

# *The reasons for the loss of activity of titanium–ruthenium dioxide anodes in sulphuric acid media*

T. LOUČKA

*Chemopetrol, Research Institute of Inorganic Chemistry, 400 60 Ústí nad Labem, Czechoslovakia*

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The interruption method has been employed to follow the change with time of the  $iR$  potential gradient corresponding to the potential fall between the anode and the end of a Haber–Luggin capillary. According to the experimental results the process of anodic discharge of oxygen on a  $\text{Ti/RuO}_2 + \text{TiO}_2$  electrode in 1 M  $\text{H}_2\text{SO}_4$  is accompanied by a loss of the active layer and by the simultaneous formations of a non-conducting, most probably oxidic, film.

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## 1. Introduction

A mechanism for the loss of activity of titanium anodes coated with a layer of  $\text{RuO}_2$  or  $\text{RuO}_2 + \text{TiO}_2$  was proposed in an earlier paper [1]. This mechanism consists of the formation of a non-conducting layer of Ti oxides at the interface between the titanium and the conducting layer of  $\text{RuO}_2$  and  $\text{TiO}_2$ . Another possible mechanism for the loss in activity is the oxidation of  $\text{RuO}_2$  in the active layer to  $\text{RuO}_4$ , which subsequently passes into solution [2]. It is also possible that both these processes may take place simultaneously. If the concept of the formation of a nonconducting layer is correct, the apparent potential rise during the loss in the anode activity is due to an increase in the  $iR$  drop. The present study aims to prove that the loss of anode activity is not caused by an increase in the anode overpotential but by the rise of the potential drop within the electrode.

## 2. Experimental

The electrodes were prepared in the same way as described earlier [1]. The Ti anode (wire, diameter = 3 mm) was coated with a layer of  $\text{RuO}_2$  and  $\text{TiO}_2$ , the mass ratio of the metals in the surface film being 1 : 1. A mercurous sulphate electrode in 1 M  $\text{H}_2\text{SO}_4$  served as the reference electrode. The measurements were made in 1 M  $\text{H}_2\text{SO}_4$ . The anode was placed along the axis of a

cylindrically shaped Pt gauze, which ensured an even distribution of electric current. The current was passed through the anode at a constant density ( $1 \text{ A cm}^{-2}$ ); current chopping (frequency 15 Hz) was carried out for 30 s after suitable time intervals. During these multiple breaks the value of the  $iR$  potential gradient, corresponding to the potential fall between the anode current supply and the end of a Haber–Luggin capillary, was assessed using a Tesla BM 430 oscilloscope. Similarly, the potential between the anode and the reference electrode was measured after each of the current chopping periods. The experiments were carried out at  $25^\circ \text{C}$ .

The changes in the Ru content in the active layer of the electrode were assessed in a parallel series of experiments by the X-ray spectroscopic method. The analyses were carried out on a PW 1410 spectrograph (Philips, Holland). The electrode samples ( $1 \text{ cm}^2$ ) were prepared from 1 mm thick Ti sheet and they were activated in the same manner as the wire electrodes.

## 3. Results and discussion

The measurement yielded the time dependence of the potential between the  $\text{Ti/RuO}_2 + \text{TiO}_2$  anode and the reference electrode and the  $iR$  drop. Both these dependences are plotted in Fig. 1. The potential between the anode and the reference electrode remains constant for a long period of

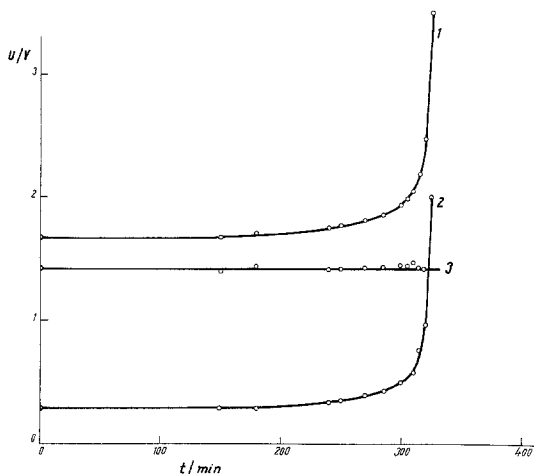


Fig. 1. Time dependences of the  $iR$  drop (curve 2) and of the potential between anode and mercurous sulphate electrode (curve 1). The corrected anode potential (curve 3) is obtained by subtracting curve 2 from curve 1.

time and then rises steeply (curve 1), consistent with earlier observations [1]. The plot of  $iR$  versus time has virtually the same shape (curve 2). The initial value of the  $iR$  gradient corresponds to the potential drop in the electrolyte and, to a small extent, also to potential gradients within the electrode, the active layer and at the  $\text{Ti/RuO}_2 + \text{TiO}_2$  interface. Since the distance between the electrode and the end of the Haber–Luggin capillary is constant, a steep increase in the  $iR$  potential gradient can be attributed only to an increase in the resistance in the electrode, in the active layer, and/or at the  $\text{Ti/RuO}_2 + \text{TiO}_2$  interface. Subtraction of curve 2 from curve 1 gives the time-dependence of the oxygen discharge potential (curve 3).

This potential is related to the mercurous sulphate electrode. It will be noted that the value remains constant even in the regions where the anode is losing its activity. In that region the dependence (curve 3) exhibits a somewhat wider spread of points ( $\pm 15$  mV). There is a lapse of time (10–15 s) between the measurements of the  $iR$  drop and of the potential and when the rate of growth of the  $iR$  potential gradient becomes significantly high, this may be sufficient to incur a certain error.

The fact that the corrected potential for oxygen discharge does not change even when the anode is losing its activity indicates that the chemical composition of the active surface layer does not change either. Thus the most obvious explanation for a rise of the  $iR$  drop is an increase in the resistance of the  $\text{Ti/RuO}_2 + \text{TiO}_2$  interface. The rise of the  $\text{Ti/RuO}_2 + \text{TiO}_2$  interface resistance can be readily explained by introducing the following relation:

$$R = R_0/(1 - \theta)$$

where  $R$  is the interface resistance,  $\theta$  is the fraction of the interface area occupied by the nonconducting oxide and  $R_0$  is the interface resistance at  $\theta = 0$ .

An evaluation of the results of X-ray spectroscopic analyses of anodically polarized electrodes and comparison with those obtained with non-polarized samples revealed that the content of Ru in the active layer after polarization decreased to roughly 1/5 of its original value. The samples, however, were polarized until the potential between the anode and the reference electrode increased from 2.5 to 8.5 V.

#### 4. Conclusion

According to the experimental results the process of anodic discharge of oxygen on a  $\text{Ti/RuO}_2 + \text{TiO}_2$  electrode in 1 M  $\text{H}_2\text{SO}_4$  is accompanied by a loss of the active layer and by the simultaneous formation of a nonconducting, most probably oxidic, film.

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#### References

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