JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 31–35

Anodic discharge of chloride ions on oxide electrodes

G. FAITA AND G. FIORI

Laboratory of Electrochemistry and Metallurgy, University of Milan, Milan, Italy.

Received 16 July 1971

The behaviour of a mixed oxide coating thermally deposited on titanium has been examined with respect to the anodic discharge of chloride ions.

The electrochemical properties are similar to those of thermal Pt and Pt–Ir alloy electrodes: chlorine evolution takes place through an electrochemical–chemical mechanism, the $2Cl_{ads} \rightarrow Cl_2$ step being rate determining.

Evidence is given about the mechanical and chemical stability of the coating and about the satisfactory reproducibility of the catalytic properties. Moreover, the current efficiency for chlorine evolution appears to be at least 99% at high current densities (up to 16,000 A/m^2).

Introduction

The anodic oxidation of chloride ions to chlorine has been already examined in two previous works in the case of Pt and Pt–Ir alloys thermally deposited on titanium matrices [1, 2]: the mechanism consists of two steps, the first one being electrochemical, the second one chemical and rate determining. It has been demonstrated that the passivation effects which characterize the Pt electrodes can be greatly decreased by using Pt–Ir alloys with very low Ir content (0·5%). In long run electrolyses (i.e., thousands of hours) where chemical and mechanical stability are important, a minimum content of 10% Ir in the alloy should be used. The present paper is concerned with the behaviour of a different type of coating suitable for the same electrochemical process. The coating consists of a mixture of metallic oxides thermally deposited on a titanium matrix.

Experimental methods

A rotating disk apparatus [3] has been used in order to remove quickly the Cl_2 bubbles from the electrode surface: in this way currents and potentials are highly stable and their values can be read with sufficient precision and accuracy. The coating of mixed oxides has been prepared according to a procedure (example No. 1) described by G. Bianchi, V. De Nora, P. Gallone, and A. Nidola in a pending patent [4].

The deposit is a solid solution of Ti, Ir, Ru oxides (13·15% Ir, 13·15% Ru, 73·7% Ti as metals); for greater convenience such a coating will be referred to as 'Ruthenium dioxide' coating in the following sections of the paper.

The electrochemical measurements were made galvanostatically. The electrode potentials were read by a Tektronix type 531 A oscilloscope and corrected for ohmic drop. The latter was read directly on the oscilloscope screen by using the well-known current interruption technique: the system was made up by a highly stabilized current regulator, a buffer resistor connected in series with the electrochemical cell, and a transistor-driven mercury relay which was connected in parallel to the electrochemical cell. Such an arrangement prevented unwanted oscillations; typical rise and fall times in the range of 1 μs were obtained.

Before each experiment the electrodes were polarized anodically at 150 mA/cm^2 for 10 min in the solution where the electrochemical measurements were made. During each run nitrogen was passed over the NaCl solutions whose pH was held at a value of 2.

Results

Fig. 1 shows the polarization curve for a thermal RuO_2 electrode: the graph of electrode potential against the logarithm of the current densities is a straight line over a wide range of current densities and its slope (i.e. the Tafel coefficient) is 40 mV/decade of current.

The experimental conditions are: 1M NaCl, pH = 2, $T = 30$°C. In the same figure analogous data are shown for Pt and Pt–Ir (4% Ir) electrodes which were prepared thermally as described in a previous paper [2] and for a graphite electrode. The latter is characterized by a complex overpotential/current relationship: the Tafel coefficient is 40 mV/decade of current only in the low current density range, whereas its value increases up to 175 mV/decade of current above 5 mA/cm^2. These data are very similar to those already quoted in the literature [5, 6]. Consequently, from a practical point of view, it is apparent that the graphite anode is far less attractive in the anodic oxidation of aqueous chlorides than the thermally prepared Pt, Pt–Ir (4% Ir) and RuO_2 electrodes. Fig. 2 shows overpotentials (η) as functions of current densities for a number of ruthenium dioxide electrodes at 20°C. in 1, 2, 3 and 4 M NaCl, at pH = 2.

It is apparent, in the case of 4 M NaCl, that the linear dependence of overpotential on logarithm of current densities still holds up to very high current densities, the typical overpotentials being quite low (i.e. 135 mV at 16,000 A/m^2.) The slope of the straight lines depends on the NaCl concentration, the values being respectively 40 mV/decade of current in 1 M solution, 37 mV/decade of current in 2 M solution, 35 mV/decade of current in 3 M solution and 32 mV/decade of current in 4 M solution. In Fig. 3 the behaviour of RuO_2 electrode in 4 M NaCl is shown as a function of temperature: the overpotential decreases with increasing temperature at constant current density, the temperature coefficient being −0·55 mV/°C.

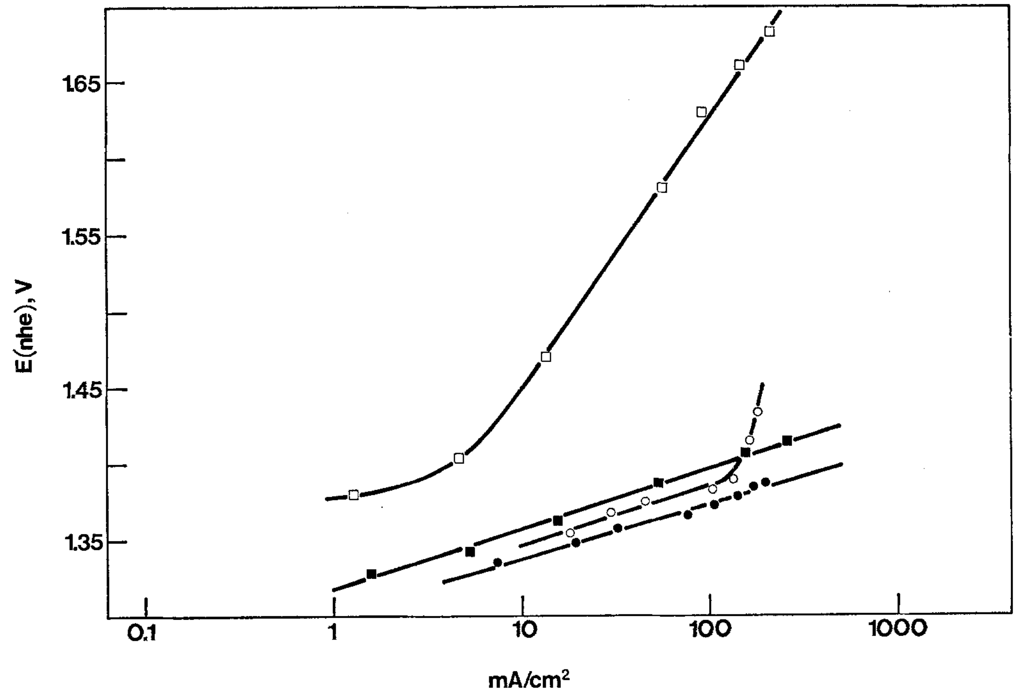

Fig. 1. Polarization curves for various electrode materials.
□ graphite in 1 M NaCl; T = 30°C; 2,800 rpm; pH = 2
■ RuO_2 in 1 M NaCl; T = 30°C; 2,800 rpm; pH = 2
○ Pt in 1 M NaCl; T = 30°C; 2,800 rpm; pH = 2
● Pt–Ir (4%) in 1 M NaCl; T = 30°C; 2,800 rpm; pH = 2

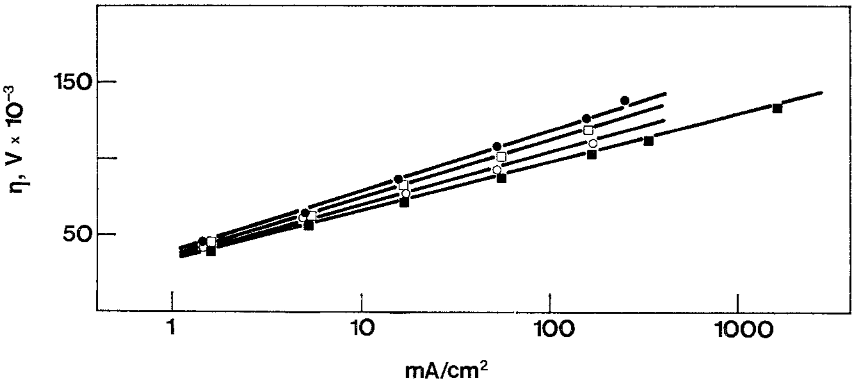

Fig. 2. Overpotential against current density as a function of NaCl concentration for a RuO_2 electrode.

● 1 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
□ 2 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
○ 3 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
■ 4 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2

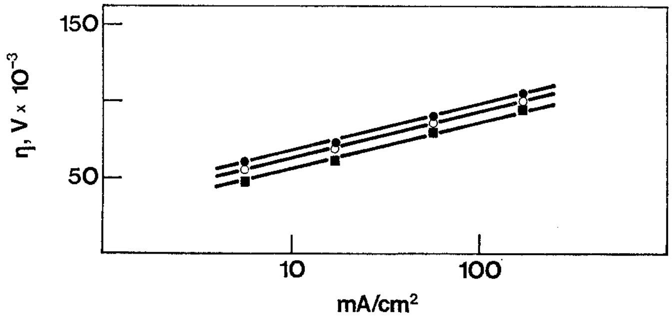

Fig. 3. Overpotential against current density as a function of temperature for a RuO_2 electrode.

● 4 M NaCl; $T = 21°C$; 2,800 rpm; pH = 2
○ 4 M NaCl; $T = 30°C$; 2,800 rpm; pH = 2
■ 4 M NaCl; $T = 39°C$; 2,800 rpm; pH = 2

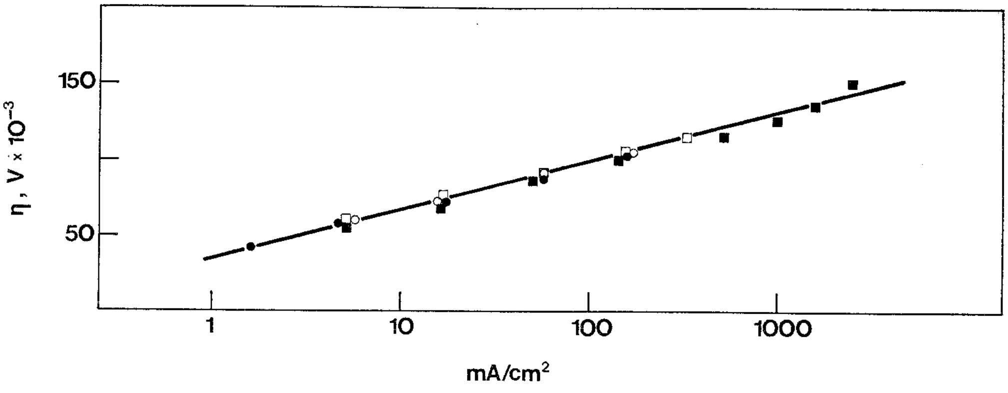

Fig. 4. Overpotential against current density for different RuO_2 electrodes.

● No. 1 in 4 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
○ No. 2 in 4 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
□ No. 3 in 4 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2
■ No. 4 in 4 M NaCl; $T = 20°C$; 2,800 rpm; pH = 2

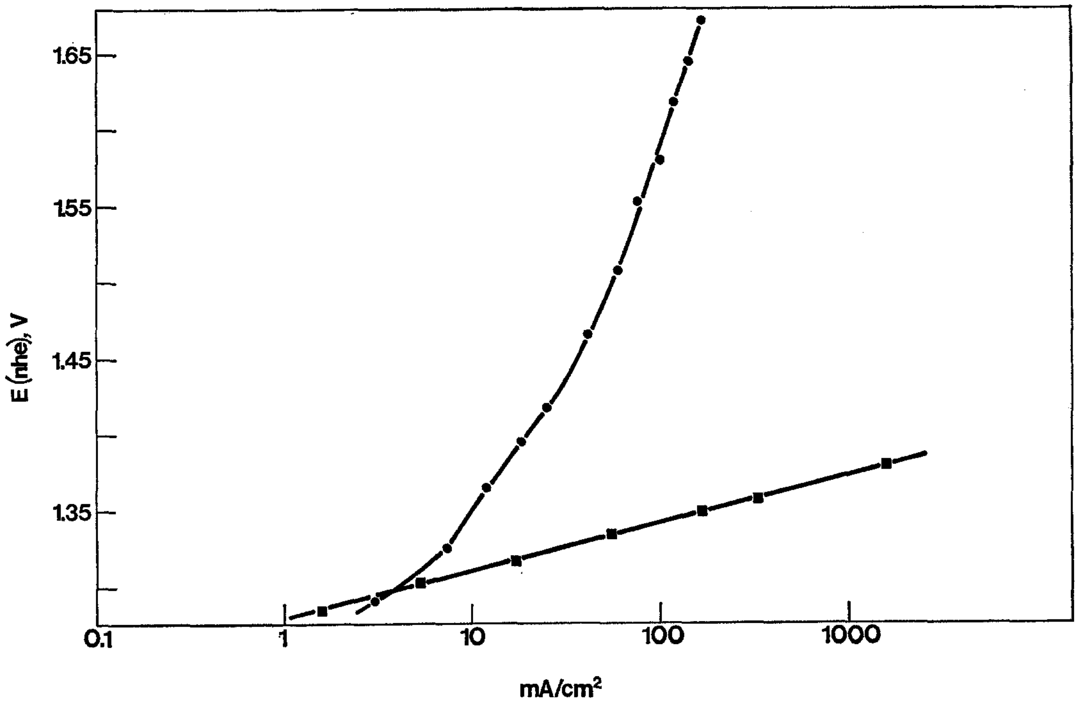

Fig. 5. Polarization curves for a ruthenium dioxide electrode in 1 M $NaClO_4$ and 4 M NaCl solutions.
● RuO_2 in 1 M $NaClO_4$, pH = 2; T = 20°C; 2,800 rpm
■ RuO_2 in 4 M NaCl, pH = 2; T = 20°C; 2,800 rpm

In Fig. 4 the polarization data in 4 M NaCl, pH = 2, are given for 4 ruthenium dioxide electrodes; the reproducibility of the data is satisfactory and the average scatter is less than ±5 mV.

Finally Fig. 5 shows the polarization curve for a ruthenium dioxide electrode in 1 M $NaClO_4$, pH = 2, at 20°C; for comparison the polarization curve for the same electrode in 4 M NaCl, pH = 2 is also drawn.

Discussion

From the experimental data shown in Fig. 1 it can be inferred that the electrochemical behaviour of thermally prepared ruthenium dioxide electrodes is quite similar to that of thermal Pt and Pt–Ir alloy electrodes [2], as regards the anodic discharge of chloride ions. The low slopes of the Tafel straight lines (30 ÷ 40 mV/decade of current) show that an electrochemical–chemical mechanism should be followed, the chemical desorption step being rate-determining:

1st step $Cl^-_{el} \xrightarrow{\bar{e}} Cl_{ads}$
2nd step $2\,Cl_{ads} \rightarrow Cl_{2,el}$ (RDS)

The rotating disk electrode and the highly concentrated NaCl solutions allow the diffusion control to be excluded from the electrochemical kinetics even at the highest current densities. It must be pointed out that unlike the Pt electrodes [7] the RuO_2 electrodes are free from hysteresis phenomena, i.e. the polarization curves obtained by increasing and subsequently decreasing current densities are generally coincident. This experimental fact allows oxidation phenomena capable of changing the composition (the Ru/O ratio), at least on the surface of the film, to be neglected.

In order to test electrode reliability, long-run experiments on laboratory scale were carried out at 165 mA/cm² and 275 mA/cm²; after a 10 hr long electrolysis no changes of overpotential were found. The resistance to the strong chlorine bubbling and to the vibrations, which are unavoidable in the rotating disk apparatus, and the absence in the brine of dissolved ruthenium, give the first evidence that the tested electrodes are characterized by good mechanical and chemical stability.

As regards the reproducibility of the catalytic properties, Fig. 4 shows the high quality of the above-described ruthenium dioxide coating. It can be observed that the thermally deposited ruthenium dioxide is stable in a range of pH and potential where, according to Pourbaix equilibrium diagrams [8], formation of RuO_4 (or ruthenates) should take place. The explanation of this unexpected behaviour could depend on the peculiar structure of the film which is a heavily doped, nonstoichiometric oxide, or on chloride ion adsorption, which should prevent the surface oxidation and consequently the solubilization of the coating. This behaviour has already been observed with platinum electrodes, where oxygen chemisorption is strongly inhibited in halide-containing solutions [9].

Finally, it is interesting to compare the polarization curves for a ruthenium dioxide electrode in 1 M $NaClO_4$ and 4 M NaCl, the pH value being 2 for both solutions (Fig. 5). The electrode displays a very high overvoltage for oxygen evolution in 1 M $NaClO_4$; if the oxygen evolution rate does not change in 4 M NaCl, it can be concluded that the current efficiency for the discharge of chloride ions is at least 99% at 16,000 A/m^2, the electrode potential being 1·38 V_{NHE}.

Acknowledgement

This work has been sponsored by Consiglio Nazionale delle Ricerche (C.N.R.), Roma, Italy.

References

[1] G. Faita, G. Fiori and J. W. Augustynski, *J. Electrochem. Soc.*, **116** (1969) 928.

[2] G. Faita, G. Fiori and A. Nidola, ibid., **117** (1970) 1333.

[3] G. Faita, G. Fiori and J. Augustynski, *Electrochim. Metall.*, **2** (1967) 437.

[4] G. Bianchi, V. De Nora, P. Gallone and A. Nidola, Patent pending; n. 690,407; 14.12.1967 (USA)

[5] L. I. Krischtalik, *Electrochim. Acta*, **13** (1968) 1045.

[6] L. J. J. Janssen and J. G. Hoogland, ibid., **15** (1970) 941.

[7] E. L. Littauer and L. L. Shreir. ibid., **11** (1966) 527.

[8] M. Pourbaix, 'Atlas d'équilibres électrochimiques à 25°C.' p. 346. Gauthier-Villars & C. Éditeur, Paris (1963).

[9] M. W. Breiter, *Electrochim. Acta*, **8** (1963) 925.