Lead-Platinum Bielectrodes for Cathodic Protection

ADVANTAGES IN MARINE APPLICATIONS

By L. L. Shreir, Ph.D.

Department of Metallurgy, Sir John Cass College, London

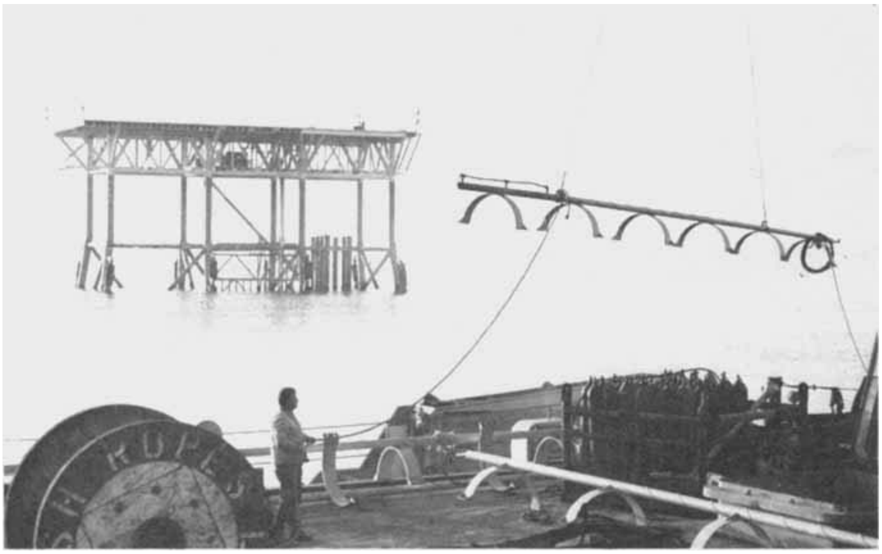
The insertion of small pieces of platinum into the surface of lead or lead alloy anodes causes a remarkable change in their behaviour as electrodes. Such lead-platinum bielectrodes are inexpensive, robust and easily fabricated and can be used successfully for the cathodic protection of marine structures. In this article the author describes the principles involved and reviews ten years of experience in a variety of applications.

It has been established for some years that lead and lead alloys can be used as inert anodes in electrolytic processes provided that a film of lead peroxide is formed and is maintained on the surface.

Lead peroxide, which is a thermodynamically stable form of lead at elevated electrode potentials, can be formed by the oxidation of $Pb^{2+}aq$ in solution at an inert electrode, such as platinum, or by the oxidation of lead itself. The oxide is chemically stable and is characterised by a high electronic conductivity (about 50 per cent that of lead) so that lead with a film of PbO_2 will act as an inert anode, provided the oxide remains in electrical contact with the metal and is reformed should a discontinuity be produced in the film. Thus anodic polarisation of lead in sulphuric acid results in the formation of a thin film of PbO_2 at the Pb/PbO_2–H_2SO_4 reversible potential; with further passage of charge the predominant reaction is oxidation of water to oxygen and there is practically no thickening of the film.

The position in chloride solutions is quite different, and both $PbCl_2$ and PbO_2 are formed simultaneously, but at low current densities a film of the latter gradually consolidates and the lead can then act as a relatively inert electrode. The presence of SO_4^{2-} in chloride solutions, as in sea-water, facilities the formation of PbO_2, and anodes of 1 to 2 per cent silver-lead and 1 per cent silver – 6 per cent antimony-lead are used for the cathodic protection of marine structures.

It has been shown however (1), that the insertion of a platinum microelectrode into lead has a remarkable effect on the anodic behaviour of the latter, and that lead-platinum bielectrodes can be anodically polarised in chloride solutions at high current densities (2). Chlorine evolution on platinum takes place at low overpotentials (3), so that this reaction occurs in preference to oxygen evolution, although the latter is the thermodynamically preferred process; platinum in contact with lead will therefore tend to act as a potentiostat and to limit the potential of the lead/solution interface to about 2.5 volts. It has been shown (4) that the PbO_2 film thickens when anodically polarised at high current densities in sea-water, and since the volume ratio of PbO_2/Pb is greater than unity, the film is under considerable expansive stress. This results in the formation of blisters which eventually rupture, with subsequent formation of $PbCl_2$ and corrosion of the exposed lead and, at constant current density, the potential of the electrode will increase since the $PbCl_2$ is nonconductive.



Among the applications for which lead-platinum bielectrodes have been found successful is the cathodic protection of the structure and well casings of North Sea drilling rigs. Here an electrode – fixed at the left-hand end of the steel frame – is being installed on one such rig. This electrode will operate at 35 amps per square foot

(Photograph by courtesy of Metal and Pipeline Endurance Limited)

This can be demonstrated by forming PbO_2 on a lead-platinum bielectrode and then removing the platinum microelectrode, when the potential immediately increases. When platinum is in contact with the lead this increase in potential cannot occur, and PbO_2 will re-form at the lead exposed at a ruptured blister without excessive corrosion.

Design and Construction of Bielectrodes

The lead-platinum bielectrode consists of an extruded bar of lead or lead alloy, 1 to 1.5 inch diameter and up to 12 feet in length, into which are inserted platinum microelectrodes at 6 to 12 inch intervals. The microelectrodes consist of small wires of platinum (with a small percentage of an alloying metal to increase hardness) 0.5 inch long by 0.030 inch diameter, inserted in the lead by drilling a 0.025 inch diameter hole, tapping in the wire until it is flush with the lead surface and then peening the surrounding lead to ensure good electrical contact.

The nature of the lead used in the bielectrode is important and recently an extensive series of tests on cast lead and lead alloys and on dispersion-hardened lead have been carried out in collaboration with D. P. Peplow of the Central Electricity Generating Board. The illustration overpage shows cast lead alloys (1 inch long by 1 inch diameter) and extruded dispersion-hardened lead (1.5 inch long by 0.5 inch diameter) on test in a water box at Marchwood Power Station. These anodes were polarised at 50 A/sq. ft for one year in order to assess the effect of the composition on the growth and spalling of the lead peroxide, and the results can be summarised as follows:

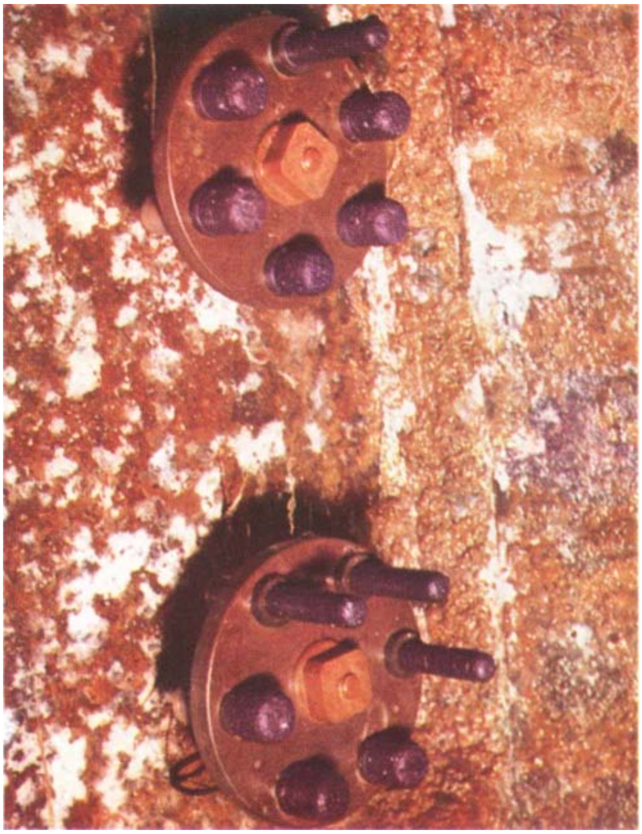
(*a*) Additions of silver are beneficial, and 0.1 per cent is almost as effective as 1 per cent.

(*b*) Additions of antimony, bismuth and tin appear to be detrimental.

(*c*) Dispersion-hardened lead and lead alloys are unsatisfactory, since pronounced spalling occurs in the direction of extrusion.

Successful Installations

The use of lead-platinum anodes in cathodic protection installations is largely confined to Metal and Pipeline Endurance Limited (MAPEL) in England, and to Lockheed Aircraft Service Corporation of Ontario, Cali-



The type of lead or lead alloy for use in platinum bielectrodes is important, and extensive tests have been carried out with a number of alloys. The anodes shown here were in use for a year, at 50 amps per square foot, in a water box at Marchwood Power Station in order to assess the effect of composition on the growth and spalling of the lead peroxide

(Photograph by courtesy of the Central Electricity Generating Board)

fornia, both of whom, on the basis of over ten years' experience, are using them for a variety of marine structures.

One of the earliest applications by MAPEL was for the cathodic protection of the cooling water culverts in a power station in Malacca, Malaya. These anodes have now been operating satisfactorily for ten years at 25 A/sq. ft. Other examples of large structures protected by MAPEL are the jetties in Europort and North Sea gas platforms such as that shown in the illustration on page 43. Here the bielectrode is mounted on a steel frame which is attached to the legs of the platform so that both are protected.

The Lockheed Aircraft Company have used these anodes extensively for the protection of bulk carriers, tankers, liners, offshore drilling rigs and oil-wells and this company has recently been awarded the contract (5) for the protection of the San Francisco Bay Area Rapid Transit Tube, a steel tube four miles long and some 130 feet in circumference which will carry rail and road traffic under the Bay; this is probably the largest cathodic protection installation ever undertaken.

Advantages of Lead-Platinum Anodes

Lead-platinum bielectrodes are cheap, robust and easily fabricated, and can be used economically in sea-water over a range of current densities, from 10 to 70 A/sq. ft; a large anode operating at a low current density is sometimes an advantage when a uniform current distribution is required on a large structure. The presence of an a.c. ripple on the d.c. produced by transformer-rectifiers causes the slow corrosion of platinum, which can be serious when the platinum is in the form of a very thin coating on a valve metal. The effect of a.c. corrosion on the relatively massive platinum microelectrode is insignificant, and this has the advantage that single-phase equipment produces no problems when lead-platinum anodes are used in a cathodic protection system.

The experience gained over the past ten years has shown that the lead-platinum bielectrode provides a cheap and reliable anode for the cathodic protection of marine structures, and it is envisaged that its importance will increase in the future.

References

1 L. L. Shreir and A. Weinraub, *Chem. and Ind.*, 1958, 1326; L. L. Shreir, *Platinum Metals Rev.*, 1959, **3**, 44

2 E. L. Littauer and L. L. Shreir, Proc. First Int. Congr. Metall. Corros., p. 374, Butterworths, London, (1961); L. L. Shreir, *Corrosion*, 1961, **17**, 90; E. L. Littauer and L. L. Shreir, *Electrochim. Acta*, 1966, **11**, 465

3 E. L. Littauer and L. L. Shreir, *Electrochim. Acta*, 1966, **11**, 527

4 D. B. Peplow and L. L. Shreir, *Corrosion Technology*, 1964, **11**, (4), 16

5 E. L. Littauer, Private communication

A Standard High Purity Platinum

NEW REFERENCE MATERIAL OF CERTIFIED COMPOSITION

In 1922, in the course of a study of methods for the preparation of high purity platinum, the National Bureau of Standards made a small trial melt which was identified in a laboratory notebook as No. 27. This was found to be thermoelectrically negative to all other specimens of platinum observed up to that time, although the temperature coefficient of resistance was only 0.003922. It is recorded that this specimen was put aside as a primary standard for thermoelectric purposes and was designated Pt 27. This has remained the standard of reference in the U.S.A. ever since, although it is extremely doubtful if any of the original sample exists.

At a conference in the U.S.A. in 1960 between the NBS and representatives of the platinum industry, an extensive programme was laid down to examine the properties of high purity platinum. In particular, it was agreed to try to relate e.m.f. against Pt 27 at 1200°C with temperature coefficient of resistance and the presence of impurities. This led to a prolonged series of tests by different bodies to assess the impurities in parts per million, by spectrographic and other means.

A batch of pure platinum was prepared by induction melting high purity platinum sponge in a zirconium silicate crucible, and casting into a platinum-lined water-cooled copper mould. The ingot was worked and drawn to wire taking the utmost care to prevent contamination. This material has been designated Standard Reference Material 680. Extensive analytical programmes, as well as tests for homogenity, were carried out, in co-operation with the NBS, by Johnson Matthey, Matthey Bishop, Sigmund Cohn, Engelhard Industries and RCA Laboratories, and a provisional certificate of analysis has been issued by the NBS giving the following impurities:

Copper	0.1 p.p.m.	Gold	<1
Silver	0.1	Magnesium	<1
Palladium	0.2	Zirconium	<0.1
Lead	<1	Rhodium	<0.2
Iron	0.7	Iridium	<0.01
Nickel	<1	Oxygen	4

Because of a certain amount of lack of agreement among the methods used, no estimate of accuracy can be made at present, but it is hoped that in six months' time a revised certificate will be issued.

In addition, a further sample designated SRM 681 containing substantially greater quantities of impurities, has been prepared for analytical reference, again with a provisional certificate of analysis.

Both of these materials in the form of 0.020 inch diameter wire may be obtained from the Office of Standard Reference Materials of the NBS, Washington, in lengths of either 4 inches or 1 metre.

Because the supply of Pt 27 has been totally exhausted, there is a need for a new standard. The NBS is making provision for platinum of substantially the same purity as SRM 680 to be prepared, and to be designated Pt 67. This will be used at NBS as the national standard for the calibration of thermocouple wires. It is probable that the new standard will give an e.m.f. against Pt 27 at 1200°C of about −9 microvolts and that it will have a temperature coefficient of resistance of 0.003927.

H. E. B.