

Development of the Noble Metal/Oxide Coated Titanium Electrode

PART III: COATED TITANIUM ANODES IN WIDELY RANGING OXYGEN EVOLVING SITUATIONS

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The first two parts of this paper on titanium-based electrodes concentrated on the development of coatings comprising noble metals and their oxides suitable for use in chloride-bearing electrolytes. This concluding part deals with similar types of electrodes which act as counter electrodes in commercial processes where the product is made on the cathode. Many electrolytes in this category involve sulfuric acid, which means that oxygen evolves at the anodes. Applications for which these electrodes are used range from those operating at very high current density, such as electrogalvanising, to others at much lower current density, such as impressed current cathodic protection of rebar in concrete.

When platinised titanium-type electrodes were first envisaged for commercial use, manufacturers fixed their sights almost exclusively on using them as a possible replacement for graphite in high current density chlor-alkali processes, in order to effect a lowering of the cell voltage and therefore produce cost savings (26). In the author's experience, other applications, for instance replacing lead-based anodes in electrowinning, were not initially considered. Such applications, mostly involving sulfuric acid-based electrolytes, call for durability under oxygen evolving electrochemical conditions. Present day, large-scale applications for titanium-based electrodes, including electrogalvanising and impressed current cathodic protection of rebar in concrete, did not then exist.

Electrowinning

In electrowinning, lead-based electrodes are used to extract metal from a solution of its salts by electrolysis, with the electropositive metal being deposited on the cathode. In this industry conditions differ from the chlor-alkali industry in numerous ways:

- Current densities, in general, are about an order of magnitude lower than in diaphragm-

type chlorine cell technology.

- The electrolyte is usually strong sulfuric acid ($\sim 150 \text{ g l}^{-1}$) at a temperature above ambient, usually $\sim 40^\circ\text{C}$, but at a significantly lower temperature than the electrolyte in chlor-alkali cells.
- The electrolyte is more likely to have an organic content.
- There may be a high manganese level (10 to 15 g l^{-1}).
- Some chloride and fluoride may be present.
- As the cathodes are periodically removed to recover the metal, there are more discontinuities in operation than in chlor-alkali production.
- There may also be anode/cathode shorting.

All in all, this is rather a formidable environment in which to introduce viable titanium-based electrodes, and the incentives for change are therefore not straightforward. However, it can be advantageous to produce a cathodic product containing only low levels of lead, and while there may be some savings in electrical cost, high levels of manganese in solution usually make this difficult because of manganese dioxide deposition on the surface of the anode.

The 'Bunker Hunt' affair in 1980, when the price of silver escalated, meant that some users

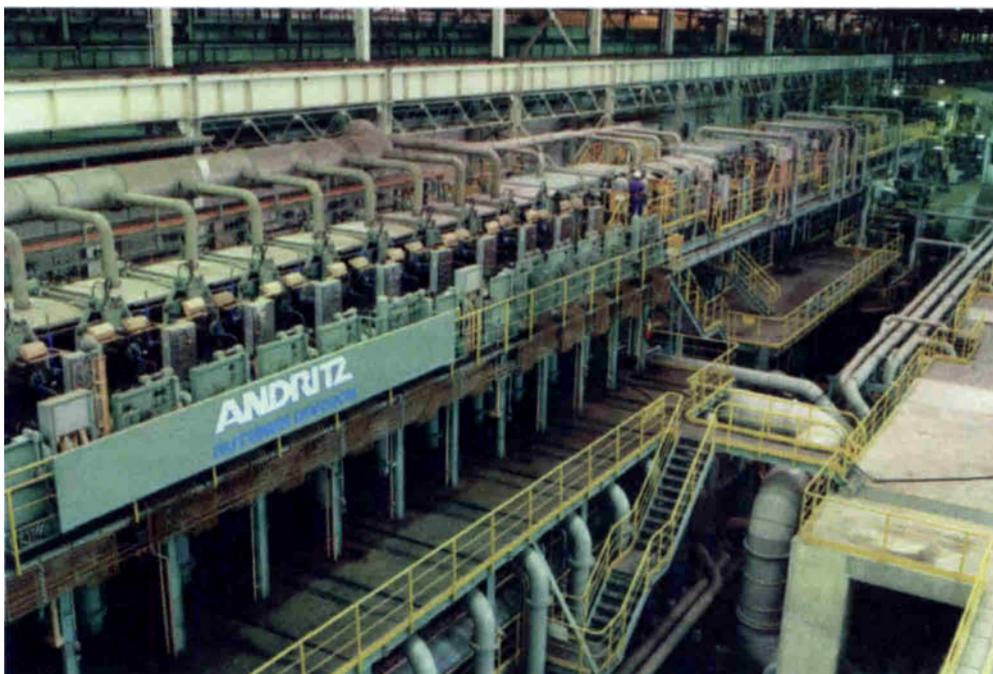


Fig. 12 A 20-cell plating section from a Gravital electrogalvanising plant in Usiminas, Brazil. The capacity is 360,000 tonnes/annum. A 20 cell unit will contain around 400 electrodes, each of size $\sim 0.5 \text{ m} \times 1 \text{ m}$
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switched to titanium-based electrodes to capitalise on the silver inventory in their lead-silver anodes. In fact, the requirements of each plant needed to be considered individually; but apart from a few plants which operated with chloride-based electrolytes and then switched to titanium-based electrodes, the majority of the world metal winning industry still uses lead-based electrodes.

Durable Electrocatalysts for Oxygen Evolving Anodes

A good place to start looking at present-day oxygen electrode technology is the early de Nora patent assigned to Bianchi and colleagues, where the preferred electrocatalyst was $\text{IrO}_2/\text{Ta}_2\text{O}_5$ codeposit (27). It is said that electrodes with this coating were incorporated into a Sulfomat cell installed in Japan by the U.S. company Ionics Inc., of Watertown, Massachusetts, but the lives of these electrodes were reputedly much shorter than those of anodes in chlor-alkali cells.

As oxygen electrodes became of greater

commercial importance, the characteristics of the electrocatalysts, iridium oxide and iridium oxide/tantalum oxide mixtures, were studied in more detail. Usually, the favoured means of depositing pure iridium oxide is by the paint/thermal decomposition route using chlor-iridium acid dissolved in an alcohol. If the decomposition temperature is too low then water-soluble iridium chloride remains, but if the decomposition temperature is too high the iridium oxide is converted to less catalytically-durable iridium metal. The window for the correct decomposition temperature is small, only about 20°C . In the preferred iridium oxide form, the electrocatalyst has a tendency to change from an attractively-low to an undesirably-high oxygen overpotential. Factors that cause passivation include:

- length of time under anodic polarisation
- increasing current density and
- decreasing acidity.

The inventors of the de Nora patent seem, like Beer with his $\text{RuO}_2/\text{TiO}_2$ patents, to have found the key parameters back in 1975. Subsequently,

Cominellis and coworkers have clarified much of the detail (28, 29). Perhaps the most important finding is that mixing tantalum oxide with the iridium oxide acts, in some way, to slow down the reduction of the iridium oxide to iridium metal. Thus, while iridium oxide by itself requires a decomposition temperature of 380 to 400°C, a codeposit of IrO₂/Ta₂O₅ can be safely put into a furnace at 450 or even 500°C, and this also results in the expulsion of more residual chloride ion.

In retrospect, the platinum in a 70/30 Pt/Ir coating appears to slow down the reduction of iridium oxide. Thus, with paints comprising chlor-platinic and chlor-iridic acids in alcohol, decomposition temperatures of 500°C can safely be used, producing coatings comprising fine scale mixtures of Pt + IrO₂.

Some evidence for the less powerful nature of iridium oxide as an oxygen electrocatalyst, compared with ruthenium oxide as a chlorine electrocatalyst, can be gauged from the finding that optimised IrO₂/Ta₂O₅ codeposits for oxygen evolution are always high in iridium oxide. A paint with a high iridium oxide content, such as 95/5 or 90/10, tends to favour the suppression of chlorine evolution in electrolytes containing trace chloride, while an optimised 'work horse' composition is nearer 50/50 wt/wt per cent.

With hindsight, an improved understanding of the titanium substrate was needed to explain accumulating experiences with titanium-based oxygen electrodes. A prerequisite for any commercial coated titanium electrode must be an adherent and durable coating. In most chloride-bearing electrolytes, even when quite acidic, the titanium is adequately durable to general corrosion, provided the design gives freedom from anodic breakdown corrosion. Highly concentrated sulfuric acid is generally more aggressive towards titanium. In engineering terms anodic polarisation (protection) allows practical usage for many years. In one reported situation (30), however, titanium, polarised at 12 volts in 10 per cent sulfuric acid at 35°C, was found to be covered with film of thickness 30 to 40 µm. Later examination showed that there was a slow but continuing pitting dissolution followed by

precipitation, which caused such thick film formation. At more elevated temperature, 70°C and above, structural corrosion may still occur but the continuing localised titanium dissolution no longer precipitates to form film.

An early warning of dire events that could happen to titanium-based electrodes was implicit in a paper by Antler and Butler who reported degradation mechanisms in platinum- and rhodium-plated titanium electrodes at accelerated high current densities during high temperature testing in simulated chlorate liquor (31). Thick titanium oxide was found to have formed underneath the noble metal coating. How could this occur if the local anodising potential on such specimens was never more than a few volts? As no similar electrode failures were found in sodium chlorate plants, the possibility of thick film formation under noble metal/oxide coatings was put to one side for many years.

Electroalvanising: The Andritz Ruthner Experience

The next episode in this story came when the Austrian company, Andritz Ruthner of Vienna, came up with a novel method of coating zinc onto one side of continuous coils of steel strip, principally for the automobile industry, but also for domestic appliances, see Figures 12 and 13. This Gravitel process also finds application for coating both sides of steel strip to different thicknesses, see Figure 14.

The Gravitel process involved zinc deposition at high current density (equivalent to mercury-type chlorine cells at 10 to 20 kA m⁻²) from made-up electrolyte compositions. Initial evaluation seemed to show that a pure iridium oxide electrocatalyst on a titanium substrate with an overlay of tantalum oxide would suffice to uprate corrosion resistance in hot sulfuric acid. Accordingly, a massive quantity of electrodes was made for – almost simultaneous – use in three plants. However, their operation showed that the nominally identical anodes behaved quite differently in each plant. In one plant, after a few months' operation, the electrodes suffered premature degradation due to 'Antler-Butler-type'



Fig. 13 A smaller electrogalvanising addition to an existing coil coating plant
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thick film formation, which physically disrupted the electrocatalyst coating. The phenomenon was initially and erroneously thought to be some form of attack from a deposit. In the second plant there was no evidence of thick film formation under the coatings, but there was a high rate of intrinsic wear and loss of adhesion by under-

mining attack. In the third plant there was neither thick film growth under the coating, nor high wear rate, and the electrodes clearly behaved as expected. How could these nominally similar electrodes behave so differently in the three plants? The explanation lay in the characteristics of the titanium substrate described earlier.

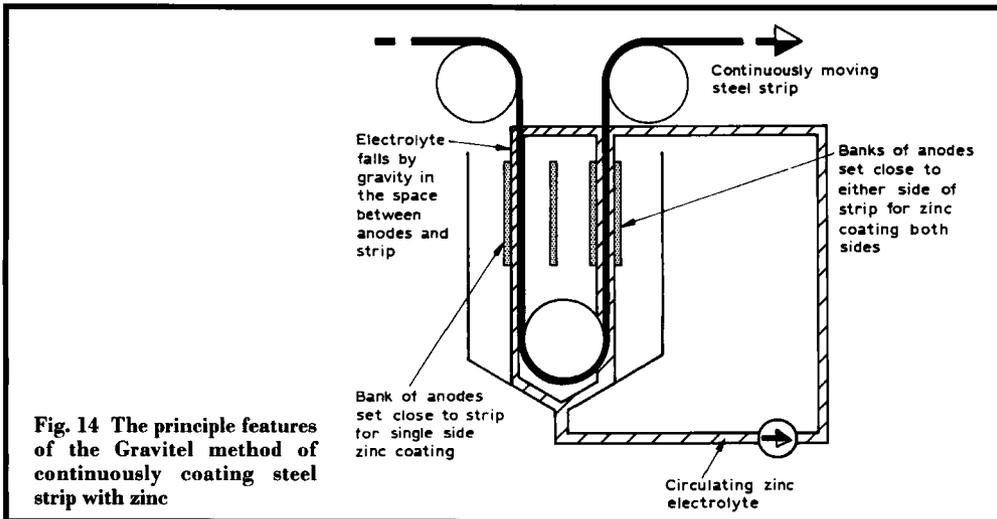


Fig. 14 The principle features of the Gravitel method of continuously coating steel strip with zinc

In the first plant, where thick film formed under the electrocatalyst, the operating temperature was about 65°C and the current density was high. Unexpectedly, even though the surface electrode potential was controlled by the noble metal oxide electrocatalyst, there was micropitting of the titanium and precipitation of film. In the second plant the electrolyte temperature exceeded 65°C and the current density was particularly high in order to meet the special needs of the plant. Thus titanium dissolved without precipitation and the iridium oxide suffered transpassivation dissolution. These resulted in electrode replacement more often than planned. The third plant, operated at lower electrolyte temperature and lower current density, did not experience the fault-causing conditions of the other two plants, at least over protracted periods.

The experience gained from these first three



Fig. 15 Typical titanium electrodes used in electrogalvanising plants. The laboratory assistant shows the size of such electrodes

Gravitel plants formed the basis both for the construction of improved electrodes and methods of use. If the etching characteristics of commercially pure titanium of differing residual impurity content are examined, etching rates increase with increasing impurity. Hence, high current density electrogalvanising anodes, see Figure 15, benefit from:

- being made from the purest titanium
- having residual surface impurities leached
- possibly having interlayers to help shield the electrolyte from the titanium, including oxide layers preformed by thermal oxidation
- having thick coatings of $\text{IrO}_2/\text{Ta}_2\text{O}_5$, to combat the effects due to the high current density.

While the first chlorate electrodes received 70/30 Pt/Ir coatings with loadings of less than 5 g m^{-2} , and most chlor-alkali electrodes use ruthenium-based coatings with loadings up to 20 g m^{-2} , loadings on electrogalvanising anodes can be 50 g m^{-2} or higher, and even then the lifetimes are not much in excess of one year. Coatings for this application are still an on-going development area.

Corrosion Protection

In addition to the use of oxygen evolving anodes in electrogalvanising, other opportunities for using electrodes occurred in electrofining, electroforming and the continuous anodising of aluminium strip for the printing industry. Another unexpected application then presented itself relating to reinforced concrete used in structural engineering. Over the years a small percentage, but huge in total, of reinforced concrete had suffered serious internal corrosion of the reinforcing bars from the presence of chloride ions. How could this most insidious and continuing corrosion situation be controlled? A consensus view in the 1980s was to use cathodic protection. Concrete is porous and contains electrolyte in pores in contact with the reinforcement. If the electrochemical potential of the steel could be controlled electrochemically, as in the protection of ships' hulls (32), then corrosion could be delayed until the damaging chloride ions had migrated away towards an anode. Hence external anodes are

Fig. 16 Mesh positioned on a support beam prior to application of a cementitious overlay. This gives an impression of the scale of usage of the mesh. The beam is part of a wharf in the Middle East

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necessary for this method of protection (33).

It has always been recommended that platinised titanium anodes, at least those operating at high current density, should be kept free from surface deposit (34). This is to prevent the formation of localised highly concentrated acidity which could damage both the coating and the titanium substrate. The application of coated titanium in concrete is only really practical by virtue of operating at current densities some five orders of magnitude lower, which limits the amount of acidity formed. Acidity is further neutralised by the proximity of highly alkaline concrete.

The commonest form of titanium-based anode for application to concrete is an open mesh not dissimilar to galvanised chicken-wire mesh, see Figure 16 (35–38). The holes in the pattern are around 5 cm × 5 cm, and the actual real surface area is about one tenth of the geometrical surface area it covers. To complete an electrochemical cell, the mesh is first applied to the active surface and then attached to the structure with a cementitious material, usually by spraying, see Figure 17. The electrolyte then makes contact between opposing electrodes via water in the pores of the concrete, which usually also helps to dissipate any anodically generated gas. Such gas may include chlorine if there is chloride in the concrete adjacent to the anode, but it is predominantly oxygen.

Electrocatalysts chosen for titanium-based anodes in concrete include 70/30 Pt + IrO₂, IrO₂ and IrO₂/Ta₂O₅. Because the current density of the application, at ~ 0.1 A m⁻², is so low

compared with, say, electrogalvanising, only very low loadings of electrocatalyst are necessary, often less than 1 g m⁻². In fact, over the last 15 to 20 years, many hundreds of thousands of square metres of reinforced concrete – in roads, bridges and buildings have been treated, with no reported failures of the titanium, which is just as well as most are designed to have lives of 25 or more years.

The present owners of the patents on the mesh form of anode have a virtual world monopoly, just as the owners of the Beer 2 patent held an almost world monopoly on codeposition methods of applying coatings. As happened with the Beer patent, numerous attempts have been made to compete with the titanium mesh form of anode by various ingenious alternative devices.

Discussion

The titanium-based electrode business is now commercially huge, involving possibly billions of dollars. In this survey, it has not been possible to cover the niceties of most applications, such as anodes in chlorate, the production of persalts, hypochlorite generation or more recent possibilities in organoelectrosynthesis, ground remediation on local and large scale, controlled ground water migration, effluent treatment, electroetching, and other uses.

With the increasing sophistication of all aspects of modern technology, it is perhaps surprising that the repetitive and laborious paint/thermal decomposition method of building up the required electrocatalyst should continue to be used. True, there are plants with a high degree

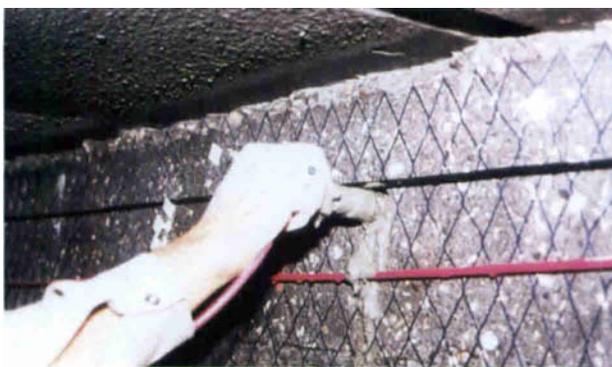


Fig. 17 Coated chicken-wire type titanium mesh positioned for use in the impressed current cathodic protection of rebar, just prior to application of a cementitious overlay

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of inbuilt automation, but attempts (and there have been many) to build up coatings quickly, for example, by heavy increments using paint/thermal decomposition, have not been successful. In fact, computerised atmosphere-controlled plasma deposition is making inroads for some applications, including cathodic protection, but it seems likely that the delicate, quasi equilibrium, high sensitivity electrocatalysts will continue to be made by the paint/thermal decomposition method for many years to come.

The Beer patents have now expired worldwide, allowing the number of electrode manufacturers to increase, although most electrodes continue to be made by a few experienced large companies who have the financial resources to guarantee their products fully.

The extensive use of noble metals and oxides as coatings on titanium has contributed to a better understanding of their electrochemistry. However, despite the growth of the noble metal/oxide coated titanium anode, the total consumption of noble metals in these industries has not attained levels that dictate world prices. Rather, the electrode market remains at the mercy of the vagaries of other applications. Few in the industry over the last 40 years will forget the marked price changes for iridium, the volatility in the price of silver, even the quite recent fall in rhodium price, but throughout the years the price of platinum has remained relatively stable.

Finally, this article has been prepared as a tribute to the few who started the commercialisation of titanium-based electrodes. There was

the irrepressible Joe Cotton, the quietly working Cliff Angell, but let no-one lose sight of the enormity of credit due to the charming, gentle, unassuming, Henri B. Beer.

Acknowledgements

It is sincerely hoped that organisations whose names have been included will not take issue over inclusion in this narrative. Appreciation is extended to the huge number of contributors to the technology. Finally the writer thanks a number of technical colleagues for reading the manuscript, including B. H. Hanson, D. A. Hughes, A. T. Kuhn and last, but by no means least, my long-established friend M. A. Warne.

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