

Lead-Platinum Bi-Electrodes

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The introduction into a lead electrode of a small piece of platinum brings about a remarkable change in the electrode behaviour. It is shown that lead-platinum bi-electrodes may well have important applications in electrolytic processes such as cathode protection.

Lead and lead alloys may be used as inert anodes in electrolytic processes provided a film of lead peroxide (specific resistance $\sim 40-50 \times 10^{-6}$ ohms cm) is formed and maintained on the lead surface. Anodic polarisation of lead in sulphuric acid results in the formation of an adherent peroxide film and, after the film has reached a limiting thickness, the electrode behaves as a noble metal, the electrode process being evolution of oxygen.

In chloride solutions, anodic polarisation of lead at constant current results in the formation of lead chloride (or oxychloride) which produces, if it remains adherent to the metal surface, a rapid increase in voltage. Under certain electrolytic conditions, the lead rapidly corrodes away. It would appear that, in chloride solutions, a thin film of lead peroxide is formed at the lead chloride/electrolyte interface and is thus insulated from the metal by the lead chloride.

A study of lead-platinum bi-electrodes has shown that if a small micro-electrode of platinum is introduced into the lead surface there is a remarkable change in the electrode processes (1). Fig. 1 shows the results obtained when pure lead and pure lead containing a micro-electrode of platinum are anodically polarised in 3 per cent NaCl at 5 A/dm² for 50 hours. Whereas the bi-electrode became coated with lead peroxide and the voltage did not exceed 5 v, the lead rapidly corroded with the formation of a white, voluminous reaction product, the voltage reaching 16 to 18.

It has been shown that insertion of a platinum micro-electrode into pure lead which has been polarised, at 2.5 A/dm², until the voltage increases to 50 results in a rapid fall in the voltage to ~ 5 . If the platinum is removed from the lead the voltage rises rapidly and the lead corrodes.

Fig. 2 shows the weight-time relationship for two lead-platinum bi-electrodes polarised at 2.5 A/dm² in artificial sea-water. After an initial dissolution of lead there is a gradual increase in weight due to the formation of lead peroxide. After 300 hours the weight remains constant, showing that film growth has ceased and that current is transported by electrons only. During this experiment the voltage did not exceed 5.

Fig. 3 shows the current-time relationship for lead and for lead containing a platinum

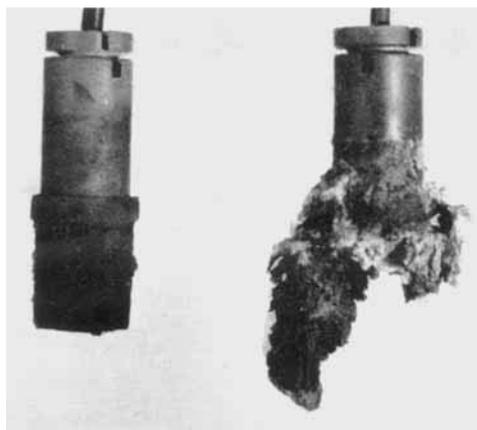
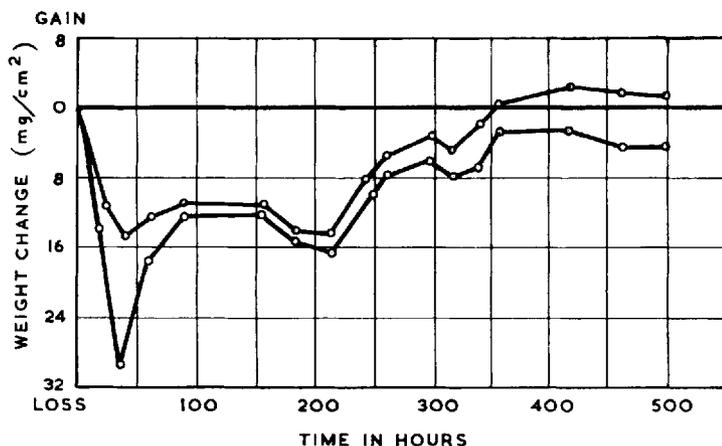


Fig. 1 Lead anodes polarised for 50 hours in 3 per cent NaCl at 5 A/dm². Left, lead containing a platinum micro-electrode; right, pure lead

Fig. 2 Weight-time relationship for two lead-platinum bi-electrodes anodically polarised at 2.5 A/dm^2 in artificial sea-water



micro-electrode maintaining the potential constant at 1.95 v (hydrogen scale). The initial increase in current with pure lead is considered to be due to the formation of Pb^{++} , which then reacts producing a coating of lead chloride of high electrical resistance on the metal surface with a consequent decrease in current. With the platinum-lead bi-electrode it would appear that, although initially the electrode process is similar, after ten minutes the lead chloride is converted into lead peroxide resulting in an increase in current.

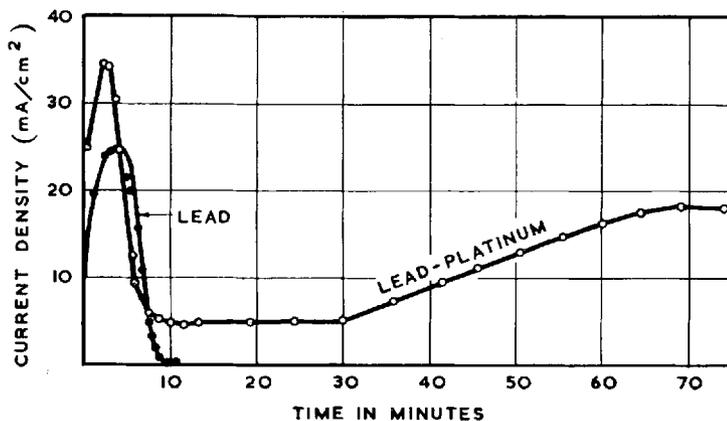
The previous considerations show that insertion of a platinum micro-electrode into the surface of a lead anode results in the formation of lead peroxide when polarised in chloride solutions. Removal of the micro-electrode results in an increase in the resistance of the film, due presumably to a non-

conducting film forming and a consequent increase in voltage.

Although several factors operating simultaneously may give rise to this phenomenon, it is suggested that one explanation is that the platinum functions as an internal 'potentiostat' and controls the potential of the lead surface (1).

It is relevant to consider the function of a platinum micro-electrode in contact with a metal which has a natural oxide film of high electrical resistance, for example titanium, zirconium or niobium. If such a bi-electrode is polarised in a chloride solution all the current passes through the platinum, and film growth, with a consequent increase in resistance, is prevented. The platinum thus controls the potential of the carrier metal. If platinum is placed in contact with lead the formation of a film of high resistance will

Fig. 3 Anodic polarisation of a lead and a platinum bi-electrode at a constant potential of 1.95 v (hydrogen scale)



immediately cause electron current to flow through the platinum with a consequent increase in its potential. This in turn will raise the potential of the lead surface to a value where lead is oxidised to peroxide and, provided the electrolyte has a high conductivity and attention has been paid to the design of the bi-electrode, the whole of the lead surface will become coated with conductive lead peroxide. Wheeler (2) has, however, recently put forward the view that the sole

function of the platinum is to make electrical contact between the lead and the peroxide.

It is considered that bi-electrodes of platinum with lead and lead alloys may have application in electrolytic processes, including cathodic protection, electroplating and electro-precipitation.

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References

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Platinum-bonded Silicides and Borides

CERMETS OF THE TRANSITION METALS

The great advantages that would follow if oxidation-resistant materials retaining great strength at very high temperatures were available are so self-evident that considerable effort and ingenuity continue to be expended in all fields which might contribute to their development.

In seeking a basis for such materials, it is tempting to look particularly to the silicides and borides of the transition metals of high melting point—titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten. Many of these compounds have melting points of 3000°C and over, and some are among the hardest materials known. In addition, many have excellent resistance to oxidation and scaling.

If these compounds are to be used, and in particular, if they are to be bonded to form acceptable cermets, it is essential, as Dr. R. Kieffer and Dr. F. Benesovsky, of Metallwerk Plansee A.G., Reutte, Austria, point out in an excellent review of recent developments (*Powder Metallurgy*, 1958, 1/2, 145-171) that the constitution of the various silicide and boride systems should be understood and

physico-chemical properties of the resulting compounds known. Immense though the task is of determining these characteristics, very great progress—reviewed by these authors—has been accomplished during the past few years. Rather less effort has been given to bonding these compounds, but the possibility of using the platinum metals remains attractive.

Kieffer and Benesovsky report briefly the results of impregnation tests of MoSi_2 , WSi_2 , TiB_2 and ZrB_2 , first pressed to compacts under 3 tons/in.² and sintered at 1500°C, with a number of molten metals in argon. In these conditions both platinum and 50:50 palladium-silver alloy gave complete impregnation, although silica alone does not wet the compounds. The one apparent disadvantage of platinum is that it tended to erode the compacts—more with the silicides than the borides—and it is suggested that one method of inhibiting this erosion might be first to alloy the platinum with silicon. It appears that further work along these lines might be well justified.

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