Platinised Titanium Electrodes for Cathodic Protection

EXTENSIVE USE HAS PROVIDED NEW INSIGHTS INTO THE ELECTROCHEMICAL PROPERTIES OF PLATINUM

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Over the past quarter of a century a combination of platinum and titanium has been used increasingly as an electrode material for the cathodic protection of steel in marine environments and underground structures. As a result of accumulated experience gained in many situations it is now possible to set guidelines within which the material may be used with confidence, thus greater application is probable.

History will record that a major achievement in electrochemistry has been the development over the last twenty-five years of an entire family of platinum coated refractory-oxide metal electrodes. The present article is concerned with the first to become commercial, platinised titanium, still extensively and increasingly being used in cathodic protection and also in many other applications such as metal finishing. There are in service perhaps in excess of 50,000 electrodes of this type, and the metal usage since inception probably amounts to over a metric tonne of platinum.

Articles in *Platinum Metals Review* have maintained a good indicator of developments. The first significant publication to appear on platinised titanium was J. B. Cotton's paper in 1958 (1). Clearly careful consideration had to be given to the commercial potential for an electrode which combined an expensive metal with titanium, then a metal in its infancy and also relatively expensive, to compete with the cheaper lead, graphite and silicon iron electrodes. The development owes much to the foresight of Joe Cotton of IMI, and also to that of Richard Lowe of Corrosion and Welding Engineering and John Morgan of Morgan Berkeley, who were prepared to mount the

necessary field trials in marine environments.

The pathway to the present position of dominance by platinised titanium as the preferred electrode for impressed current cathodic protection of steel in marine environments—oil platforms, jetties, ships and pumps—has not always been straightforward. There were early indications (2) of electrode life foreshortening by the effect of current ripple from commercial power sources. Romuald Juchniewicz, in this journal (3), described the effect of superimposed 50Hz AC ripple. This was to be the first of several accounts on the topic, which continue to appear because of the increasing variety of current waveforms used in automatic control systems.

Fortunately, in practice, current ripple has not proved to be a significant problem because ripple frequencies on commercial power supplies are in general higher than those likely to foreshorten anode life. Twenty years after Cotton's first paper, Lionel Shreir (4) reviewed progress with the platinised electrode in marine service, and more recently Peter Sly (5) has provided a pointer, in the proposed application of platinised niobium in open hole deep well ground beds, to a way in which the platinised electrode is likely to find new and increasing

Fig. 1 Smooth corrosion-free hulls minimise the power necessary to move ships through the water. Modern vessels, such as the tanker illustrated here in dry dock, are in many cases fitted with impressed current cathodic protection methods for corrosion protection. Platinised titanium counter electrodes used in part of such a system can be seen as four small horizontal strips in line with the propeller shaft

Photograph by courtesy of British Petroleum

application in the cathodic protection of underground structures such as storage tanks, buried pipelines and oil well casings.

The Manufacture of Electrodes

In twenty-five years there have been undoubted improvements in methods of electrode manufacture. Platinum coating of titanium by electrodeposition is still widely used, but titanium, like aluminium and other refractory-oxide metals, remains basically a difficult metal on which to electrodeposit coatings. The technique involves a preroughening to a high degree, with the formation of re-entrant angles, so that the electrodeposit mechanically locks onto the surface, though no doubt there is also some weak Van der Waal attraction. Adhesion is not, however, usually by metallurgical or strong chemical bonding. The trick in obtaining a sound electroplate is to achieve good initial strike and a very helpful

way of ensuring this is to pre-coat the etched titanium with a very thin layer of an electrically conductive primer formed by thermal decomposition (6). Electroplating of adherent platinum deposits from aqueous baths onto such treated surface then becomes a much more certain operation.

Electrodeposition provides coverage of platinum onto widely varying sizes and shapes of substrate; furthermore, the method also allows the recoating of what are relatively expensive substrates when existing anodes have come to the end of their useful life by virtue of consumption of the platinum. However, there are limits to the thickness of electrodeposits that can be applied from aqueous baths. The bulk of anode coatings are in the 1 to 5 microns range and occasionally up to 10 microns. For thicker coatings of up to 20 microns, demanded for example by requirements in the cathodic protection of North Sea offshore oil platforms,
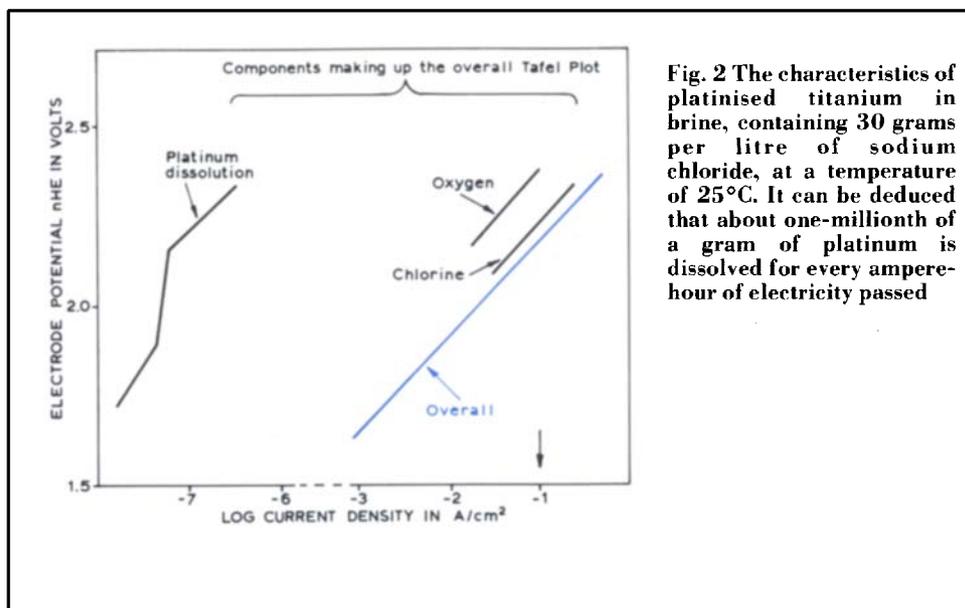
Fig. 2 The characteristics of platinised titanium in brine, containing 30 grams per litre of sodium chloride, at a temperature of 25°C. It can be deduced that about one-millionth of a gram of platinum is dissolved for every ampere-hour of electricity passed

a coating by metallurgical co-processing is used. This method, too, has undergone development, and a product now made for land-based uses, including ground beds and bridge deck protection, includes small diameter, principally 1 to 4 mm, platinised copper-cored titanium (and copper-cored and solid niobium) sheathed with 1 to 2.5 microns thickness of platinum.

Factors Influencing the Durability of Platinum Coatings

In the early days of exploitation of platinised titanium there was a belief that platinum, acknowledged as a noble metal for many centuries, would be totally insoluble and last for ever. The immediate governing factor was the minimum thickness that could be electrodeposited to provide a visible uniform coverage of platinum; at the time this turned out to be about 2.5 microns.

Although it would be unwise to say that any scientific topic is ever totally understood, nevertheless it would be realistic to say that platinised titanium electrode preparation and usage has now turned from an art to a rather sophisticated science.

In reality, platinum was found to have a small but finite anodic consumption (dissolution) rate. Piecing together the available published literature it is now clear that the metal, in for example the most commonly encountered electrolyte—brine—is passivatable, with so-called active, passive and transpassive characteristics. It took a long time to come to terms with the fact that, used in low overpotential mode, platinum was operating in an "active" corrosion region. Such is the nobility of platinum that practical application of the metal, for instance alloyed with iridium to minimise the onset of passivation, has been widely possible for example in the electrolysis of brine to form sodium chlorate. There is a measurable dissolution that is significantly higher than for iridium and ruthenium oxides. However, when platinum is raised to passive potentials the anodic corrosion rate becomes very much lower, and it is in this condition that the material finds its bulk application. A breakdown of the relative Tafel plots for platinum operated in 3 per cent sodium chloride is illustrated in Figure 2, from which it can be deduced that for every ampere-hour (Ah) of electricity passed by platinum, principally as chlorine evolution, there is dissolution of about 1 millionth of a gram of platinum.

During twenty-five years of usage of platinised titanium it has transpired that platinum, long-held to be corrosion-proof, can

be dissolved in some quite unexpected ways over and above immersion in the "king of waters" (aqua regia). Categorised, these fall under the general headings of:

(i) Disturbance to the passivation film (depolarisation) caused by current waveform variations.

(ii) Operation in dilute brine with simultaneous evolution of chlorine and oxygen.

(iii) Operation in liquors that contain specific organic compounds.

Current Waveform

Losev and collaborators (7) got to the root cause of the likely effect of current waveform in a paper published in 1963. Using a radiotracer method it was demonstrated that mere interruption of applied anodic current would cause some loss in protectiveness of the passive film, resulting in a short but intense period of platinum solvation, see Figure 3. The topic of ripple has since been widely investigated. When platinised titanium first became available it was feared that the current oscillations from commercial rectifiers would prevent the electrode
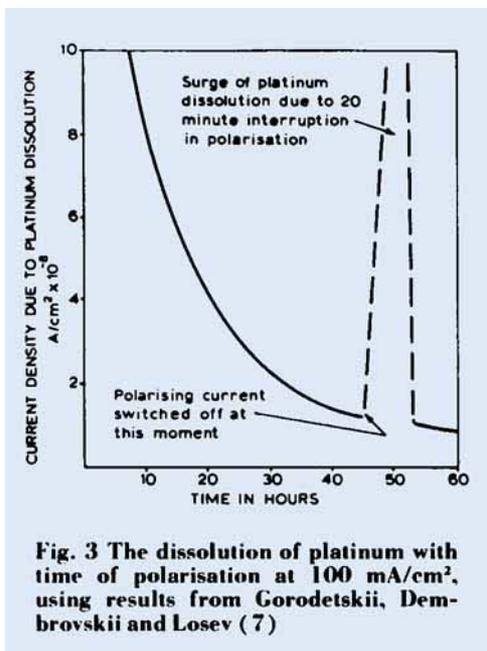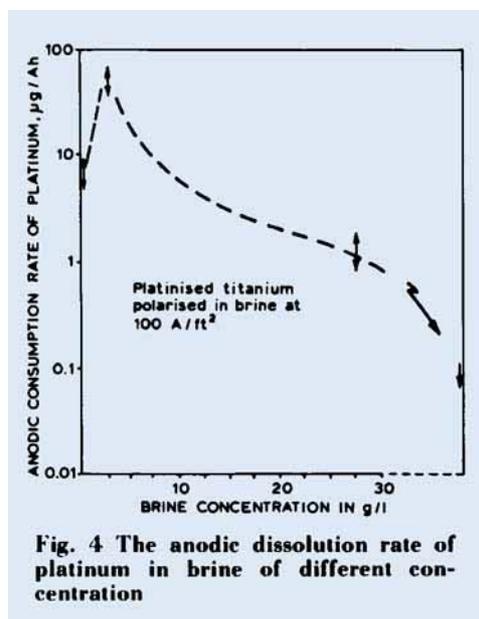

Fig. 4 The anodic dissolution rate of platinum in brine of different concentration

from being viable. This has turned out not to be the case (8) because, in general, the frequency of the inherent ripple was too high to effect any practical increase in dissolution rate. Use of lower frequency AC, for example the 2 to 5Hz square wave pulsing systems of some modern automated cathodic protection units, does however need more careful consideration of effects on platinum anodic corrosion rate, and spurious negative peaks or deliberate reversals of current are to be avoided completely.

When, in the late 1960s, platinum electroplated titanium was tried in the direct AC boiling of supply waters using 50Hz AC, it seemed to take many by surprise that this procedure was a ready means of converting a platinum substrate into an orangy coloured platinum oxide at a high rate.

Conjoint Evolution of Oxygen and Chlorine

Some earlier applications of platinised titanium electrodes were in plant utilising water from estuaries, for example the cathodic protection of power station condenser boxes and in electrochlorinators. The higher than expected platinum consumption rates were variously

Fig. 3 The dissolution of platinum with time of polarisation at 100 mA/cm², using results from Gorodetskii, Dembrovskii and Losev (7)

ascribed to dilute seawater, mixing of ocean and river water in estuaries, and to low temperatures. Lowering of temperature proved to have a minimal effect on consumption of platinum, but the diluteness of the sodium chloride produced the quite unexpected finding that simultaneous evolution of chlorine and oxygen increased the platinum consumption rate by more than the separate effects of evolving either pure oxygen or pure chlorine, illustrated in Figure 4. Such a synergistic effect is paralleled by stress corrosion, where the conjoint action of stress and corrosion (for example the caustic cracking of steel) produces greater damage than the separate effects of stress and corrosion. Thus in concentrated salt solution the anodic wear rate of platinum is less than 0.1 μg/Ah. In sulphuric acid, or in river water, the wear rate under oxygen evolution is about 5 μg/Ah. In seawater (about 1/10 saturation) the consumption rate of platinum is about 1 μg/Ah but at brackish water concentrations, that is to say a few grams per litre of dissolved solids, consumption rate can rise into the several tens of μg/Ah.

The Presence of Certain Organic Compounds

This is yet another situation where a sensitivity of platinum to unusually high anodic consumption rates was associated with conditions not previously appreciated until the more widespread use of platinised titanium. It was required to protect a mild steel vessel containing a feedstock of 0.25 per cent brine plus sugar. The platinised titanium that was specified for the apparently normal operating conditions failed prematurely and repeatedly. This was the basis for subsequent experimentation that showed that, diluteness of brine apart, sugar greatly accentuates the anodic corrosion rate not only of platinum, but also of other noble metals and the principal oxide electrocatalysts of ruthenium and iridium. Juchniewicz (9) and co-workers, working with stronger brine, have shown subsequently that it is common sugar, rather than any anodic decomposition products, that is responsible for

the increase in anodic consumption of platinum.

Subsequently, other organic compounds have been identified as affecting the anodic consumption of platinum, including particular brightening/levelling agents used in nickel electroplating solutions, diesel fuel contamination of brine, and certain organic compounds in organoelectrosynthesis reactions such as, for example, adiponitrile in sulphuric acid.

Discussion

The increasing and widely varying applications of platinised titanium electrodes have, as just described, highlighted new aspects of the behaviour of platinum. The effect of current ripple, conjoint evolution of oxygen and chlorine and specific organic compounds, are largely misunderstood in mechanism. Yet the discovery of these effects, far from diminishing the uses of platinised titanium electrodes, has set guidelines within which the material is used with increased confidence. At the anodic consumption rate of about 1 μg/Ah, the norm in seawater, platinised titanium electrodes have found a seemingly permanent niche. Few would argue against this type of electrode being the preferred high current density material for marine uses. However, the same could not be said over selection of electrodes for use underground in the cathodic protection of tanks, pipelines and oil well casing or of reinforcing steel in bridge decks and multi-storey car parks. Here the choice falls more naturally on graphite, silicon iron and magnetite. Yet platinised titanium, or platinised titanium-type electrodes, might well find some use.

Considering land-based situations in more detail, few electrodes in cathodic protection systems are used buried directly into soil or rock. Rather, to achieve a low resistance contact, electrodes are embedded in coke to form an extended surface area carbon ground bed. The electrical connection to the bed is achieved by applying to a centrally located electrode a current at densities of the order of A/m^2, or not more than a few at most. Much use

Fig. 5 Producing oilwells, such as the one illustrated involving a lufkin pump, are lined with steel pipework down to the oil-bearing strata. To prevent corrosion of the steel on the rock side, and the possibility of perforation with loss of oil and perhaps contamination of important water horizons, cathodic protection methods are being increasingly applied, with deep well ground beds located nearby

Photograph by courtesy of Shell

is now made in the United Kingdom of the fine coke known as "Sunbrite Singles" which is a domestic smokeless fuel, but another special fluidiseable coke is also used known as "Loresco". In order to feed current to the coke the electrode may well be called upon to operate in part electrochemically as well as electrically.

There is advantage to be gained in using something less brittle than graphite, silicon iron or magnetite. A more manageable engineering material, such as a length of pliable platinised titanium, has many attractions, both in transportation and installation. In the case of deep well as opposed to shallow ground beds, a miniaturised non-brittle electrode needs a smaller diameter hole, hence saving in drilling costs, and also in the cost of any lining that may be required.

Another form of deep ground bed that is being used increasingly around the world is the so-called "open hole" variety, and here again the miniaturised higher current density operating platinised titanium (or niobium) anode, in the form of rod or mesh, is being installed. As described by Sly (5), the platinised anode is simply suspended in the hole which must, self

evidently, be at a depth at which water collects around the anode. Quite apart from the cost savings in limiting the diameter of hole drilled, the anode and cable can readily be hauled to the surface for inspection and replaced if found necessary. When the platinum has been consumed, the substrate can be recoated.

In 1980 Warne and Berkeley described platinised titanium mesh feeders to two satisfactory ground bed systems that were dug up for purely investigational purposes and found, after 15 years, to have the platinum electroplated titanium mesh in unworn and still as-new condition (10). This must augur success for the long term.

There is an increasing requirement for reliable, long life ground beds. In cathodic protection the bed current requirements vary from a few to a few hundred amperes. There is speculation that ground beds of great depth and many hundreds, perhaps thousands of amperes, might be needed in electrophoretic methods of tertiary oil recovery. The platinised titanium electrode, having established itself in the marine field, seems set for increasing exploitation in the ground bed application. Unlike the marine field,

the chemistry of the environment varies much more widely in the ground application.

Conclusion

In twenty-five years, the platinised titanium electrode has grown steadily in stature. Of the many lessons that can be learnt from its successful applications two that come particularly to mind are: the need to make bold decisions when the first steps are taken to launch a new product, and the fact that much more knowledge has been amassed on the chemical/electrochemical behaviour of platinum, providing academics with a wealth of phenomena to investigate over the coming years.

Platinum is indeed a technically fascinating metal, no doubt still hiding many more secrets.

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Hydrogen Detector Uses Silver-Palladium Probe

Embrittlement caused by hydrogen inclusions is a well known phenomenon which affects many metals and alloys including steel, titanium, zirconium and uranium. The mechanism by which embrittlement occurs varies with the metal or alloy under attack, and in certain alloys failure can result from the incorporation of less than 10 ppb of hydrogen. This can happen at any stage in the initial manufacture or subsequent processing, or by corrosion during service. Its effects could be catastrophic in the case of high strength steels and titanium alloys used in the nuclear, petrochemical, power generation and aircraft industries. Clearly, there is an industrial requirement for probes able to detect minute traces of hydrogen.

A recent development by the Lawrence Electronics Company of Seattle, Washington, has resulted in a probe which utilises the unique properties of the platinum group metals, particularly palladium and its alloys, to rapidly dissociate and absorb hydrogen (G. M. Lawrenson and J. F. Lawrence, Proc. 18th Annu. Airline Plat. Met. Finish. Forum, Orlando, Florida, March 16th–18th, 1982; reprinted as SAE 820604; see also T. Archbold, J. Sukalac and J. C. Picard, Third Int. Cong. Hydrogen Mater., Paris, June 1982).

The probe, which may for example be used to measure the hydrogen gas given off during the corrosion of steel or present in steel as a result of cadmium plating, incorporates a glass encapsulated ion gauge with a 25 weight per cent silver-palladium capillary needle which acts as diffusion membrane between the sampling environment and the detector. A tungsten filament inside the capillary heats the silver-palladium to a temperature at which hydrogen has high diffusivity. Therefore the hydrogen enters the test chamber where it is ionised by the electron current flowing between the electron emitter and the electron collector. The H^+ ions are attracted to the hydrogen collector where an electric current proportional to the hydrogen pressure is generated. The high sensitivity and short response time of the detector enables it to be an effective means of measuring hydrogen present in parts per billion.   D.J.A.