Development of the Noble Metal/Oxide Coated Titanium Electrode

PART I: THE BEGINNING OF THE STORY

By P. C. S. Hayfield

Bickenhill, West Midlands, England

The titanium-based electrode was invented some forty years ago. Since then it has been incorporated into a wide variety of industrial processes on a huge scale, principally in the chlor-alkali industry. Deriving from industrial, as opposed to academic, work, the saga of its commercial exploitation has involved patenting and secrecy on a massive scale. Despite there being numerous contributors to the overall technology, just a few individuals are holders of the hundreds of patents that were taken out. It is not intended that this article should contain comprehensive details of patents and other published literature, but rather be an attempt to portray, as accurately as possible, the excitement generated as the technology unfolded. However, it is bound to be inevitable, bearing in mind the complexities and the scope of commercial involvement, that not all readers will be satisfied with every detail, so apologies are offered in advance to those who may inadvertently feel themselves slighted.

By the early 1950s, the commercial production of titanium by the Kroll process was well advanced in both the U.S.S.R. and the U.S.A. However, around this time, the Metals Division of the British firm ICI decided to develop its own method of production, with the most likely principal use being seen as the aerospace industry. By the mid 1950s, following rapid development through the techniques of arc melting, consumable electrode melting and electron beam melting, a high quality, commercially pure titanium was being produced.

It then fell to J. B. Cotton, who was Head of the Corrosion Section of the Central Research & Development Department in the Metals Division of ICI, to assess both the corrosion and electrochemical properties of this newly commercially-available metal.

Cotton and his team, by then having gained an enviable reputation for selecting successful copper-based alloy tube that came to be used in the condenser cooling systems of ships and power stations, were soon able to demonstrate – using jet impingement and other test methods – that titanium possessed both exceptional corrosion and erosion resistance towards seawater (1).

The Noble Metal/Titanium Bielectrode Concept

Titanium anodises when it is used as the anode in a range of non-halide containing aqueous environments. This usually results in the growth of thin films of oxide which exhibit interference colouring when viewed in white light. After anodising, the anode can no longer pass useful current. It was observed that if unanodised titanium was attached to an already anodised electrode, current passed only until the fresh titanium had anodised. When a soluble metal, such as copper, was attached to the anodised titanium, current would flow until all the copper had dissolved; this is the concept behind the now widely adopted titanium anode basket used for metal plating applications. In some aqueous halide solutions, including seawater, titanium exhibits the phenomenon of anodic breakdown corrosion. Cotton experimented with attaching
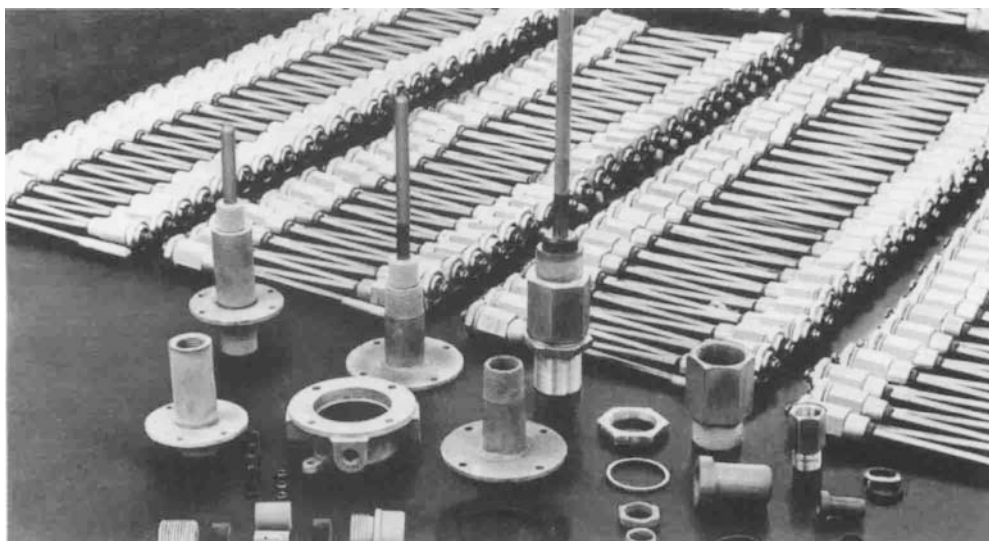
Fig. 1 Platinum electroplated titanium rod anodes as used typically in the cathodic protection of water boxes in power generating plant

carbon to titanium to bleed off current and hence minimise the risk of possible breakdown corrosion. But he soon came to appreciate that attaching carbon resulted in an anode being produced, and from there it was a short step to spot welding a small piece of platinum wire to the titanium and showing that current passed through the platinum. The concept of the platinum coated titanium bielectrode had thus been recognised.

Fortunately for Cotton, within his group there was a highly experienced plating specialist called C. H. Angell, who was able to successfully coat adherent platinum onto titanium at a time when it was considered difficult to plate any metal adherently onto titanium. As there was a possibility of commercially exploiting such a platinised titanium bielectrode in cathodic protection, patent protection was sought (2).

After several months, it came to the attention of the Metals Division that, totally independently of the ICI work, an employee of Magneto Chemie in The Netherlands, H. B. Beer, had taken out a patent on rhodium plated titanium, see Table I for major milestones in the development (3). Its priority date was just a few weeks before that of the ICI patent. It is thought that Beer, working in the unusual surroundings

of a building constructed around a disused windmill, had come across the bielectrode concept during studies on making scents.

The consequence of this situation was that an agreement was struck between the small-sized Magneto Chemie and two Divisions of the much larger ICI organisation, General Chemicals (chlorine producers) and Metals, under which the development of titanium-based electrodes to replace graphite electrodes in chlorine cells was to be shared. Beer was to work on coating formulations while others were to concentrate upon assessing the commercial viability of the coatings on titanium electrodes. The agreement stayed in force for several years, not being terminated until 1965. International Nickel and Engelhard gave early assistance during these formative years in the development of titanium-based electrode technology.

Electrodeposited Platinum Coatings

Although the management of the Metals Division of ICI permitted the registering of a first patent (2), there was not even lukewarm enthusiasm for the platinum electroplated titanium electrode which was being offered commercially for cathodic protection uses, ahead of its utilisation in the chlorine cell industry.

The argument ran: platinum is expensive, and titanium both expensive and relatively scarce, so how can a bielectrode comprising the two metals ever be commercially viable, compared with existing lead-based and other electrodes? However, the possibility that platinised titanium might operate at substantially higher current densities than existing anodes, encouraged Cotton's enthusiasm.

This optimism was supported by several other workers in the cathodic protection industry. G. Waite was possibly the first to mount electrodes, for trial, on a ship's hull, and this use was also helped when J. H. Morgan included a section on titanium-based electrodes in his book (4); one illustration showed an electrode vigorously evolving chlorine at high current density.

The product was technically improved over many months, but the questions of how much platinum to apply and how long the coating would last, went unanswered. At that time it was the vogue in the metallurgical industry to try radiotracer technology of the kind used by Losev and colleagues at the Karpov Institute in Moscow (5), but short term results were inconclusive.

Accurate determination awaited results from long term polarisation trials, lasting several years, at the ICI seawater corrosion laboratory at Brixham, and at the Brighton Seawater Laboratory of the S. E. Board of the Central Electricity Generating Board, where intermediate non-destructive monitoring of residual platinum loading was independently performed. In broad terms, the anodic corrosion rate for platinum electroplate coatings in seawater was found to be between 1 and 2 µg for every ampere hour of electricity passed (µg A^{-1}h^{-1}). Put another way, only between one and two millionths of the current passed through the anodes, used for chlorine evolution, was involved in platinum dissolution.

In industry there was no time to wait for the results of these long polarisation trials – so the first commercial anodes were platinum coated, in a sodium hexahydroxyplatinate bath, until visually there seemed to be continuous coverage. This occurred after deposition of about 55

g m^{-2}, which is a nominal 2.5 µm thickness. At the time it was thought that as platinum was so noble the bielectrode would be able to last indefinitely.

Superimposed AC on DC

R. Juchniewicz of the Gdansk Polytechnic (6, 7) suggested that the effects of AC ripple superimposed on current from commercial transformer/rectifiers was likely to shorten significantly the life of the commercial platinised titanium bielectrode, and this indeed was worrying news. By then the manufacture of platinised titanium bielectrodes for cathodic protection had been transferred to Marston Excelsior Ltd, a wholly-owned Metals Division subsidiary.

To preserve the reputation of the new product, it was felt necessary to advise electrode users to limit superimposed AC ripple to not greater than 5 per cent of DC; in some instances this necessitated the provision of costly smoothing equipment. But it was later found that superimposed AC ripple was not as serious as initially alleged (8), the explanation involving the AC frequency. Juchniewicz's work used AC of 50 Hz and lower frequencies, whereas the ripple from most industrial DC supplies is 100 Hz and higher. Platinum forms a surface oxide during anodic polarisation which, while thin, is capable of reduction to finely divided platinum if depolarised over a long enough period. At 50 Hz and lower frequencies, including stops/starts, platinum oxide will reduce to a form in which it can be lost mechanically. But depolarisation at 100 Hz and higher is too short a period for the reduction to occur, and no example has even been recognised where superimposed ripple has been the cause of premature electrode failure.

Brine Dilution Effects

Unexpectedly high platinum corrosion occurred to electrodes placed in tidal estuaries. The anodic corrosion rate of platinum rises from ~ 1 to 2 µg A^{-1}h^{-1} to 50 or higher µg A^{-1}h^{-1}, for chloride concentrations varying from near 30 g l^{-1} (seawater) to around 2 to 3 g l^{-1}, respectively. In effect, platinum forms an equilibrium or quasi

Table I	
Important Dates	
1958	Rhodium electrodeposition on titanium (Beer)
1958	Platinum electrodeposition on titanium (Cotton et al)
1960	Paint/thermal decomposition method of coating (Angell et al)
1965	First mixed metal oxide coatings (Beer)
1967	Second mixed metal oxide coatings (Beer)
1968	First titanium-based electrodes (70/30 Pt/Ir coated) in commercial chlor-alkali cells (chlorate)
1984	Titanium-based anodes in electrogalvanising
1986	Titanium-based anodes in the cathodic protection of rebar in concrete

equilibrium state when evolving chlorine, and a rather different state for oxygen evolution. During cojoint oxygen and chlorine evolution, which occurs in dilute brine, there is interference in the formation of surface layers and this leads to accentuated metal dissolution.

Deposits

In one of many well-documented applications, large numbers of rod-type platinised titanium anodes, see Figure 1, were installed to protect a steel jetty in the Middle East. With the years, shifting sands led to some anodes, initially in clear water, becoming silted over. Whenever this happened, platinum was lost preferentially and the underlying titanium began to corrode. This was explained by the formation of high acidity near the surface of the electrodes, which were struggling to operate at high current density.

Organics

As if superimposed AC ripple, brine dilution and local acidity were not enough unexpected hazards to affect the life of platinised titanium electrodes, it was disappointing to have to add others, including organics, to the list. A first instance came when platinised titanium was supplied in small-coil form as auxiliary anodes as part of the nickel plating on the insides of kettles.

For seemingly unexplained reasons at the time, such electrodes had particularly short lives. The cause was traced to a particular organic brightener addition, naphthalene trisulfonic acid (9).

It was hoped that this was an isolated example, but it was not. In retrospect, organic chemists should not have been surprised that a platinised titanium anode used in the cathodic protection of a steel vessel containing a feedstock of dilute brine and sugar failed prematurely. However, it was totally unexpected to those involved. In desperation, a succession of different types of coated titanium, described later, were used, but all, to varying extents, had anodic dissolution rates significantly increased in the presence of sugar. The various decomposition products of sugar, including fructose and gluconic acid, do not exert similar activation.

The list of specific organics which have a deleterious effect on the anodic behaviour of noble metal/oxide electrocatalysts continues to increase. It now includes certain oils, wetting agents and concentrated seaweed.

Improvements to Technology

In the manufacture of most platinum electroplated titanium, the titanium is first chemically etched to form a surface with reentrant angles -- to aid the mechanical adhesion of subsequently applied coatings. Even this simple process of chemical roughening has involved much development.

Beer was the first to suggest that an equi-axed titanium grain size of 0.03 to 0.05 mm was the

optimum, a specification now used worldwide. Etchants have ranged widely, including hydrochloric acid at ambient temperature (3 days), hot oxalic acid (8 hours), hot sulfuric acid (1 hour) to the so-called Piontelli alkaline anodic etch (few seconds). The acid etches cause the formation of a surface film of electrically conducting titanium hydride, but once samples are washed in water and exposed to air, a skin of electrically resistive titanium oxide soon forms. Surfaces partially coated with hydride and oxide cause coarse nucleation of the deposit during subsequent platinum electrodeposition.

A simple and expedient way to overcome such coarse, porous deposits, is first to coat the titanium with a thin electrically conducting layer using the paint/thermal decomposition process described later. This so-called paint/electroplate method (10) is now widely practised, resulting in improved coating adhesion, less porous deposits and visual platinum coverage at much lower overall loading than hitherto possible. The decreased porosity confers significant improvement to resistance against the coating being undermined in acidic environments.

Metallurgically Co-processed Platinised Titanium

In parallel with the development of the platinum electroplated titanium electrode at the Metals Division of ICI, another part of the organisation sought to promote uncoated titanium sheet electrodes for the formation of "starter cathodes" in the copper refining industry. Here, titanium was required to be attached to copper hanger bars. This cannot be done by autogenous welding as brittle intermetallics form.

Therefore, A. C. Barber of ICI decided upon encapsulation of copper by titanium, so that clad bars could be spot welded to titanium sheet. To achieve such cladding an ingot was prepared, comprising a core of copper and an outer skin of titanium, which could be metallurgically co-processed (hot extrusion followed by cold drawing) to make the copper-cored titanium. A variation of the sequence was to wrap platinum foil around the titanium to make platinised copper-
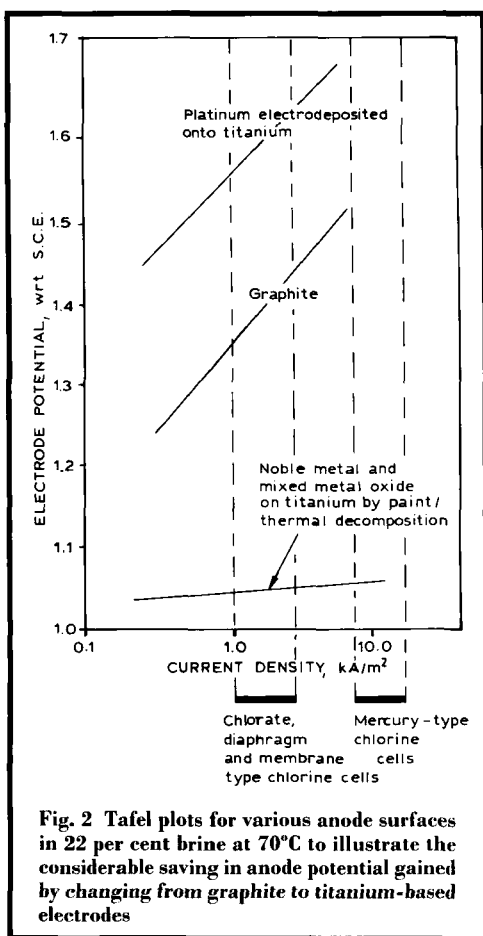
cored titanium (11). By this route much thicker platinum can be applied to titanium than is possible by electrodeposition, and further, the coatings are not porous. An excellent example of the product is the platinised niobium used for cathodic protection of a North Sea oil platform (12).

It has been suggested recently that platinised titanium has been a commercial disappointment (13). While it is true that there are now electrocatalyst coatings which are displacing platinum in respect of cost, durability and other characteristics, platinum electroplated titanium has been, and continues to be, a highly successful commercial product. Not only does the high hardness (occluded hydrogen) of the platinum confer important abrasion resistance, but in a wide range of applications, the product has become predictable and dependable, and unlikely to be replaced.

Probably a longer term assessment than can be written at present will view platinised titanium as an important phase in the development of later generations of coatings. Until the advent of the bielectrode, both wrought platinum and clad platinum copper had restricted use because of cost. The advent of more affordable electrodes greatly increased both the size and diversity of application, and the electrochemical characteristics of the metal have also been much clarified. In the 1950s, the situations where platinum was found, anodically, to dissolve unexpectedly fast were not foreseeable. Nevertheless, the conditions which affect platinum electroplate also have relevance to later generations of coatings.

Paint/Thermal Decomposition Coating Methods

Platinum electroplated titanium, with the platinum in passivated mode, is characterised by a high chlorine overpotential (14), see Figure 2, making it unattractive for use over graphite in the chlor-alkali industry, to lower manufacturing costs. Angell was the first to propose an alternative to electrodeposition as a method of coating (15). He put forward the concept, not novel in itself, of taking a solution containing a

Fig. 2 Tafel plots for various anode surfaces in 22 per cent brine at 70°C to illustrate the considerable saving in anode potential gained by changing from graphite to titanium-based electrodes

believed that 70/30 platinum/iridium (Pt/Ir) electroplate was an alloy when in fact it is a fine scale mixture of platinum and iridium. More importantly, and certainly not appreciated at the time, all paint/thermally decomposed coatings, with the singular exception of platinum, were in noble metal oxide, rather than metallic, form. All the paint/thermally deposited coatings exhibit low chlorine overpotential, and in addition, ruthenium electroplate possessed low chlorine overpotential.

Again, it has been suggested (13) that because of the simplicity of the paint/thermal decomposition route the method is trivial, but while it may be a simple concept, its practical execution is complex in detail.

It may now seem straightforward to dissolve completely a noble metal salt in a solvent, of either water or alcohol, but in the early 1960s this was not so. A close interplay was required between the producer and the user to achieve full solubility. Adherent deposits produced by the paint/thermal decomposition route are so thin, that any undissolved particles form major local discontinuities which may weaken the durability of the electrode. Even in modern-day coating plants, paints must be shaken or barrelled over several days and then decanted before the liquid is considered usable. When painting there is a natural instinct to want to shake or stir paint before its application, but for electrodes this must always be resisted. Paints generally have a short shelf life, and any storage should be at low temperature, less than say 5°C.

In the Metals Division of ICI, in the early 1960s, it was possible to purchase an oily, resinate-based platinum-containing paint which was used in the ceramics industry. However, Beer preferred to make up his own composition. A typical route, later patented, might include dissolving chlor-platinic acid in an alcohol, such as amyl alcohol, and then adding a natural oil, linalool, which has the rather exotic name of 'ex Bois de Rose'. After repetitive paint/thermal decomposition sequences to build up a significant loading, Beer proposed improvement to the coating by a post heat treatment (16). While the charge was still at the final decomposition

soluble noble metal salt, applying it as a paint to the titanium surface and then heating it in air to decompose the salt to the metallic state. An element of good fortune existed, in that at the temperature for thermal decomposition, 400 to 500°C, titanium does not significantly oxidise in air. By comparison, the painting technique cannot be readily applied to niobium because its inherent rate of oxidation is too fast.

Displayed in Table II are results that had accrued in the Metals Division of ICI by February 1963. These take the form of chlorine overpotentials at 1 and 10 kA m⁻² current density, in 22 per cent brine, for a range of electrodeposited and paint/thermal decomposition coatings. It is necessary to be cautious in understanding the information. At that time it was

Table II
Chlorine Overpotential Measurements for Electrode Surfaces, in February 1963

Surface	Overpotential in saturated brine at 70°C, mV		Surface	Overpotential in saturated brine at 70°C, mV	
	1 kA m⁻²	10 kA m⁻²		1 kA m⁻²	10 kA m⁻²
Platinum	12	24	Flame sprayed	71	271
paint (05X)	11	25	platinum	57	195
70/30 Pt/Ir	8	11	Nominal 70/30	43	81
paint (IR-1)	8	12	Pt/Ir electroplate	60	106
Platinum	21	41	Platinum	38	63
paint	27	43	electroplate	42	93
Ruthenium	25	41	Ruthenium	18	28
paint	27	42	electroplate	20	33
Iridium	19	30	Iridium	32	52
paint	17	28	electroplate	33	92
Rhodium	26	40	Rhodium	213	306
paint	28	42	electroplate	221	324

temperature, ammonia was introduced, followed by butane, and finally the atmosphere changed back to air for 60 hours, prior to cooling to ambient temperature. The ammonia/butane part often led to a 'flash over' or slight explosion as rapid local oxidation ensued. When, for a few months, the Beer route was introduced into production at the Witton site of the Metals Division, it was considered prudent on safety grounds to have a fire tender standing by should the processing get out of control.

Nowadays it is commonplace to accept both noble metal oxides as well as noble metals as electrocatalysts, but this was not always the case, as there was a reluctance to move away from platinum.

The second part of "Development of the Noble Metal/Oxide Coated Titanium Electrodes", will examine the history of the platinum-containing paints used to coat electrodes in mercury cells, diaphragm and chlorate cells for the production of chlorine, and the advent of RuO_2/TiO_2 electrodes. It will be published in the April 1998 issue of Platinum Metals Review.

References

1 J. B. Cotton and B. P. Downing, Transactions of the Institute of Marine Engineers, 1957, 69, 311–319

2 J. B. Cotton, E. C. Williams and A. H. Barber, British Patent 877,901; 1958

3 H. B. Beer, British Patent 855,107; 1958

4 J. H. Morgan, "Cathodic Protection: Its Theory and Practice in the Prevention of Corrosion", Leonard Hill (Books) Limited, London, 1959

5 V. V. Gorodetskii, M. A. Dembrovskii and V. V. Losev, Zh. Prikl. Khim., 1963, 36, 1543–1549

6 R. Juchniewicz, First International Congress on Metallic Corrosion, Butterworths, London, 1962, p.368

7 R. Juchniewicz, Platinum Metals Rev., 1962, 6, (3), 100

8 R. Juchniewicz and P. C. S. Hayfield, Third International Congress on Metallic Corrosion, Moscow, 1966, 73–82

9 M. A. Warne and P. C. S. Hayfield, Trans. Metal Finish., 1967, 45, 83–92

10 M. A. Warne and P. C. S. Hayfield, British Patent 1,351,741; 1970

11 A. C. Barber, British Patent 1,457,511; 1973

12 R. M. Vennett, R. W. Seager and M. A. Warne, Mater. Perform., 1983, 22, 22–30

13 G. K. Chandler, J. D. Genders and D. Pletcher, Platinum Metals Rev., 1997, 41, (2), 54–63

14 J. A. Bittles and E. L. Littauer, Corros. Sci., 1970, 10, 29–41

15 C. H. Angell and M. G. Deriaz, British Patent 885,819; 1960; British Patent 984,973; 1963

16 H. B. Beer, British Patent 964,913; 1962