthenium-based coatings corrode more quickly in the presence of sugar, as does platinum electroplate. Fortunately the warning of the possible increased corrosive effects due to sugar meant

that it was not added in plants equipped with ruthenium oxide-based coatings.

Using titanium-based electrodes in chlor-alkali cells caused a number of unfortunate incidents. For instance, diesel fuel spilled from dumper trucks used to take salt from a salt dome caused 'blinding' (deposition of film on the surface) of anodes in a mercury-type plant, thereby raising net chlorine overpotential to economically unacceptable levels. When the chlorine compressor in a diaphragm-type chlorine facility failed, the emergency procedure was to divert chlorine in the plant into sodium hydroxide solution where it was safely converted to sodium hypochlorite. Somehow the hypochlorite in one plant was inadvertently fed back into the chlor-alkali cells. Such an accident indelibly reminds one that alkaline brine strongly attacks ruthenium-based electrodes! Despite losing ~25 per cent of the anodic coating in just a few hours, the plant went on to function normally for the next 5 years without the need for anode replacement.

Membrane-Type Chlorine Cells

The introduction of membrane-type chlorine technology, see Figures 9 and 10, has also seen wide use of Beer 2 RuO₂/TiO₂ coatings. Because the ion exchange membrane is usually highly alkaline, conditions of use can exist where the anolyte may also go alkaline, for example, during a shut-down. Upon re-energising the plant,



Fig. 9 The external view of an FM21-SP electrolyser unit of a membrane-type chlor-alkali cell. Each cell incorporates mixed metal coated titanium anodes
Courtesy of ICI Chemicals and Polymers Ltd.

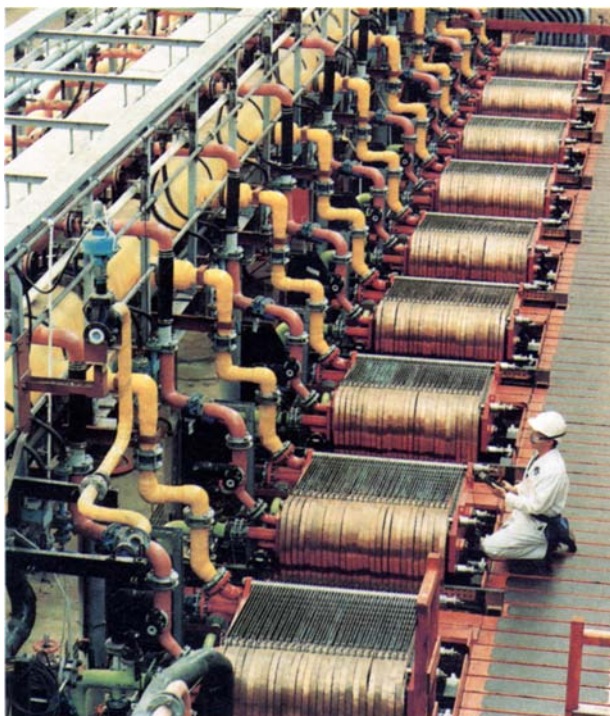


Fig. 10 A general view of a membrane chlor-alkali cell room which uses many of the FM21-SP electrolyser units
 Courtesy of ICI Chemicals and Polymers Ltd.

alkalinity in the anolyte encourages oxygen, rather than chlorine, formation; and at above a pH of about 12, see Figure 11, the anodic reac-

tion produces only oxygen, even in saturated brine. Hence, upon start-up of a membrane-type plant with alkaline anolyte there can be either only oxygen produced, or cojoint oxygen and chlorine. Even if the alkaline conditions are only transient, there can be significant dissolution of the anode coating. To improve overall durability, at a small loss in anode efficiency, some RuO_2 in Beer 2 $\text{RuO}_2/\text{TiO}_2$ codeposit may be replaced by IrO_2 . The colour change from light grey to near black is usually an indication that the coatings contain some IrO_2 . It is likely that a range of proprietary modifications to coatings are now used

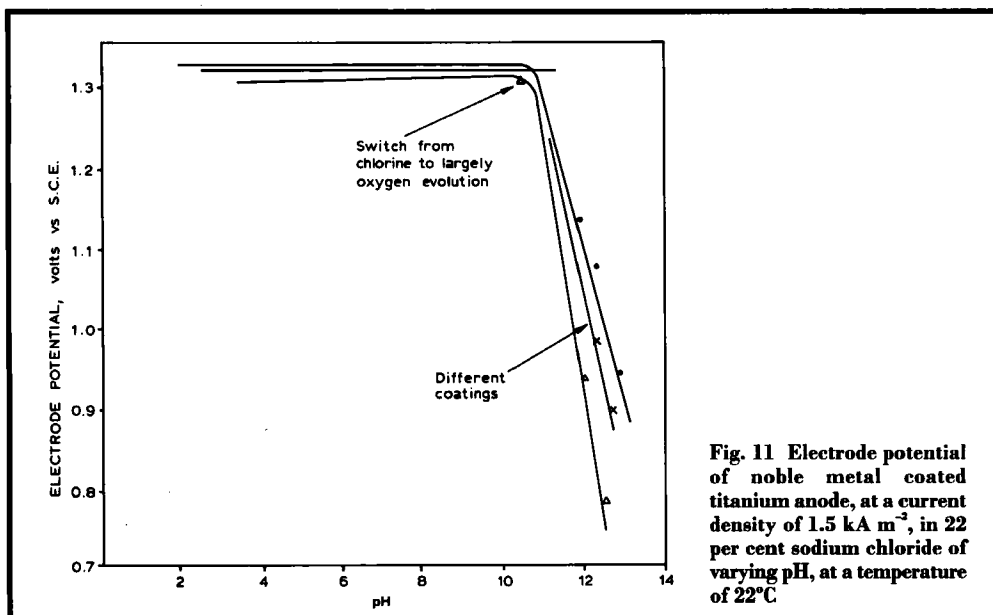


Fig. 11 Electrode potential of noble metal coated titanium anode, at a current density of 1.5 kA m^{-2} , in 22 per cent sodium chloride of varying pH, at a temperature of 22°C

in the many membrane-type chlorine cells.

There is no longer justification for continued heavy expenditure on chlorine cell anode coatings. This does not mean that further worthwhile improvements cannot be made (25). Apart from the continuing desire for cost effective use of noble metals, the industry has to live with fluctuations in the noble metal base prices in deciding which coating to use for specific applications.

The concluding part of this paper will appear in the next issue of *Platinum Metals Review* and will deal with the development of oxygen electrodes for widely ranging types of electrochemical application, some of which function at very high current density – electrogalvanising – and others at extremely low values, such as impressed current cathodic protection of rebars in concrete.

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Electroless Platinum Deposition for Medical Implants

The metallisation of polymers enables such materials to be used in a wide range of industries, such as automotive, and in electronic applications. Most recently, the electroless deposition of metal onto polymers is finding use in medical applications for fabricating electrodes used in implantable medical devices. Platinum, being biologically inert, is one of the metals used to coat implantable electrodes. However, as metallic deposition only takes place on conducting surfaces, it is necessary to metallise, or seed, the non-conducting polymer prior to electroless deposition. A suitable catalyst is thus required to provide the insulating surface with conducting properties.

In commercial electroless platinum deposition a tin sensitizer and a palladium chloride, PdCl₂, activator are used to provide the catalytic centres, but tin is toxic and therefore unsuitable for use in medical implants.

Now, researchers based at the Royal North Shore Hospital in Sydney, Australia, describe a method for the electroless deposition of platinum onto films and fibres of polyethylene terephthalate (PET) using a new tin-free catalyst to activate the PET surface (Z. Rao, E. K. Chong, N. L. Anderson, M. G. Stevens, R. Driver and K. V. Paulose, *J. Mater. Sci., Lett.*, 1998, **17**, (4), 303–305). The catalyst was made by dissolving PdCl₂ into dimethylsulfoxide (DMSO).

The electroless deposition of platinum onto PET involved a number of steps with thorough

rinsing in de-ionised water between each step. The PET films or fibres were first carefully washed to remove wax or oil residues, followed by etching in a hot alkaline bath consisting of sodium hydroxide and a surfactant. The etching roughened the PET surface and this allowed better adhesion for the platinum coating, by mechanical interlocking between the coating and the surface. The PET samples were then dipped into the DMSO-Pd catalyst, followed by dipping into a reducer of an aqueous solution of hydrazine at room temperature. Lastly, catalysed samples were immersed in an electroless platinum deposition bath preheated to 60°C.

The resulting electrolessly plated platinum coatings were characterised by various techniques and compared with commercially available samples. Peel tests to evaluate the adhesion showed it to be good for platinum coatings of up to 200 nm thickness, but thicker coatings were less adhesive.

Palladium was present on the PET surface in metallic form but with an irregular distribution. These very fine palladium particles or clusters may act as catalytic sites for the subsequent electroless platinum deposition. However, as platinum deposition appeared to start simultaneously over all the catalysed PET surface, the role of the palladium is unclear, and further studies are required. This tin-free catalyst may thus find use in producing adhesive platinum coatings for implantable medical applications.