

# ***Ruthenium dioxide: a new electrode material.***

## ***II. Non-stoichiometry and energetics of electrode reactions in acid solutions***

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RuO<sub>2</sub> films on Ta and Pt as supports have been prepared by thermal decomposition of RuCl<sub>3</sub> at different temperatures in various atmospheres. Bulk and surface electronic properties of these films have been deduced from their behaviour as electrodes with respect to reactions involving or not involving the adsorption of reactants and/or products, (for example Fe<sup>2+</sup>/Fe<sup>3+</sup>, I<sup>-</sup>/I<sub>2</sub>, H<sub>2</sub>/H<sup>+</sup> and some simple organic reactions). Results indicate that the non-stoichiometry of the oxide film is a function of the temperature of preparation and also of the atmosphere of annealing. In particular, smaller fractions of Ru<sup>3+</sup> are obtained as the temperature of preparation is increased and/or the atmosphere of annealing is made more oxygenated. Kinetics of electrode reactions suggest an essentially metallic nature for RuO<sub>2</sub> films. They behave very well with redox systems but exhibit poor electrocatalytic features in that rates of reactions involving adsorption steps are usually lower on RuO<sub>2</sub> films than on noble metals. Possible reasons for this are discussed in detail.

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### **1. Introduction**

The growing interest in RuO<sub>2</sub> electrodes [1–5] is essentially due to their ability to work well as anodes at the highest current densities in chlor-alkali cells [6, 7]. In Part I [8] of this series, the intrinsic behaviour of RuO<sub>2</sub> film electrodes prepared by the thermal decomposition (in the air) of RuCl<sub>3</sub> on metallic supports has been studied in acid solutions of inert electrolytes. In this paper, results relative to the behaviour in the presence of active electrolytes are reported.

Bulk electronic properties have been deduced from the kinetics of redox systems such as Fe<sup>2+</sup>/Fe<sup>3+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> for which it is known that no chemibonds are formed between electrode surface and reactants. Adsorption features have been investigated through the behaviour of systems such as H<sub>2</sub>/H<sup>+</sup> and I<sup>-</sup>/I<sub>2</sub> whose

kinetic mechanisms usually involve one or more adsorption steps. The two above systems react in potential ranges more than ½ V apart, the former in the hydrogen adsorption region and the latter just before the oxygen adsorption region for noble metals. Some preliminary experiments on the adsorption and oxidation of organic substances have also been made.

The main purpose of this work is to elucidate some electric, electronic and surface features of RuO<sub>2</sub> film electrodes through their electrochemical behaviour with the above systems. In particular, the interest is centred on the possible role of the metallic support on which the RuO<sub>2</sub> is thermally deposited, and on the effect of temperature and environment on the RuCl<sub>3</sub> decomposition.

### **2. Experimental**

#### *2.1. Generalities*

Preparation of electrodes, the cell, and basic problems in making up base solutions have been

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described in detail in Part I [8].

## 2.2. Types of electrodes

2  $\mu\text{m}$  thick films of  $\text{RuO}_2$  on Ta and Pt as supports were used. A 0.1 mm thick Pt foil of 2  $\text{cm}^2$  total area and a Ru plate prepared as described in Part I were used as comparison electrodes.  $\text{RuO}_2$  films on Ta were deposited at 450 and 550°C. At 650°C the deposited layer invariably scaled off due to the marked oxidation of the underlying metal.  $\text{RuO}_2$  films at 550 and 650° were prepared on Pt. All the above films were then annealed at the same temperature in the air. However, films on Ta at 450°C were also annealed in pure nitrogen, and pure oxygen, respectively.

## 2.3. Solutions and electrolytes

Experiments with a supporting electrolyte only were performed in 1 M  $\text{HClO}_4$  solutions. 0.1–1 M  $\text{H}_2\text{SO}_4$  was usually employed as the supporting electrolyte for redox couples. 0.1 M  $\text{Fe}^{2+}$ , 0.1 M  $\text{Fe}^{3+}$  solutions were prepared from  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NH}_4)\text{SO}_4 \cdot 12\text{H}_2\text{O}$  (reagent grade Erba chemicals).  $5 \cdot 10^{-3}$  M  $\text{I}_2$ ,  $5 \cdot 10^{-2}$  M KI solutions were used for the  $\text{I}^-/\text{I}_2$  system. The hydrogen evolution was carried out from 1 M  $\text{HClO}_4$  solutions.

## 2.4. Reference electrodes

A hydrogen electrode in the same solution worked as the reference electrode for inert electrolyte solutions. With redox systems, a platinized platinum electrode in the same solution was used. In this case, the potential read on the voltmeter, in general, gave directly the value of overvoltage for the reaction under study. All potentials were read on an Amel electrometer.

## 2.5. Experimental techniques and apparatus

The electrolytic hydrogen evolution has been studied by means of steady-state potentiostatic measurements with the aid of a 557 Amel potentiostat. Exchange currents for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{I}^-/\text{I}_2$  were measured from the slope of the linear portion of the relationship between  $i$  and  $\eta$  at low overvoltages obtained galvanostatically. Cyclic

voltammetry experiments were carried out as described in Part I [8].

## 3. Results

### 3.1. Effect of temperature and environment of preparation

Fig. 1 shows the voltammetric curves in inert electrolyte solutions for three  $\text{RuO}_2$  electrodes on Ta deposited at 450°C but annealed in nitrogen, air and oxygen, respectively. It can be seen that the charge  $q_i$  consumed by the electrodes between 0.3 V and the oxygen evolution is to a first approximation independent of the direction of variation of the potential, but it decreases as the oxygen content of the annealing atmosphere is increased. The general shape of the curves and the characteristic potentials remain unchanged. The effect on the value of  $q_i$  is large in going from air to oxygen, but it is almost negligible in going from air to nitrogen.

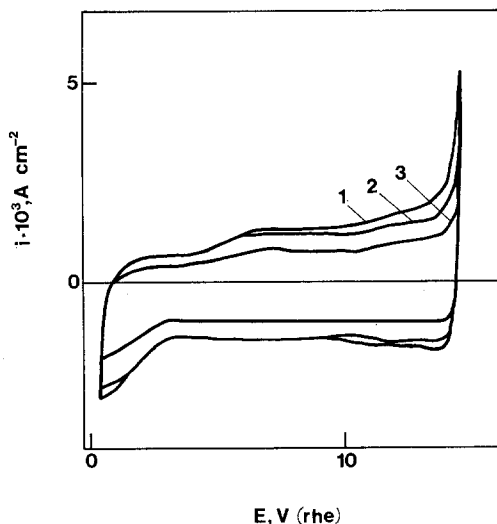


Fig. 1.  $I/E$  curves at  $40 \text{ mV s}^{-1}$  for  $\text{RuO}_2$  films deposited on Ta at 450°C and annealed at the same  $T$  in different atmospheres. (1)  $\text{N}_2$ ; (2) air; (3)  $\text{O}_2$ .

Fig. 2 refers to three  $\text{RuO}_2$  electrodes on Pt deposited at different temperatures. Again, the curves are similar, but the charge  $q_i$  appears to decrease as the firing temperature is increased. Although the absolute value of  $q_i$  may be somewhat different for different sets of electrodes due

to the particular way of preparation, within a set of electrodes the way  $q_i$  changes according to Figs. 1 and 2 appears to be reproducible. In other words, a decrease in  $q_i$  with increasing  $T$  and oxygen content of atmosphere appears to be a well-established experimental fact.

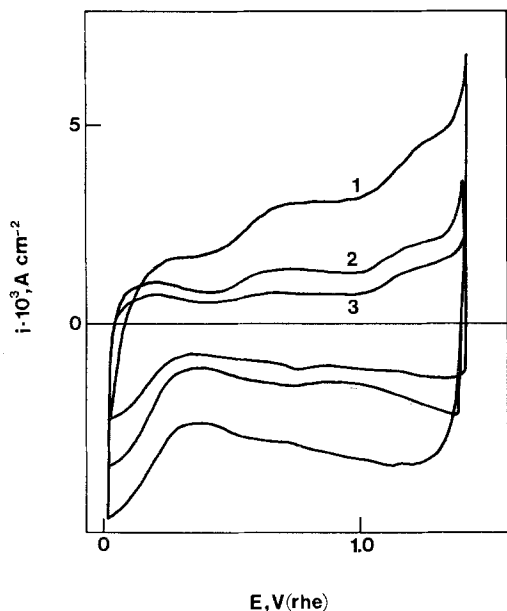


Fig. 2.  $i/E$  curves at  $40 \text{ mV s}^{-1}$  in  $1 \text{ M HClO}_4$  for  $\text{RuO}_2$  films deposited on Pt at different  $T$ . (1)  $450^\circ\text{C}$ ; (2)  $550^\circ\text{C}$ ; (3)  $650^\circ\text{C}$ .

### 3.2. Redox systems

Figure 3 shows the voltammetric curve of  $\text{RuO}_2$  films in stirred solutions containing the ferro/ferricyanide redox couple. The curve evidences the very good reversibility of redox systems on  $\text{RuO}_2$  electrodes. Although an intrinsic current for charging and discharging the oxide layer is always present, the current due to the redox reaction comes out clearly and the anodic and cathodic waves can be well-distinguished around the reversible potential. It is of interest to note that the reversible potential is established at open circuit on all of the  $\text{RuO}_2$  electrodes as easily and rapidly as on such metallic electrodes as Pt and Ru. This behaviour is displayed by Fig. 4 where the steady state anodic curves for the oxidation of ferrocyanide at Pt and  $\text{RuO}_2$  are presented. The curves for the two electrodes superimpose if currents are referred to the geometric area. Even far from the limiting current, nothing apparently points to a dramatic difference

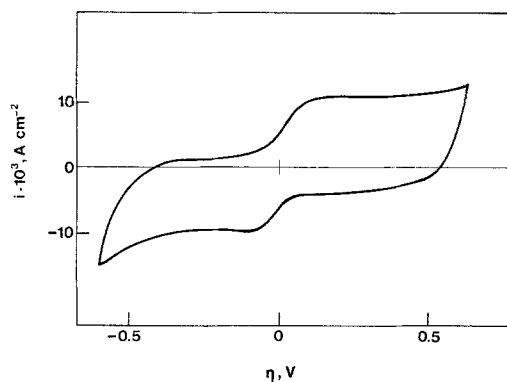


Fig. 3.  $i/\eta$  curve at  $40 \text{ mV s}^{-1}$  for a  $\text{RuO}_2$  film electrode in  $0.01 \text{ M K}_4\text{Fe(CN)}_6$ ,  $0.01 \text{ M K}_3\text{Fe(CN)}_6$ ,  $0.1 \text{ M H}_2\text{SO}_4$  stirred solution.

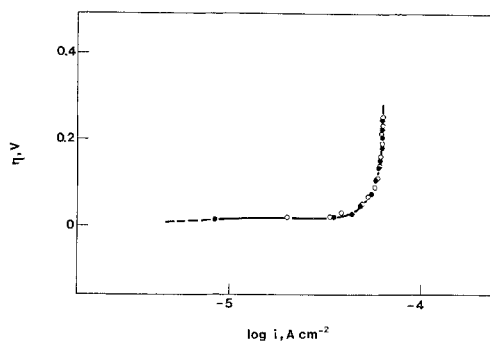


Fig. 4. Quasistationary potentiostatic  $i/\eta$  curves for  $\text{RuO}_2$  films and Pt in  $0.005 \text{ M K}_4\text{Fe(CN)}_6$ ,  $0.1 \text{ M K}_3\text{Fe(CN)}_6$  solution. (○) Pt; (●)  $\text{RuO}_2$ .

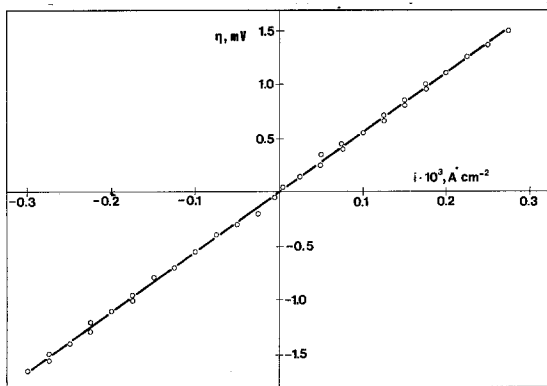
between electrochemically active and geometric area. However, this observation can only be qualitative.

In view of the reversibility of redox reactions on  $\text{RuO}_2$  electrodes,  $i_0$  values for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple have been derived from the slope of the linear portion of the  $i/\eta$  experimental relationship. Fig. 5 shows a typical example of an  $i/\eta$  curve displaying the perfect symmetry of the anodic and cathodic branches. This has been observed with all electrodes studied.  $i_0$  values were measured at five different temperatures ranging from  $20$ – $40^\circ\text{C}$  and  $\log i_0$  plotted against  $1/T$  to obtain the heat of activation,  $\Delta H^\ddagger$ . Fig. 6 shows a typical Arrhenius plot for a  $\text{RuO}_2$  film prepared at  $450^\circ\text{C}$ . Table 1 summarizes the results for all electrodes studied.

The value of  $i_0$  found for Pt is within a factor of 2 reported by Bockris *et al.* [9] with the same electrolyte and the same experimental

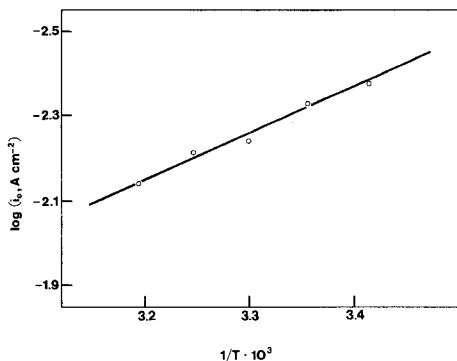
Table 1. Kinetic parameters for the  $Fe^{2+}/Fe^{3+}$  redox reaction in 0.1 M  $Fe^{2+}$ , 0.1 M  $Fe^{3+}$ , 1 M  $H_2SO_4$  solution at 25°C

Electrode	$i_0 \cdot 10^3$ (A cm <sup>-2</sup> )	$\Delta H^\ddagger$ (Kcal mol <sup>-1</sup> )
Pt	3.2	5.5
Ru	7.6	5.0
(Ta)RuO <sub>2</sub> , 450°C, air	4.7	5.2
(Ta)RuO <sub>2</sub> , 450°C, O <sub>2</sub>	5.2	5.7
(Ta)RuO <sub>2</sub> , 450°C, N <sub>2</sub>	5.3	4.2
(Ta)RuO <sub>2</sub> , 550°C	0.055	—
(Pt)RuO <sub>2</sub> , 550°C	6.8	5.6
(Pt)RuO <sub>2</sub> , 650°C	6.0	6.6

Fig. 5. Typical galvanostatic  $i/\eta$  curve for RuO<sub>2</sub> film electrodes in 0.1 M  $Fe^{2+}$ , 0.1 M  $Fe^{3+}$ , 1 M  $H_2SO_4$  stirred solution at 25°C.

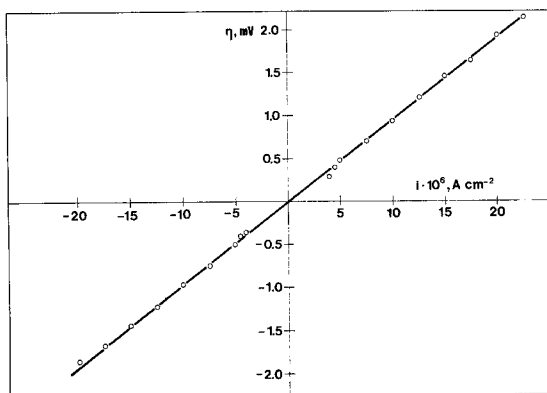
method. All of the RuO<sub>2</sub> electrodes (except that prepared at 550°C which seems to be anomalous) exhibit almost identical  $i_0$  values. There is just a factor of 1.4 between the lowest and the highest value of  $i_0$ .

Inspection of the  $\Delta H^\ddagger$  values reveals that this quantity is unaffected by the nature of the electrode and is on average the same as that observed on various metallic electrodes [10].

Fig. 6. Typical Arrhenius plot for the  $Fe^{2+}/Fe^{3+}$  redox reaction at RuO<sub>2</sub> film electrodes.

### 3.3. $I^-/I_2$ system

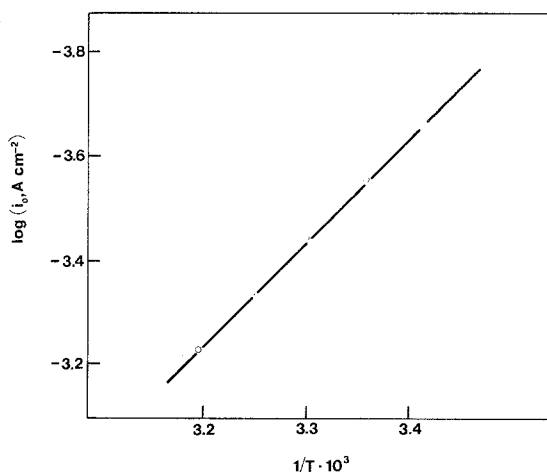
This system also exhibits a very good reversibility on RuO<sub>2</sub> electrodes. In fact, the equilibrium potential is rapidly attained upon immersion. Fig. 7 shows that the relationships between  $i$  and  $\eta$  in the region of low overvoltage are perfectly linear and symmetrical with respect to the equilibrium potential.

Fig. 7. Typical galvanostatic  $i/\eta$  curve for RuO<sub>2</sub> film electrodes in 0.005 M  $I_2$ , 0.05 M KI, 1 M  $H_2SO_4$  stirred solution at 25°C.

$i_0$  values have been derived from similar plots at different temperatures. A typical Arrhenius plot is shown in Fig. 8.  $i_0$  values for the various electrodes and the corresponding heats of activation,  $\Delta H^\ddagger$ , are summarized in Table 2. It can be seen that  $i_0$  at typical metals is at least one order of magnitude higher than at RuO<sub>2</sub>. Neglecting RuO<sub>2</sub> on Ta at 550°C which again seems to be anomalous, it appears hard to differentiate the various RuO<sub>2</sub> electrodes on the basis of the  $i_0$  values. Just tentatively, the  $i_0$ 's for RuO<sub>2</sub> on Ta appear on the whole lower than those for RuO<sub>2</sub> on Pt. Accordingly,  $\Delta H^\ddagger$  for the former may be somewhat

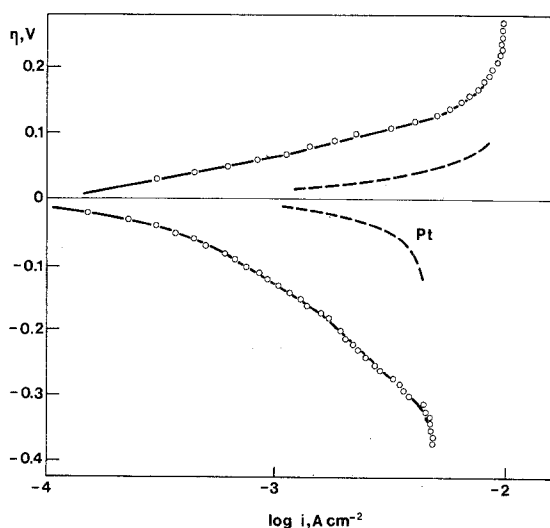
Table 2. Kinetic parameters for the  $I^-/I_2$  reaction in  $5 \cdot 10^{-3} M I_2$ ,  $5 \cdot 10^{-2} M KI$ ,  $1 M H_2SO_4$  solution at  $25^\circ C$ 

Electrode	$i_0 \cdot 10^4 (A cm^{-2})$	$\Delta H^\ddagger (Kcal mol^{-1})$
Pt	38.0	4.5
Ru	39.0	6.0
(Ta)RuO <sub>2</sub> , 450°C, air	2.7	9.3
(Ta)RuO <sub>2</sub> , 450°C, O <sub>2</sub>	1.1	11.0
(Ta)RuO <sub>2</sub> , 450°C, N <sub>2</sub>	9.7	5.8
(Ta)RuO <sub>2</sub> , 550°C	0.2	(2.0)
(Pt)RuO <sub>2</sub> , 450°C	4.8	6.2
(Pt)RuO <sub>2</sub> , 550°C	4.5	4.8
(Pt)RuO <sub>2</sub> , 650°C	5.0	6.7

Fig. 8. Typical Arrhenius plot for the  $I^-/I_2$  reaction at RuO<sub>2</sub> film electrodes.

higher than  $\Delta H^\ddagger$  for the latter. Within a single-group of RuO<sub>2</sub> electrodes, a further differentiation appears to be even less evident. It can be tentatively suggested that a decrease in  $i_0$  and an increase in  $\Delta H^\ddagger$  occurs with increasing  $q_i$ , the charge measured according to Figs. 1 and 2. However, this classification is less certain than the differentiation between RuO<sub>2</sub> and metals.

The different behaviour of RuO<sub>2</sub> and metals is strikingly evident in Fig. 9 which presents a typical steady-state potentiostatic curve for a RuO<sub>2</sub> electrode compared to the curve for Pt. Curves for Ru have been observed to be similar to those of Pt. The reaction clearly goes more easily on Pt than on RuO<sub>2</sub>, though the final limit is in both cases the diffusion of the species to the electrode surface. In particular, the curves for Pt are more symmetric with respect to the equilibrium potential. However, this may just be due to the high value of  $i_0$  compared to  $i_{lim}$ . This also prevents a mechanistic

Fig. 9. Quasistationary potentiostatic  $i/\eta$  curves for a RuO<sub>2</sub> film deposited at  $450^\circ C$  on Ta, and for Pt in  $0.005 M I_2$ ,  $0.05 M KI$ ,  $1 M H_2SO_4$  stirred solution.

analysis for Pt to be made on the basis of Tafel slopes. On RuO<sub>2</sub>, due to the low value of  $i_0$ , the Tafel lines can be easily identified. The anodic Tafel slope is below 120 mV, whereas the cathodic slope is slightly higher than 120 mV. This picture is quite general for RuO<sub>2</sub> electrodes. This difference in slope may indicate some difference between cathodic and anodic mechanisms, provided the transfer coefficient equals 0.5.

These electrochemical systems have been used in this work as a means of characterizing the electrodes and not as objects in themselves. Therefore, their kinetics have not been studied in more detail than that necessary for a qualitative understanding of the problem, yet it is still possible to attempt to derive the mechanisms occurring on the various electrodes from the Tafel slope values. Neglecting the equilibrium between  $I_2$  and  $I^-$ , and

writing the possible steps as follows:



the rate determining step at Pt may be [11] Reaction 3, or Reaction 1, both steps occurring with high coverage by adsorbed atomic iodine. On  $RuO_2$ , on the contrary, Reaction 2 is probably the r.d.s. in the cathodic direction, while the oxidation may be governed by Reaction 3. The experimental value of the Tafel slope for Reaction 3 would indicate an intermediate coverage of the surface with atomic I.

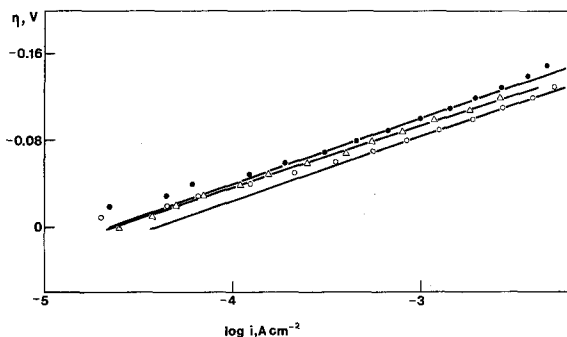


Fig. 10. Quasistationary potentiostatic  $i/\eta$  curves for the electrolytic hydrogen evolution from 1 M  $HClO_4$  solutions on  $RuO_2$  films deposited on Ta at  $450^\circ C$  and annealed in different atmospheres. (●) air; ( $\Delta$ )  $N_2$  (○)  $O_2$ .

### 3.4. Electrolytic hydrogen evolution

Figure 10 shows typical  $\log i/\eta$  curves for the cathodic evolution of  $H_2$  on  $RuO_2$  films. Tafel lines exhibit slopes,  $b$ , of about 60 mV. Apparently, the value of  $b$  depends on  $q_i$  in that an increase in  $b$  can be perceived as  $q_i$  decreases. The effect of the underlying metal is more pronounced. Fig. 11 shows that  $b$  for  $RuO_2$  on Pt is much lower than  $b$  for  $RuO_2$  on Ta. This fact appears to be experimentally well-established. Fig. 12 shows a typical Arrhenius plot in the case of a  $RuO_2$  electrode on Ta.

Table 3 summarizes the results for  $i_0$  and  $\Delta H^\ddagger$ . It can be seen that  $i_0$  on Pt is about two orders of magnitude higher than those on Ta-supported  $RuO_2$ .  $RuO_2$  on Pt, in turn, exhibits a  $i_0$  value about one order of magnitude higher than that measured with  $RuO_2$  on Ta. Thus,  $i_0$  values and,

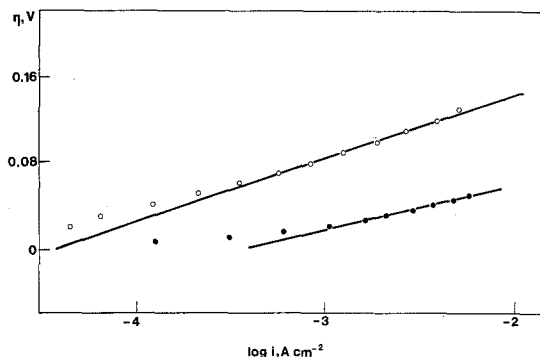


Fig. 11. Quasistationary potentiostatic  $i/\eta$  curves for the electrolytic hydrogen evolution from 1 M  $HClO_4$  solutions on  $RuO_2$  films deposited on different supports. (○) Ta; (●) Pt.

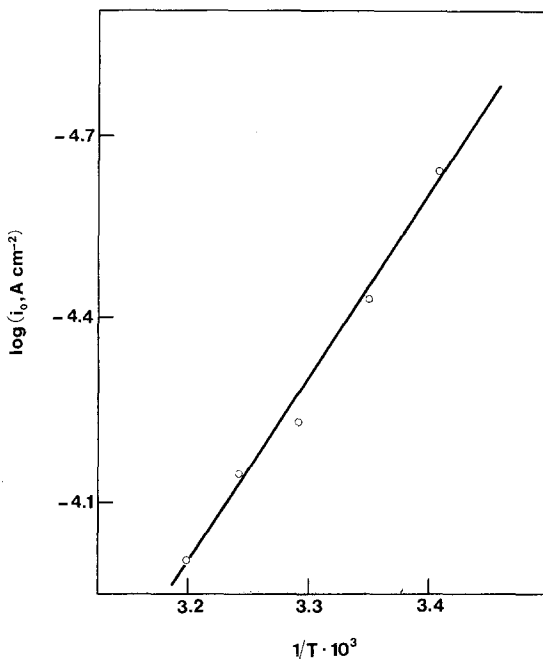


Fig. 12. Typical Arrhenius plot for the electrolytic hydrogen evolution from 1 M  $HClO_4$  solutions on  $RuO_2$  film electrodes.

even more,  $\Delta H^\ddagger$  values suggest a possible role played by the nature of the support. In fact,  $\Delta H^\ddagger$  for  $RuO_2$  on Ta is higher than that for  $RuO_2$  on Pt which, in turn, is similar to the heat of activation found on the metals. Within a single group of electrodes it is again hard to recognize a differentiation. Tentatively,  $\Delta H^\ddagger$  seems to depend slightly on  $q_i$  in the sense that it appears to increase as  $q_i$  decreases.

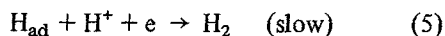
It must be noted that the experimental determination of  $\Delta H^\ddagger$  for this system is rather difficult

Table 3. Kinetic parameters for the hydrogen evolution reaction in 1 M HClO<sub>4</sub> at 25°C

Electrode	$i_0 \cdot 10^3$ (A cm <sup>-2</sup> )	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )
Pt	2.5	6
Ru	0.5	7
(Ta)RuO <sub>2</sub> , 450°C, air	0.037	17
(Ta)RuO <sub>2</sub> , 450°C, O <sub>2</sub>	0.022	22
(Ta)RuO <sub>2</sub> , 450°C, N <sub>2</sub>	0.023	15
(Pt)RuO <sub>2</sub> , 550°C	0.16	7

inasmuch as the equilibrium conditions are poorly characterizable. In fact, the rest potential of RuO<sub>2</sub> in a solution saturated with H<sub>2</sub> is 0.6–0.8 V more positive than the reversible potential. Thus, RuO<sub>2</sub> does not equilibrate with hydrogen, which points to some inability for these oxide films *in solution* to dissociate molecular hydrogen. This, however, does not indicate *per se* a basic inability to chemisorb atomic hydrogen too. In fact if RuO<sub>2</sub>, once subjected to a strong hydrogen discharge, is released, it keeps the reversible potential of hydrogen for a time generally dependent on the extent and duration of the cathodic treatment. However, precisely because of this behaviour, it can be realized how it may be difficult to standardize the surface state of RuO<sub>2</sub> and thus have complete confidence in the absolute experimental value of  $\Delta H^\ddagger$ .

In conclusion, the most certain experimental observation is the value of the Tafel slope of about 60 mV which, together with the other facts above, points to the ion + atom reaction [12]:



as the r.d.s. for the electrolytic hydrogen evolution on RuO<sub>2</sub>.

### 3.5. Organic reactions

Some preliminary experiments have been made with this class of substances to enlarge the qualitative picture of the surface properties of RuO<sub>2</sub>. Fig. 13 shows that RuO<sub>2</sub> film electrodes are able to oxidize organic substances. Similar curves have been obtained with many simple molecules. This type of reaction is presumably a direct charge-transfer oxidation in view of the range of potential where it occurs. Below 1 V, even if any reaction occurred, this would be at any rate masked by the large intrinsic current due to charging processes [8]

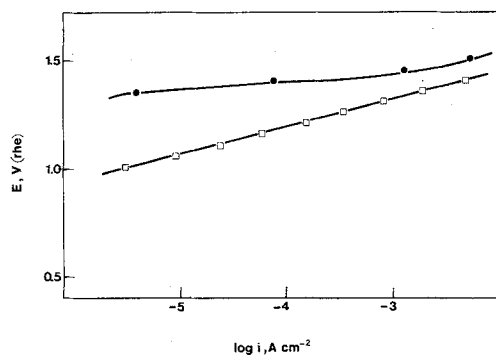


Fig. 13. Quasistationary potentiostatic  $i/\eta$  curves for RuO<sub>2</sub> films in 1 M HClO<sub>4</sub> solutions with and without added CH<sub>3</sub>OH. (●) no CH<sub>3</sub>OH; (○) 0.1 M CH<sub>3</sub>OH.

(Figs. 1 and 2). Both steady-state and voltammetric measurements could hardly evidence anything in this range of potential.

It is known that many organic molecules dehydrogenate on Pt below 1 V resulting in strong chemisorption bonds with the metal surface [13, 14]. In order to determine whether something similar can occur also on the surface of RuO<sub>2</sub>, steady-state  $i/\eta$  curves have been determined with ferrocyanide in solution in the presence of and in the absence of glyoxal which on Pt gives particularly strong chemisorption phenomena [15, 16]. Fig. 14 shows in fact that the cathodic current due to the reduction of ferrocyanide decreases sensibly indicating a partial blocking of surface sites. No particular difference can be found in the anodic curves. It must be recalled that the reversible potential for the ferrocyanide/ferricyanide system is very close to the range of potential where oxygen adsorption on Pt starts. For this reason, at potentials positive to the equilibrium value, desorption of the organic adsorbate by oxidation is expected [17].

Fig. 15 shows the same experiments with RuO<sub>2</sub> electrodes. It can be seen that the curves in the presence and in the absence of glyoxal are

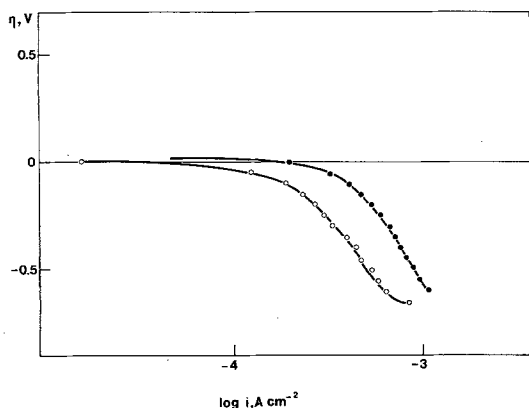


Fig. 14. Quasistationary potentiostatic  $i/\eta$  curves for the ferricyanide reduction on Pt in 0.05 M  $\text{K}_3\text{Fe}(\text{CN})_6$ , 0.05 M  $\text{K}_4\text{Fe}(\text{CN})_6$ , 0.1 M  $\text{H}_2\text{SO}_4$  solution with and without added glyoxal. (●) no glyoxal; (○) 0.01 M glyoxal.

superimposed. This would point to the absence of any blocking effect on the electrode surface by organic chemisorption, or alternatively, that the adsorption phenomena may be much weaker than on Pt.

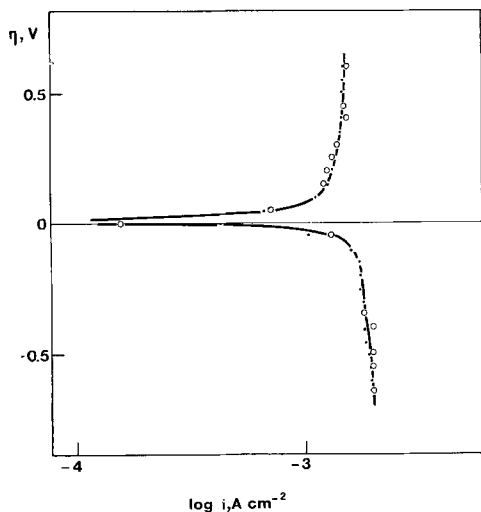


Fig. 15. Quasistationary potentiostatic  $i/\eta$  curves for the ferro/ferricyanide redox system on  $\text{RuO}_2$  film electrodes in 0.05 M  $\text{K}_4\text{Fe}(\text{CN})_6$ , 0.05 M  $\text{K}_3\text{Fe}(\text{CN})_6$ , 0.1 M  $\text{H}_2\text{SO}_4$  with and without added glyoxal. (●) no glyoxal; (○) 0.01 M glyoxal.

## 4. Discussion

### 4.1. Non-stoichiometry

It has been shown in Part I [8] that the charge  $q_i$

needed to change the potentials of  $\text{RuO}_2$  electrodes from 0.3 to about 1.35 V (oxygen evolution) can be assumed to be a measure of the degree of non-stoichiometry of the oxide layer. In this respect, the effect of the firing temperature and annealing environment can be easily understood. In fact, a lower value of  $q_i$  would indicate a lower fraction of Ru formally present as  $\text{Ru}^{3+}$ , i.e. a lower degree of non-stoichiometry. Results show that  $q_i$  decreases as  $T$  is increased and this is reasonable in that the decomposition of  $\text{RuCl}_3$  will be faster and more complete the higher the temperature [2]. Furthermore,  $q_i$  decreases as the annealing atmosphere is made more oxygenated. This result too can be explained according to the above picture in that a long annealing process would allow the oxidation reaction to proceed further, particularly as the annealing atmosphere consists of pure oxygen. In this case, the composition of the layer is likely to change somewhat across the thickness in that the non-stoichiometry may increase towards the interior of the film. The difference between the case of annealing in nitrogen and that in air is small because, it must be recalled, some decomposition occurs in the air.

### 4.2. Role of the support

Although the effect of the nature of the support seems to be small, it is all but negligible, particularly in reactions with electrode-reactant chemical interaction steps. In fact, as shown in Part I, no systematic effect of the support on the  $q_i$  values can be observed. However, with the  $\Gamma/\text{I}_2$  system and even more in the case of the hydrogen discharge, the reaction rate with  $\text{RuO}_2$  on Pt appears to be closer to that with Pt than to that with  $\text{RuO}_2$  on Ta. In other words, Ta seems to behave as a really inert support, whereas some role is played by Pt. This metal is likely to be more easily incorporated into the oxide layer thus giving rise to modifications in the surface properties. On the contrary, bulk electric properties do not appear to be modified, as proved by the constancy in  $i_0$  and  $\Delta H^\ddagger$  for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  reaction.

In the case of Ta as the support, results show that its use must be restricted to firing temperatures below 500°C. In fact, at 650°C the oxide on Ta grows so rapidly that the adhesion of the  $\text{RuO}_2$  layer is prevented. The oxidation of the support appears to be important also at 550°C in that,



although the adhesion of the RuO<sub>2</sub> layer is possible, results with Fe<sup>2+</sup>/Fe<sup>3+</sup> and particularly with I<sup>-</sup>/I<sub>2</sub> indicate the presence of a marked barrier layer. No particular problems seem to arise at 450°C as suggested by the values of the parameters for the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox reaction.

### 4.3. Electronic properties

Bulk electronic properties of the RuO<sub>2</sub> film electrodes can be derived from the analysis of the parameters of the redox reactions. Since no chemibonds are formed on the electrode surface, the reaction rate is in this case independent of chemisorption features. It has been shown elsewhere [10] that the value of  $\Delta H^\ddagger$  for this type of reaction is essentially determined by the properties of the system in solution rather than by the nature of the electrode.  $\Delta H^\ddagger$  practically results from the reorganization energy of solvent molecules around the ion changing its charge. The fact that  $\Delta H^\ddagger$  is the same for all RuO<sub>2</sub> films examined and its value equals that found with metal electrodes suggests that these layers can be considered as essentially metallic in nature. This, together with other experimental observations, means that the electron concentration is high enough to prevent a detectable potential drop across the layer. This result is substantially in agreement with conductivity measurements on RuO<sub>2</sub> films [2] which give for the resistivity values about 0.1  $\Omega$  cm (corresponding to a resistance of the order of 10<sup>-5</sup>  $\Omega$  for a 2  $\mu$ m thick layer) and a temperature coefficient of conductivity practically equal to zero. Although these features do not allow RuO<sub>2</sub> films to be defined as typical metals, the general behaviour is as a whole typically metallic.

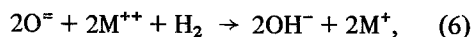
The accuracy of the results do not enable more detailed analysis to be made. It is however possible to infer from the constancy of  $i_0$  for Fe<sup>2+</sup>/Fe<sup>3+</sup> that the bulk electronic properties are not influenced by the degree of non-stoichiometry of the layer. If concepts applied to metals [10] could be extended to RuO<sub>2</sub> films, then results would apparently suggest that the energy of electrons at the Fermi level is independent of the type of the film and very close to that of Pt. In other words, the work function of RuO<sub>2</sub> films may be close to 5 eV and practically unaffected by the procedure of preparation. However, the true value for  $\Phi$  (work

function) can only be derived from correlations between  $\Phi$  and log  $i_0$  for the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple [10] if the value of  $i_0$  for RuO<sub>2</sub> referred to the true area is known, a prerequisite to which is a knowledge of the surface roughness factor. BET measurements [2, 5] give for this factor a value of about 200, but it is unlikely that this value corresponds to the true electrochemical active area which may be one order of magnitude lower. The procedure of preparation may give rise to sites accessible to the rare gas used in BET measurements but not to substances in solution. On the other hand, BET measurements refer to the state of the surface in contact with a gas phase, whereas the surface of an oxide is generally subjected in solution to a strong hydration [18–21] which in some respects could be equivalent to a 'smoothing' effect [22]. Further, the fact that in Fig. 4 the curve for RuO<sub>2</sub> at  $i < i_{lim}$  coincides with that for Pt suggests that the electrochemically active surface area might not be too far from that of the geometric surface.

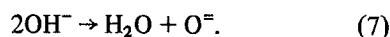
### 4.4. Surface properties

It is more difficult in this case to draw any definite conclusions. Experimental data are not clear-cut and to some extent they may even suggest contrasting views. The observed inability to dissociate molecular hydrogen and chemisorb organic substances points to poor catalytic properties of RuO<sub>2</sub> films. However, the fact that electrochemically formed atomic hydrogen is retained on the surface indicates a chemisorption power certainly higher than that for sp-metals. This apparent contradiction could be due to water strongly chemisorbed on the surface, whose desorption would absorb a large fraction of the total chemisorption heat.

Some irreversibility in hydrogen adsorption can be foreseen also from the behaviour of oxides in hydrogen adsorption from the gas phase. In principle, chemisorption corresponds to reduction [23]:



and desorption is in general possible only as water:



On the other hand, surface valences are presumably saturated in solution [24] by adsorption of H<sub>2</sub>O, H<sup>+</sup> or OH<sup>-</sup>, i.e.  $\equiv M(H_2O)(OH)_2$  so that an oxide

electrode tends in principle to be reversible to oxygen and not to hydrogen. Results seem to support this view.

Irreversible adsorption of hydrogen also appears likely on the basis of the poor resistance of these electrodes to strongly cathodic polarizations, even though the reaction exhibits on the whole a certain degree of reversibility in that an anodic polarization can restore the characteristics of the electrode. It is thought [8] that the hydrogen discharged cathodically can penetrate into the lattice resulting in some reduction of the layer, but it can be taken out by a subsequent anodic polarization.

It is really hard to quantify the adsorptive power of RuO<sub>2</sub> films.  $\Delta H^\ddagger$  data would indicate that this may be higher on RuO<sub>2</sub> than on typical transition metals, although the absolute value of  $\Delta H^\ddagger$  can be to some extent uncertain. A higher value of  $\Delta H^\ddagger$  would indicate a lower value of M–H bond strength if the r.d.s. were Reaction 4. If the r.d.s. were Reaction 5, a high value for  $\Delta H^\ddagger$  would mean a high value for the M–H bond strength due to the increasing difficulty for removing H<sub>ad</sub> [25]. Now, the experimental value of  $\Delta H^\ddagger$  seems very high compared to that found on Hg [26] which exhibits a very low  $E_{M-H}$ . A even lower  $E_{M-H}$  on RuO<sub>2</sub> should result in a higher  $\eta$  than on Hg, and this is not the case.

Although such high values for  $\Delta H^\ddagger$  may be partly due to experimental reasons, slopes of Tafel lines seem to suggest [12] Reaction 5 as the r.d.s. If this is the case, analysis of the 'volcano' curve [27] for the relationship between  $\log i_0$  and  $E_{M-H}$  would suggest that RuO<sub>2</sub> should be located on the descending branch on the right-hand side of the Pt group, i.e. among metals adsorbing hydrogen more strongly than Pt. This would seem to contrast with the proved inability of RuO<sub>2</sub> to dissociate H<sub>2</sub>, but can be easily understood if this inability is attributed not to a low value of  $E_{M-H}$  but to a high value of the activation energy for dissociation due to the geometry of active sites or more probably to the preformed layer of strongly chemisorbed water molecules. Accordingly, organic molecules would not be chemisorbed because of an unfavourable heat of desorption of water molecules rather than because of an intrinsic inability as for sp-metals. Further along these lines, if the r.d.s. for the anodic and cathodic reactions of iodine are actually those suggested above, the behaviour of

RuO<sub>2</sub> films would again be explainable in terms of surface bonds with atomic iodine being more strongly bonded than in the case of Pt. However, experimental results indicate for this reaction a high degree of reversibility and this requires a sufficiently low activation energy for iodine dissociation. This could be due to a more favourable geometric factor and also to a substantially lower bond energy in the case of the iodine molecule [28].

If the non-stoichiometry does not appear to affect the rate of single electron exchange reactions, it can however have some influence on the surface properties. Since experimental results in this respect are not clear-cut, it is just tentatively suggested that the increase in Tafel slope with decreasing  $q_i$  may be explained in terms of a parallel increase in  $E_{M-H}$  [12, 27]. In other words, the energy of chemisorption of hydrogen would increase as the fraction of Ru<sup>3+</sup> decreases. Again, if RuO<sub>2</sub> can be treated as a metal, the above observation can be understood in the light of ideas developed elsewhere [23, 27]. It has been shown that the hydrogen adsorption heat decreases with increasing number of  $d$  electrons in the metals along a transition row. Now, as the number of Ru<sup>3+</sup> increases, the number of  $d$  electrons increases and thus the adsorption heat decreases. This interpretation could reasonably be applied to the case of I<sup>-</sup>/I<sub>2</sub>. The role of  $d$  electrons is frequently emphasized in hydrogen adsorption on metal oxides [23, 29, 30].

Most of the above discussion is based on the consideration of RuO<sub>2</sub> as a typical metal, i.e. the chemical identities of cations and anions would merge. This can in fact occur as orbitals of anions and cations interact to give common electron bands [31]. However, there exist metallic oxides which owe their properties to the presence of a  $d$  band due to interaction of orbitals of the cation sublattice only [31]. In the latter case, the concept of surface site would be more relevant and geometric factors could become more important than energetic factors. Data [31–33] which could enable the location of RuO<sub>2</sub> in one of the two above classes are unfortunately rather uncertain, although the Ru–Ru distance in the oxide lattice [2, 34] makes the formation of a  $d$  band due to cations rather unlikely.

## 5. Conclusion

The above discussion probably goes beyond the

realistic conclusions which can be drawn from the experimental results presented and therefore may be somewhere speculative. A firm point appears to be the consistently metallic behaviour of RuO<sub>2</sub>. This makes these films good electrodes for simple electron exchange reactions (redox processes) in a relatively large potential range due to the apparent high resistance to oxidation and, partly, to reduction. On the contrary, electrocatalytic properties of RuO<sub>2</sub> films come out from the present results to be rather poor, and reactions involving chemisorption steps are slower than on metals.

Resistance to oxidation is very high whereas that to reduction is less satisfactory. This makes these electrodes work well as anodes. In fact, many anodic reactions proceed with difficulty on metals because of the concomitant reaction of surface oxidation. This characteristic can make RuO<sub>2</sub> a good anode even in spite of its intrinsically poor electrocatalytic properties. Also in the case of organic substances, the absence of molecular demolition connected with dehydrogenation and chemisorption, makes the use of these electrodes in the field of electro-organics promising. An easier control of the anodic reaction is probably also in aqueous solution.

As regards the reasons why RuO<sub>2</sub> appears to be a poor electrocatalyst, nothing definitive can be stated on the basis of the present results. Most of the conclusions on this subject have in fact been drawn on the basis of observations regarding the hydrogen discharge reaction. However, hydrogen is a particular reactant in the field of oxides and the results obtained with it may be misleading. It is not possible to go beyond the tentative suggestion that the poor electrocatalytic properties could result from a higher rather than a lower adsorption power with respect to that observed with noble transition metals. In other words, RuO<sub>2</sub> would be comparable to transition metals with few d electrons rather than to sp-metals. On the other hand, due attention should be paid to the possibility of a change in the surface properties of RuO<sub>2</sub> with changing potential, if the non-stoichiometry is also a function of the applied voltage. Definite proof of these views requires further experimental work.

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