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Platinum-iridium catalyzed titanium anode. II. Oxygen evolution

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The oxygen evolution reaction on titanium based Pt–Ir catalyzed DSA has been investigated. The steady state polarization curves of the electrodes with the various contents and different pH values of electrolyte have been determined.

A good Tafel linearity with slopes of 40 and 120 mV dec^{-1} were obtained. The conclusion is drawn that the second electrochemical step is rate-determining. The overvoltage of the oxygen evolution reaction at 1 A cm^{-2} compares most favourably with published data for other materials.

1. Introduction

The preceding communication [1] reported the behaviour during the electrolytic preparation of chlorate of a dimensionally stable anode (DSA) based on titanium and coated with a platinum-iridium alloy (60:40 wt. %) as a catalyst. Another process of practical relevance is the electrolysis of water and the present communication reports on the use of these same electrodes as anodes for oxygen evolution from acid and alkaline aqueous solutions.

2. Experimental

The anodes used were those which efficiently sustained chlorate electrolysis for 400 days at 300 mA cm^{-2} at 60°C. During this interval, 20 –50 % of the alloy corroded away. The surface concentration of alloy varied between 0·08 and 0·8 mg cm^{-2}. The process of oxygen evolution was investigated over the pH range 0·5 – 13·6 in an electrolyte consisting of NaOH and $HClO_4$ to a total concentration of 1 N. Steady-state polarization measurements were made in a cell normally used for kinetic investigations by supplying a controlled current and comparing the electrode potential with an SCE connected via a Luggin capillary. The results presented below however, are on the standard hydrogen scale. The platinum wire counter-electrode was in the same compartment as a consequence of which the pH of the solution did not change even after prolonged electrolysis. Air was bubbled through the cell throughout the measurements. The cell was maintained at 25 ± 0·1°C.

Stable steady-state values of electrode potential were readily established and no hysteresis was observed as is characteristic of the polarization of platinum, for example. For comparison, some measurements were made on electrodes of nickel, smooth platinum and on a DSA based on ruthenium oxide (De Nora-Milan) in 1 N NaOH solution.

3. Results

The polarization of the electrodes was found to depend strongly on the surface concentration of catalyst (Fig. 1). A Tafel relationship was obtained over more than three decades of current density having a slope of 120 mV dec^{-1} for an alloy concentration of 0·75 mg cm^{-2}. As this concentration was reduced, the slope increased but electrodes could operate at as low a content as 0·076 mg cm^{-2}.

However, the remaining data presented were all obtained with 0·75 mg cm^{-2} of the alloy.

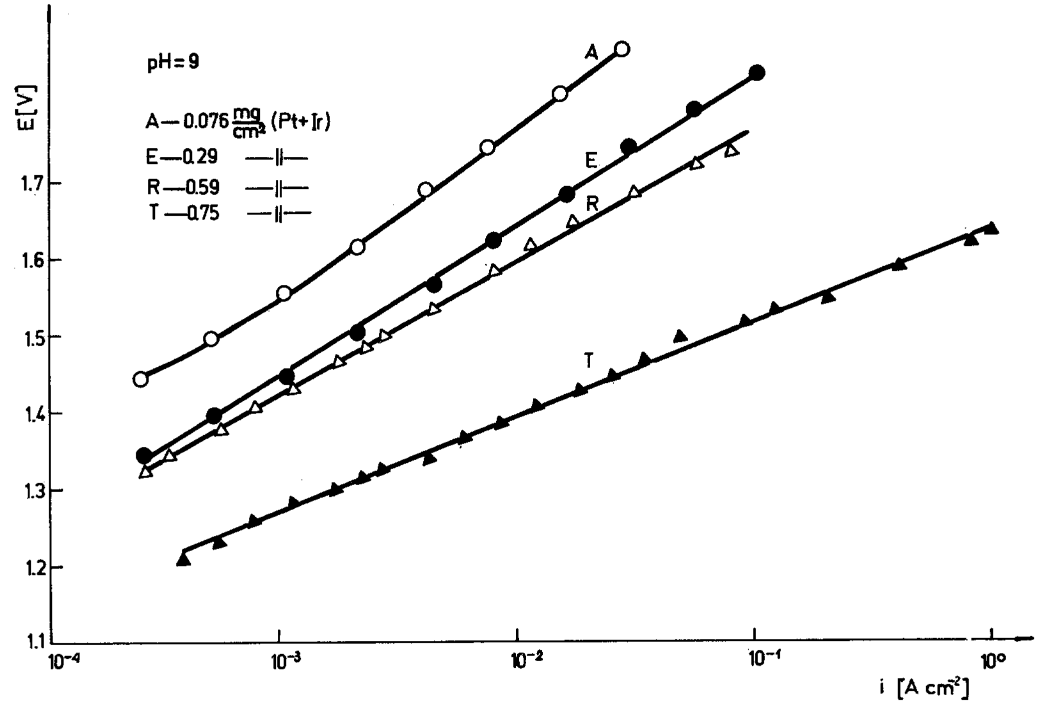

Fig. 1. Tafel lines for oxygen evolution on Pt–Ir DSA in 1 N $NaC10_4$ of pH 9 for different catalyst content at the surface. Curves: 1 – 0·076 mg cm^{-2}; 2 – 0·29 mg cm^{-2}; 3 – 0·59 mg cm^{-2}; 4 – 0·75 mg cm^{-2}.

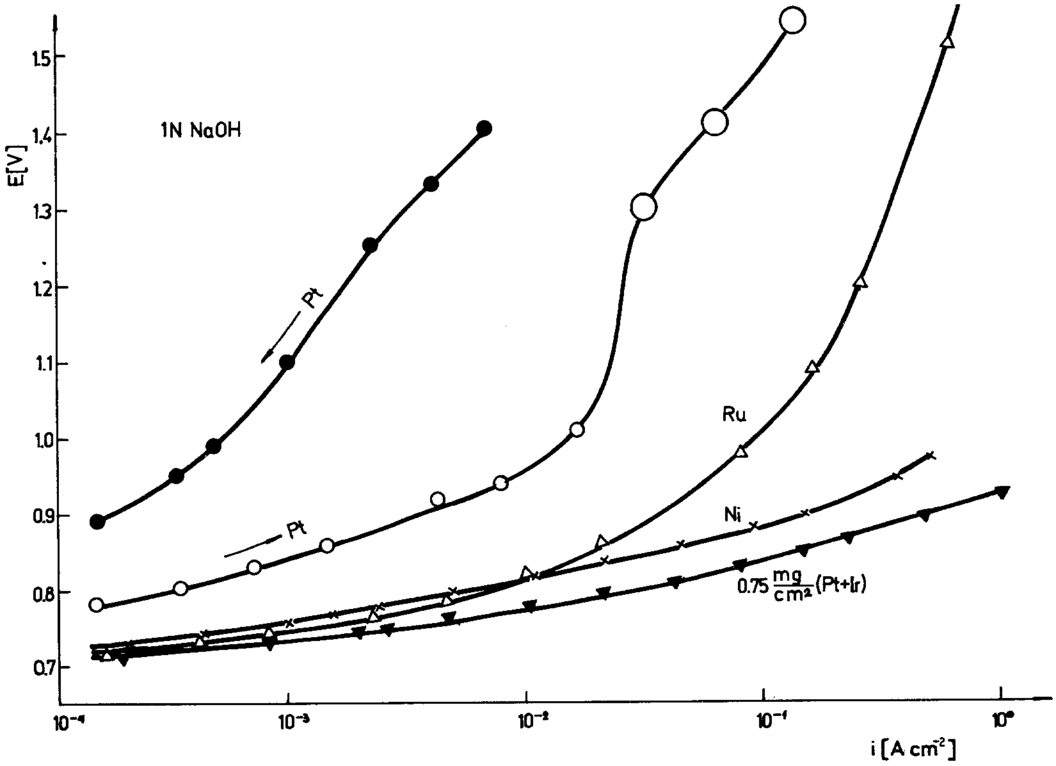

Fig. 2. Polarization curves for oxygen evolution on different electrodes in 1 N NaOH solution.

The characteristics in 1 N NaOH are compared in Fig. 2 with those of other electrodes. Pure platinum exhibits a considerable hysteresis and is a rather poor anode for this process. It is interesting to note that the ruthenium oxide based DSA has comparable behaviour at low current densities but significantly poorer properties in the region of commercially relevant current densities (0·1–1 A cm^{-2}).

The polarization characteristics also depended strongly on the pH of the solution (Fig. 3). Different behaviour is exhibited in acid and in alkaline solutions. In the latter at fairly low pH, limiting currents are observed with the transition of the polarization into the region characteristic of the acid medium.

4. Discussion

The polarization characteristics shown in Fig.3 give information on the processes occurring at the Pt–Ir based DSA. The ready establishment of these characteristics and the absence of hysteresis indicate that the electrode surface does not undergo irreversible oxidation as found with pure platinum [2] and the conclusion is that the presence of iridium has a stabiliizing effect on platinum.

The existence of the pH–dependent limiting current density, which is sensitive to stirring, and the transition to the other polarization level in alkaline solutions leaves no doubt that in the acid and alkaline regions two different processes take place:-

$$2\,H_2O = O_2 + 4\,H^+ + 4e \qquad (1)$$

and the discharge of OH$^-$:

$$4\,OH^- = O_2 + H_2O + 4e\,. \qquad (2)$$

It should also be noted, however, that the shift of polarization by about 800 mV between pH 0·5 and 13·6 parallels that expected for the reversible potential of oxygen evolution by either of the

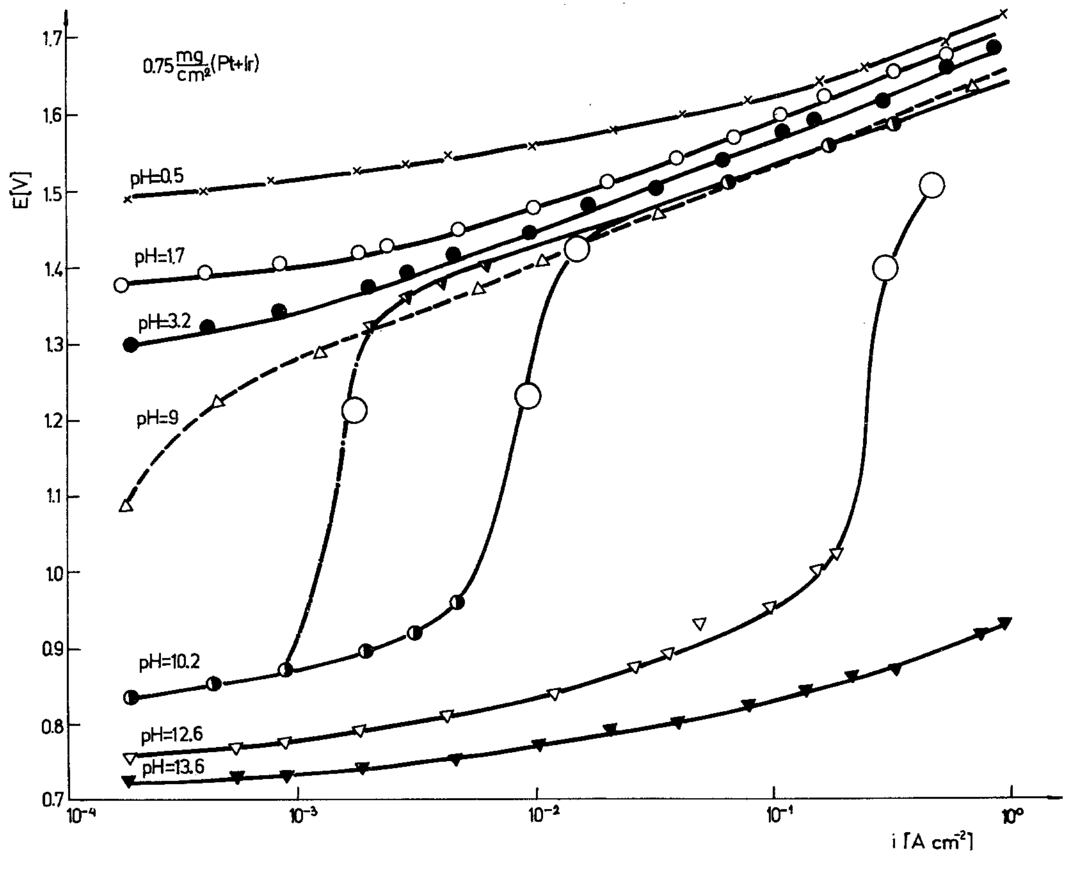

Fig. 3. Polarization curves for oxygen evolution on Pt–Ir DSA with 0·75 mg cm^{-2} alloy in 1 N (HC1O$_4$ + NaOH) solutions of different pH.

processes (60 mV dec^{-1}). In other words, the overpotential seems to remain constant. This indicates that the alloy has equally good catalytic properties with respect to both water and OH$^-$ discharge, suggesting that the rate-determining step may be the same in both processes. Several facts are indicative of reaction mechanism.

Thus, (1) in the low current density region, all the Tafel lines have a slope of 40 mV dec^{-1}; (2) in the same region, polarization is pH dependent, i.e. it increases with decrease in OH$^-$ concentration and increase in H$^+$ ion concentration; (3) in the high current density region, the Tafel slope is 120 mV dec^{-1}; (4) the polarization is practically independent of pH (95 mV difference over 10 pH units), i.e. all Tafel lines converge*.

Such a well-defined Tafel slope of 40 mV dec^{-1} suggests strongly that it is the second electron exchange in the line, which is rate-determining [3]. Hence, the reaction path should be one in which at least the first two steps could be said to be

$$H_2O \rightleftharpoons OH_{ads} + H^+ + e \qquad (3)$$

$$(\text{or } OH^- \rightleftharpoons OH_{ads} + e \text{ in alkaline region})$$

and

$$OH_{ads} \xrightarrow{rds} \dots + e\,. \qquad (4)$$

This is in accordance with the finding that the rds should be the same for the discharge of water and of OH$^-$ ions.

It also agrees with the recorded pH dependence of polarization in the low current density region, for the increase in the concentration of H$^+$ ions suppresses the first step in the first case, while the decrease in OH$^-$ ion concentration shifts the equilibrium to the left in the second case. Thus this leads to first order kinetics with respect to pH in both cases.

The change in the Tafel slope to 120 mV dec^{-1} and the absence of a dependence on pH in the higher current density region can also be interpreted on the same basis. Two reasons can be put forward.

As the concentration of OH$_{ads}$ increases towards saturation of the surface it will become independent of the concentration of H$^+$ (or OH$^-$) or of potential. When the concentration of electroactive intermediate becomes potential independent the transfer coefficient is known to change from 1·5 → 0·5, characteristic of a symmetrical barrier and, as a consequence, the slope changes from 40–120 mV dec^{-1}.

An alternative explanation can be found in the fact that in such a mechanism there is always a current density region in which the first step becomes slower than the second (whose rate increases faster with potential than that of the first) and takes over the control, with the Tafel slope changing to the value found.

Both these explanations are also in accord with the fact that the transition from the lower slope to the higher one takes place at lower current densities the higher the pH.

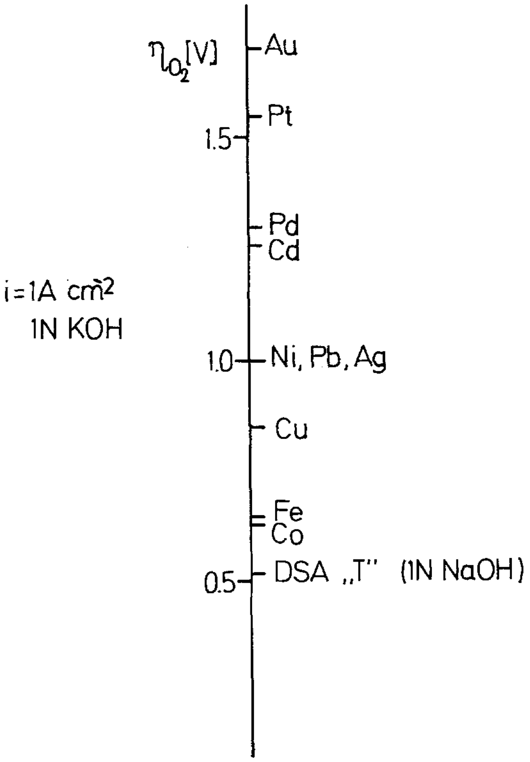

Fig. 4. Comparison of oxygen overpotentials in 1 N KOH solutions at different metals [4] with that at Pt–Ir DSA (0·75 mg cm^{-2} of alloy) in 1 N NaOH.

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* Several authors have investigated the behaviour of pure iridium with respect to oxygen evolution [3,4]. It is interesting to note that Damjanović, Day and Bockris [3] also found a Tafel line with two different slopes (40 mV dec^{-1} and 120 mV dec^{-1}) and a narrow transition region. However, polarizations were somewhat higher than those found in the present work with the Pt–Ir alloy. Thus, in the lower slope region there is a difference in current density at a constant potential, of about half an order of magnitude, while in the higher slope region the difference is close to two orders of magnitude.

However, if the first cause was operative with the second step rate-determining under all conditions, at the very high pH values the transition should have taken place at current densities below the investigated current density region and the Tafel slope in alkaline solutions should have already come to 120 mV dec^{-1}. The fact that this is not so suggests strongly that the second mechanism is the operative one. In this case the rate constant of the first step could be much larger in the case of OH^- discharge than in the case of discharge of water and the transition of slopes at pH 14 could be above the current densities investigated as found in experiments.

The practical significance of the data obtained can be seen in Fig. 4 where overpotential at 1 A cm^{-2} is compared with those on a series of metals taken from the literature [4]. It is seen that the Pt–Ir based DSA has a far smaller polarization than metals commonly used as catalysts in oxygen evolution. There is a difference (0·1 V) between it and cobalt, the best catalyst known hitherto. When the small amount of the noble alloy catalyst used per cm^2 and its resistence to corrosion are taken into consideration the efficiency of such electrodes in the electrolysis of water becomes evident.

5. References

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