The Anodic Behavior of Lead-Platinum and Lead-Palladium Bielectrodes in Chloride and Sulfate Solutions

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In recent years the electrolytic anodes with platinum coating on the metallic bases, such as tantalum, titanium and tungsten, have attracted extensive attention in the fields of sodium chloride electrolysis and cathodic protection against corrosion.

Shreir1) found that the lead anodes in chloride electrolytes were prevented from corroding when a platinum, indium or graphite microelectrode was introduced.

While tentative explanations have been made of the effects of platinum, it is considered, in view of the complications involved, that further experimental studies are necessary in order to get a clearer understanding of the reaction mechanisms.

Experimental

Lead anodes with an area of 1 cm² were prepared at a purity of 99.99%. Test specimens of platinum and palladium, as well as the lead anodes, were then immersed into the surfaces of resinous blocks.

The potential was determined by means of a saturated calomel electrode in a sodium chloride solution or in laboratory sea water and by means of a 1 N mercurous sulfate electrode in a sodium sulfate solution.

Results and Discussion

Lead Electrode in 0.5 N Sodium Chloride. —The anodic current of the lead electrode in the passive region was smaller than that in the active region, though the latter came below the anodic current of the other two electrodes. Figure 1 shows the anodic polarization curve for lead in 0.5 N sodium chloride.

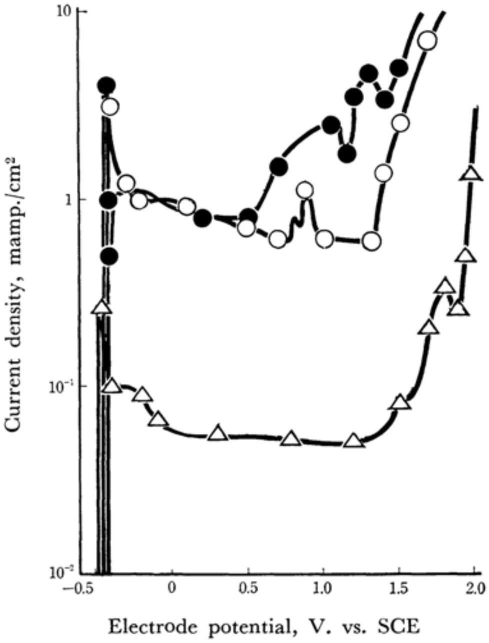

Fig. 1. Anodic polarization curve of lead electrode, lead-platinum bielectrode and lead-palladium.
△ Pb, ○ Pb-Pt bielectrode
● Pb-Pd bielectrode
Electrolyte: 0.5 N NaCl 100 cc.
Rate of potential change: 0.005 V./min.

This result suggests that lead chloride, formed and then dissolved in the active region, deposits on the electrode surface as illustrated in the following formulae:

$$\mathrm{Pb} \rightarrow \mathrm{Pb}^{2+} + 2\mathrm{e}$$
$$E = -0.368 + 0.0295 \log A_{\mathrm{Pb}^{2+}} \qquad (1)$$

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1) L. L. Shreir, *Corrosion,* **17,** 118t (1961).

$$Pb^{2+} + 2Cl^- \rightarrow PbCl_2$$
$$E = -0.510 + 0.0295 \log A_{Cl^-} \qquad (2)$$
$$K = 1.6 \times 10^{-5}$$

The palladium anode in a 0.5 N sodium chloride solution gave an incipient current in the potential region from 1.1 to 1.2 V., this was 500 mV. higher than the current for platinum. As has been decribed above, this means that the chloride ions are absorbed on the firmly-formed lead chloride layer, which is thus changed into lead dioxide. As the potential region from 1.4 to 1.9 V. is transpassive, the isolated lead present in the porous lead chloride layer will be dissolved as quadri-valent lead ions, according to the following reactions:

$$Pb \rightarrow Pb^{4+} + 4e$$
$$Pb^{4+} + 4OH^- \rightarrow PbO_2 + 2H_2O$$

The quadrivalent lead ions which are hydrated in the vicinity of the electrode are discharged and then deposited on it in this potential region. The lead dioxide formed still displays a fine appearance at first, but the film immediately decomposes as a result of the discharge of chloride ions.

It is considered that, in the passive region, the formation of metallic lead and chloride in the defective anode layer are involved in the absorption reaction of hydroxide ions. Fleischmann and Liler2) established, using a lead acetate electrolyte, that lead dioxide easily neucleated and grew up on the platinum anode. They suggested the following reaction processes:

$$OH^- - e = OH_{ads} \qquad (3)$$
$$Pb^{2+} + OH_{ads} + OH^- - e = Pb(OH)_2{}^{2+} \qquad (4)$$
$$Pb(OH)_2{}^{2+} = PbO_2 + 2H^+ \qquad (5)$$

Reaction 4 presumably controls the reaction rate. Feitknecht and Gäumann3) proposed the following reactions:

$$OH^- = OH + e \qquad (6)$$
$$PbO^+ + 2OH = Pb(OH)_2{}^{2+} + O^- \qquad (7)$$
$$Pb(OH)_2{}^{2+} = PbO_2 + 2H^+ \qquad (8)$$

For the anodic reaction of the Pb electrode in the presence of chloride ions, the authors inferred, instead of formulae 4 and 8, that:

$$\begin{aligned}&Pb^{2+}\ (\text{in layer}) + OH_{ads} + OH^- - e \rightarrow\\&\quad Pb(OH)_2{}^{2+},\ Pb(OH)_2{}^{2+} + 4Cl^- \rightarrow\\&\quad [PbCl_4(OH)_2]^{2-} \rightarrow PbO_2 + 4Cl^- + 2H^+\end{aligned} \qquad (9)$$

and

$$\begin{aligned}&PbCl_4 + 2OH^- - 2e \rightarrow\\&[PbCl_4(OH_{ads})_2]^{2-} - 2e \rightarrow\\&PbO_2 + 2Cl^- + 2H^+ + Cl_2\end{aligned} \qquad (10)$$

Platinum and Palladium in Solutions of Sodium Chloride, Sodium Sulfate and Artificial Sea Water.—If palladium does not dissolve as well as platinum, the evolution potential of chlorine gas for palladium will be about 1.02 V., that is, 0.03 V. less than that for platinum. The evolution potential of oxygen on palladium is 0.075 V., and on platinum, 0.80 V. (referred to the mercurous sulfate electrode). It was found that the incipient anodic current for palladium appeared at 0.9 V., while that for platinum appeared at 0.9 V., too. Heumann and Schürmann4) reported that the current-potential curves for the palladium anode in electrolytes containing chloride ions exhibited an active region, a primary passive region, and a secondary passive region; these correspond, respectively to the dissolution of palladium into the divalent state, the chlorine evolution from the passive electrode, and the oxygen evolution. They stated the experimental results as follows: For the palladium anode in 0.5 N hydrochloric acid, the anodic current begins at the potential of 0.62 V. and passes through a

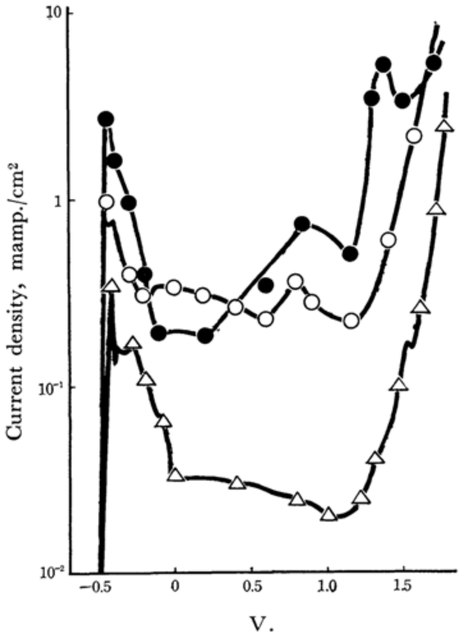

Fig. 2. Anodic polarization curve of Pb, Pb-Pt bielectrode and Pb-Pd bielectrode in artificial sea water.
△ Pb, ○ Pb-Pt, ● Pb-Pd
Electrolyte: artificial sea water: 100 cc., 30°C
Rate of potential change: 0.005 V./min.

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2) M. Fleischmann and H. R. Liler, *Trans. Faraday Soc.*, **54**, 1370 (1958).

3) W. Feitknecht and A. Gäumann, *J. Chim. Physique, Physicochim. Biol.*, **49**, 135 (1956).

4) Th. Heumann and R. Schürmann, *Ber. Bensen Ges. Phys. Chem.*, **67**, 601 (1963).

maximum current density of about 0.04 amp./cm² at 1.4 V. *in the active region*; then it decreases towards the minimum value of 0.01 amp./cm² at 1.6 V. Another maximum in current density (0.06 amp./cm²) comes at the anodic potential of 1.75 V., after which the current again descends to 0.04 amp./cm². A further rise in the potential results in a monotonous increase in the anodic current.

Figure 2 depicts the anodic polarization curves for all the electrodes in aritificial sea water. On account of the dissolved oxygen, the current for the lead electrode becomes negative in the potential region from −0.8 to −0.55 V. The reaction mechanism was discussed in a previous report.[5] In our present experiments, the transpassivity region ranged between 0.6 and 0.9 V. when oxygen gas evolved on the electrode. The behavior of the lead platinum bielectrode is very like that of the lead electrode, but lead-palladium is so different that the anodic current begins to rapidly increase at −0.23 V. and the polarization curve is reflected at 0 V., above which point the transpassive region ranges from 0.8 to 1.1 V. Vetter[6] considered that the anodic current on the lead-palladium bielectrode indicated palladium dissolution but not lead dissolution in the potential region from −0.2 to 0 V., since the active region of palladium is in the potential region around −0.2 V.

The Influence of the Current Density on the Corrosion Rate of Palladium in Artificial Sea Water.—If palladium dissolves in the bivalent form, the dissolved ion amounts, according to Faraday's law, to 1.9903 g. at the current of 1 amp. for 1 hr. and 7.6416 g. at the current of 1 amp./dm² (32 mamp./3.2 cm²) for 5 days. The practical corrosion, however, weighed 0.00064 g., about 8/1000000 of the theoretical dissolved quantity. The difference in amount of electric charge between the calculation and the practical corrosion is caused by the gas evolution.

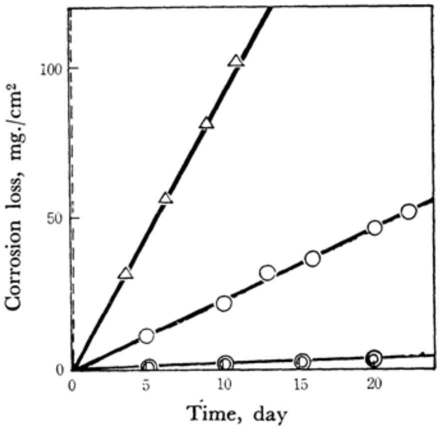

Fig. 3. Corrosion rates of Pd in artificial sea water.
◎ 1 amp./dm², ○ 5 amp./dm²
△ 10 amp./dm²
---- theoretical deposit amount of Pd²⁺ at 1 amp./dm²
Electrolyte: artificial sea water 500 cc., room temp.

Summary

A potentiostatic method was used to investigate the behavior of lead electrodes and lead-platinum and lead-palladium bielectrodes in sodium chloride and sodium sulfate solutions and in sea water. The experimental results showed lead-palladium bielectrode to be of practical use in the electrolysis of sea water.

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[5] E. Sato and T. Shiina, *J. Electrochem. Soc. Japan*, **32**, 148 (1964).

[6] K. J. Vetter and D. Berndt, *Z. Elektrochem.*, **62**, 378 (1958).