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The reason for the loss of activity of titanium anodes coated with a layer of RuO_2 and TiO_2

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The galvanostatic method has been employed for following the time change of the ATA potential in 0·5 N H_2SO_4. On the basis of the experimental data it is proposed that the loss of ATA activity results from the formation of a non-conductive oxide film at the titanium–active layer interface.

1. Introduction

During the last years there have been many studies of the electrochemical properties of titanium anodes coated with a layer of ruthenium and titanium oxides, i.e. activated titanium anodes (ATA). With respect to the extensive industrial use of these anodes it is important to know why they lose their electrochemical activity after a certain time. (This is manifested by increasing anode potentials). This knowledge could then be exploited in the course of producing ATA, or possibly during the production of electrodes from used anodes.

According to certain data [1] the loss of electrochemical activity of the ATA occurs because of the oxidation of ruthenium dioxide to ruthenium tetroxide and thus, the dissolution of one component of the active layer. According to thermodynamical calculations [2], the oxidation of RuO_2 to RuO_4 occurs at potentials more positive than 1·387 V (versus the standard hydrogen electrode).

According to other data [3, 4], it seems possible that in the course of electrolysis a layer of the titanium oxide having a valve effect is formed. This layer would also increase the anode potential.

In the present work the reasons for the loss of the ATA activity were studied in detail.

2. Experimental

A galvanostatic method (i = constant) was used for ATA activity measurements. A SVÚOM–VPZ potentiostat in the galvanostatic connection served as a source of the constant current. The potential difference between the working and reference electrode was recorded on a Rikadenki (Kogyo Co. Ltd) six-line recorder. The same instrument was used to record the current between the working and the auxiliary electrode. The change of the potential with time served as a measure of the ATA activity.

All the measurements were performed at constant temperature, in an ordinary glass vessel with a three-electrode connection. The mercurous sulphate electrode in 0·5 N H_2SO_4 was chosen as the reference electrode. A cylindrical Pt gauze with a geometrical surface of about 30 cm^2 served as the auxiliary electrode. An activated Ti wire, 2 mm in diameter, served as the working electrode. The activated titanium wire was situated at the centre of the cylindrical auxiliary electrode, in order to obtain an even distribution of the anodic current density.

Two types of activated titanium anode were prepared. These were anodes with a layer of the RuO_2 only and anodes with a layer of RuO_2 and TiO_2, the ratio of the metals being 1 : 1 by mass. The electrodes were prepared by applying ethanol solutions of $RuCl_3$ or $RuCl_3 + TiCl_3$, respectively, on to a titanium wire, which was subsequently heated at a temperature above 400° C.

All the measurements were made in 0·5 N H_2SO_4 solution prepared from analytical grade sulphuric acid and distilled water. During each measurement the temperature was 20 ± 1° C. The measurement consisted in following the time change of the working electrode potential for different current densities. The current densities in the range 0·1–1·5 A cm^{-2} were used.

3. Results

A typical relationship between the potential of an activated titanium anode in 0·5 N H_2SO_4 and time for a current density of 0·5 A cm^{-2} is shown in Fig. 1. In this case the active layer on the titanium contains both RuO_2 and TiO_2 (metal ratio 1 : 1).

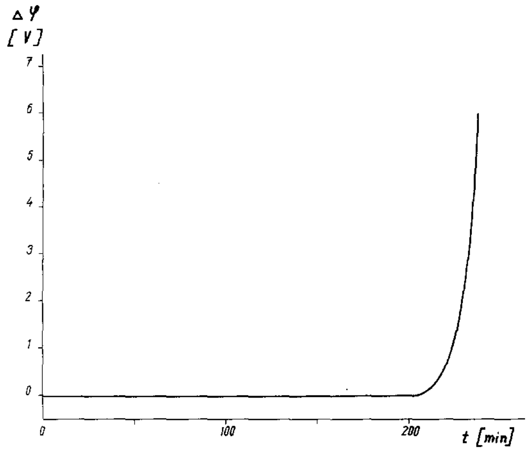

Fig. 1. The time change of the ATA potential in 0·5 N H_2SO_4 at 0·5 A cm^{-2} (RuO_2 + TiO_2).

The change of the activated titanium anode potential is defined by the Equation

$$\Delta\phi = \phi - \phi_0 \qquad (1)$$

where ϕ_0 is a potential of the ATA at time $t = 0$, ϕ is a potential of the ATA at time t. The ATA potential remains unaltered for quite a long time but then increases rapidly. At first sight, these curves are similar to those corresponding to the potential changes on electrodes forming non-conducting oxidic films on their surfaces [5].

Fig. 2 shows the dependence of $\Delta\phi$ on $\Delta\phi t$. This is a straight-line relationship, except as $t \to 0$, which may be expressed by the Equation

$$\Delta\phi = a + k\Delta\phi t \qquad (2)$$

or

$$\Delta\phi = \frac{a}{1 - kt} \qquad (3)$$

where k is the slope of the straight-line (Fig. 2) and a is the intercept on the y-axis. Equations 2 and 3 are not valid for small values of t.

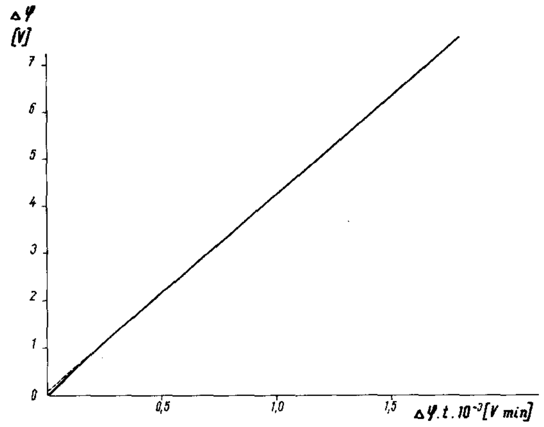

Fig. 2. Dependence of $\Delta\phi$ on $\Delta\phi t$ for an ATA (RuO_2 + TiO_2) in 0·5 N H_2SO_4 for a current density of 0·5 A cm^{-2}.

Curves of the same type are obtained for all current densities in the range 0·1–1·5 A cm^{-2} for the ATA with a layer formed by RuO_2 and TiO_2, or with RuO_2 itself, albeit with different values of the constants a and k.

By plotting the current density i as a function of ln k we can obtain the straight-line relationship shown in Fig. 3, for which

$$i = a_0 + b \ln k \qquad (4)$$

or

$$k = a_i \exp\frac{1}{b} \qquad (5)$$

where b is the slope (Fig. 3). For the ATA with a layer of RuO_2 and TiO_2 $b = 0{\cdot}311$ A cm^{-2}.

In the industrial use of ATA, the service time* represents one of the governing factors. In the present work the service time is defined as a time when, on a theoretical basis, the potential increases to an infinite value. This value can also be determined experimentally with a relatively high precision. The service time determined in this way is denoted by τ. A plot of service time versus current density is shown in Fig. 4. As can be expected, the service time drops with increasing current density.

The service time of the ATA can also be defined by means of the charge Q which passes through the electrode for the time τ. Then

$$Q = i\tau. \qquad (6)$$

By plotting this charge Q versus the current density i, we can obtain the dependence shown in Fig. 5.

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* The time of operation before the anode potential increases significantly (i.e. by 200–300 mV).

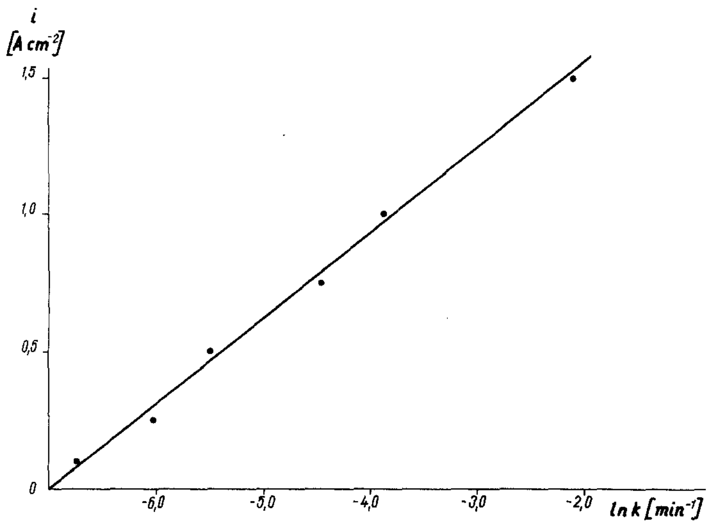

Fig. 3. Dependence of the current density i on $\ln k$ for an ATA (RuO_2 + TiO_2) in 0·5 N H_2SO_4.

4. Discussion

The increase in the ATA potential in 0·5 N H_2SO_4 occurs after several hundred minutes under laboratory conditions, whereas in the industrial electrolysis of alkali chlorides the service times of ATA can be several years. This may be related to the evolution of oxygen in the case of the 0·5 N H_2SO_4 solution. In contrast, during the electrolysis of alkali chlorides the evolution of oxygen is negligible.

The shapes of the ATA potential as a function of time curves are very similar to those obtained when a non-conducting film is formed on an electrode surface. (See also empirically established relations.)

Therefore we may speculate that a part of oxygen discharged on the active layer–electrolyte interface, is leaving the electrode surface in the form of bubbles that enter the solution, whereas a part of it is adsorbed on the surface and penetrates through the active layer towards the active layer–titanium interface by diffusion or migration. Oxygen is then chemisorbed on the surface of the titanium and this results in the formation of a non-conducting oxide layer.

The suggested mechanism is supported also by the results of work on the behaviour of titanium

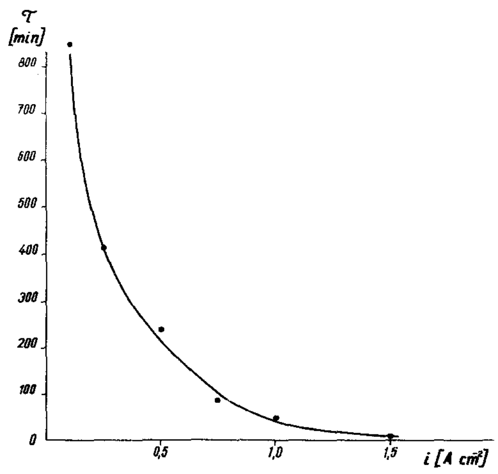

Fig. 4. Dependence of the service time τ of an ATA (RuO_2 + TiO_2) on the current density in 0·5 N H_2SO_4.

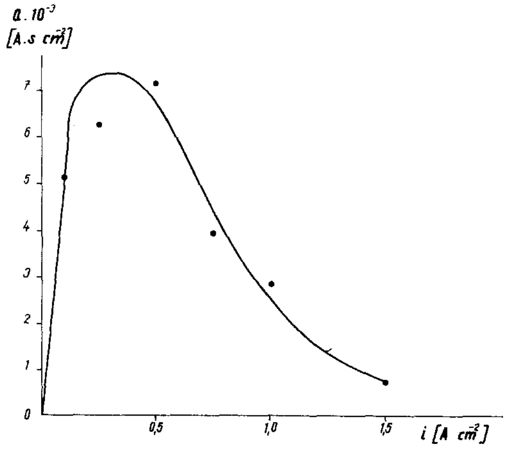

Fig. 5. Dependence of the ATA service time (Q) on the current density in 0·5 N H_2SO_4.

or tantalum anodes coated by MnO_2 [6] or PbO_2 [7], for which a similarly formed oxide layer is postulated.

The rate of oxygen discharge is much lower during the industrial electrolysis of alkali metal chlorides. On the basis of the mechanism suggested above, the service life of anodes should be proportional to the amount of oxygen in the anode gas. The situation is more complex in practice since the service life of anodes depends largely on other factors such as the number of faults, the pH and the frequency of circuit breaking.

References

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