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Ruthenium dioxide: a new electrode material. I. Behaviour in acid solutions of inert electrolytes

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The electrochemical behaviour of RuO_2 film electrodes, prepared by the thermal decomposition of $RuCl_3$ on metallic supports has been investigated in solutions of inert electrolytes. Steady-state potentiostatic i/E curves, cyclic voltammetry and charging curves are presented. The procedure for the preparation of electrodes is described.

RuO_2 film electrodes exhibit oxygen overvoltages much lower than, and hydrogen overvoltages almost equal to, those on Pt electrodes. Results of measurements in the range of potential between oxygen and hydrogen evolution suggest that modifications arise which, while occurring within the whole film and not only at the surface, involve only a small fraction of the metal atoms. An explanation of this behaviour is advanced in terms of non-stoichiometry of the oxide layer.

1. Introduction

During the last few years considerable interest has arisen in the commercial application of RuO_2 film electrodes as a consequence of the excellent results obtained in chlor-alkali cells [1, 2]. Recently, this interest has broadened and efforts are being made to gain some insight into the mechanism of behaviour of this oxide. However, the very few studies published remain restricted to chlorine evolution from brines as regards mechanism and efficiency [4, 5].

In a preliminary note [6], a brief account was given of the work carried out in this laboratory on the intrinsic behaviour of RuO_2 film electrodes. Electrochemical data anticipated conclusions on the solid-state properties obtained by measurements of chemical composition, structural factors and electrical resistivity. It is hoped that this will become the first of a series of papers describing results obtained in these investigations.

Among the oxides of transition metals, RuO_2 holds a particular position for, together with a few other oxides [7] (eg. IrO_2, TiO) it exhibits a metallic conductivity of the order of 10^4 ohm^{-1} cm^{-1} in single crystals [8, 9]. This is also found in films [3] prepared by the decomposition of $RuCl_3$, although some 1000 times less. The metallic features of RuO_2 films are easily demonstrated by electrochemical measurements [6]. In the present initial study results are presented for RuO_2 film electrodes.

2. Experimental

2.1. *Preparation of electrodes*

These were prepared by depositing a thin layer of RuO_2 (usually 2 μm thick) on 0·1 mm thick plates of Ti, Ta or Pt of 2 cm^2 total surface area. Plates were fastened to a glass tube by a very thin wire

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of the same metal also covered with RuO_2. The supporting metals were selected to enable their role to be studied. No such effects were observed in inert electrolytes and hence they are not referred to further. However, better mechanical adherence of the RuO_2 is obtained with Ta and Ti. It should be noted that RuO_2 and TiO_2 are isomorphous [10].

The RuO_2 films were prepared by thermal decomposition of $RuCl_3$ in air at 350°C [11, 12], deposited mechanically on the support. To ensure maximum adhesion, depending on the metal, the support was sand-blasted, treated with aqua regia or 25% HCl, then washed and rinsed with triply distilled water and dried in the air. The required amount of $RuCl_3$ was dissolved in 20% HCl (about 25 $g l^{-1}$) and dried by gentle heating. This residue was dissolved in isopropanol and the resultant brown, limpid solution brushed onto the support, layer by layer. After each layer was deposited, the solvent was evaporated at about 50°C, then the electrode was kept for 10 min at 350°C in an oven with forced air circulation. After cooling, the procedure was repeated until no more solution remained. The electrode was finally annealed at the same temperature for some hours to ensure that the layer was uniform in composition and structure. The film showed a satisfactory resistance to gentle scraping.

The apparent thickness of the RuO_2 films has been calculated on the basis of the specific gravity of crystalline RuO_2 (6·97 $g cm^{-3}$) [13]. The mechanical resistance is satisfactory for thicknesses lower than 10 to 20 μm and for layers prepared by a large number of partial depositions. Layers of greater thickness usually scaled after a short period of use.

The RuO_2 films are black with some blue lustre as with single crystals. X-ray analysis showed the presence of all the principal RuO_2 peaks, while those of Ru were absent. However, the degree of crystallinity increases with the change from a glass to a metal support. Some epitaxial growth is also apparent. From this point of view the best support appears to be Ti.

Optical inspection of the films reveals a satisfactory uniformity and compactness with a low apparent porosity.

In this respect it is useful to note that aqueous solutions of $RuCl_3$ can be decomposed by the same procedure. However, the higher surface tension of the solvent prevents the solution from spreading fully on the surface of the support, and the higher evaporation temperature makes the resultant film more porous and mechanically less resistant.

2.2. *Cell*

This had three compartments, the reference electrode was separated from the main body by a glass stopcock and a glass frit. No grease was used. Prior to each run, the cell was washed with concentrated sulphuric acid containing a few permanganate crystals, then rinsed many times with triply distilled water. Between runs, the cell was kept in an oven at 130°C. After each run, the working electrode was rinsed with triply distilled water and dried between two pieces of filter paper.

All experiments were carried out at $25 \pm 0{\cdot}1$°C in an air thermostat.

2.3. *Solutions*

1 M $HClO_4$ solutions (pH = 0·55) were usually employed. They were prepared volumetrically by diluting 60–70% reagent grade $HClO_4$ with triply distilled water. Before runs the solutions were degassed with high purity nitrogen which had been passed through active charcoal and a trap containing the same solution as that in the cell. However, the presence of oxygen dissolved in solution appeared to have no detectable effect on the behaviour of RuO_2.

2.4. *Reference electrode*

A hydrogen electrode in the same solution was used. Potential values were read on a 610A Keithley electrometer.

2.5. *Experimental techniques and apparatus*

Steady-state potentiostatic measurements, cyclic voltammetry and charging curves were obtained. Potentials were applied from a 557 Amel potentiostat modulated by a 202A HP function generator. Non-stationary i/E curves and chronopotentiometric measurements were recorded on Leeds and Northrup X/t and XY instruments.

3. Results and discussion

3.1. *Rest potential*

The rest potential of RuO_2 film electrodes in acid solutions was about 0·95 V (rhe). This potential was rapidly attained as electrodes were dipped into the solution and was reproducible within a few tens of mV. When the electrode was subjected to short alternate discharges of O_2 and H_2 and then open-circuited from the hydrogen region, the potential reached a value of about 0·9 V after 2 h. When the electrode was released from the oxygen region, the value of the open-circuit potential was about 1·1 V after 2 h. The rate of recovery of the starting rest potential appeared to depend on the duration of O_2 or H_2 discharge. Hydrogen discharge produced more marked and prolonged modifications than oxygen discharge. An electrode kept at −0·05 V for 15 h showed, 1 h after release, an open-circuit potential of about 0·5 V, increasing very slowly. However, if the electrode was maintained under O_2 evolution at 1·6 V for 15 h, the potential decreased rather rapidly after release to 1·35 V, on open-circuiting. The rest potential in this case was easily recovered after a very short excursion of the electrode potential to the cathodic region above the hydrogen discharge, whereas in the other case a rapid passage through the anodic region before the oxygen evolution did not yield the same result.

The value of the initial rest potential can be interpreted on the basis of the standard potential for the reaction:

$$2RuO_2+2H^++2e \rightleftharpoons Ru_2O_3+H_2O \quad (1a)$$

RuO_2 would rapidly equilibrate with the solution by exchanging protons at the interface. A similar situation has been observed for ReO_3 [30] which is an electronic conductor [7]. In the case of an electrode surface, reaction 1 would better represent the true situation as:

$$RuO_2+H^++e \rightleftharpoons RuOOH \quad (1b)$$

The standard potential for reaction 1a has been reported [14] as 0·94 V (nhe). The changes resulting from H_2 or O_2 discharge are to be attributed to the adsorption of atomic oxygen which corresponds to the formation of higher oxides, and to the adsorption of atomic hydrogen. The latter corresponds to the reduction of Ru_2O_3 with a consequent shift of the electrode potential towards the standard potential of the Ru/Ru_2O_3 couple which has been given [14] as 0·74 V (nhe). Recent data [15] on the free energy

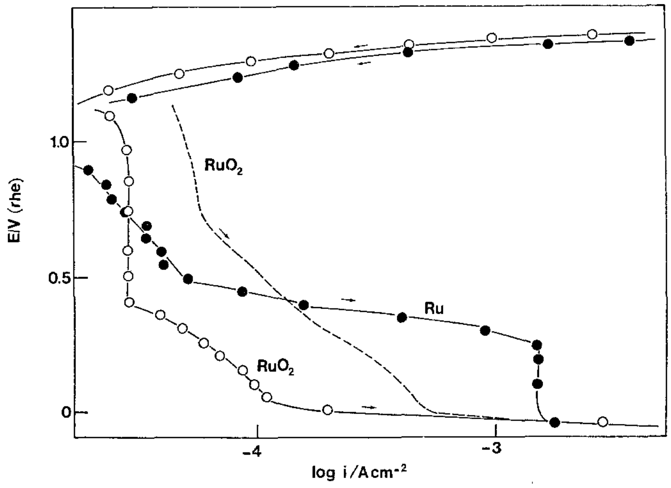

Fig. 1. Quasi-stationary potentiostatic i/E curves for RuO_2 films and Ru in 1 M $HClO_4$. Polarization time at each potential: solid curves, 5 min; dashed curve, 30 s. Arrows indicate the direction of change in potential.

of formation of RuO_2 enables a value of 0·43 V to be calculated for the standard potential of the reaction:

$$RuO_2 + 4H^+ + 4e \rightleftharpoons Ru + 2H_2O \qquad (2)$$

Modifications due to hydrogen discharge are therefore more marked and probably extend to atom layers below the surface. It is for this reason that the equilibrium potential is only recovered with difficulty.

3.2. *Steady-state potentiostatic measurements*

The most striking feature of these measurements is that in the range of potentials between O_2 and H_2 discharge, a high current is supported by the electrode, which does not seem to be explicable in terms of simple parasitic reactions such as reduction of oxygen dissolved in solution, organic impurities, adsorbed surface films, etc. The modifications occurring should involve the bulk of the electrode. Fig. 1 shows the steady-state potentiostatic i/E curve for RuO_2. The curve for a Ru electrode prepared by electrodeposition of a 2 μm thick Ru layer on a Pt plate is also reported for comparison. Measurements were made by maintaining the electrode for 30 min at 1·4 V, bringing the potential to 1·5 V and then going to cathodic values in 50 mV steps. Striking similarity was observed between the two curves. The current in the intermediate range of potentials is higher on Ru than RuO_2.

Hydrogen overvoltage on RuO_2 is almost as on Pt, while the overvoltage for oxygen evolution is much lower on RuO_2 and Ru than on Pt [16]. An essential difference between RuO_2 and Ru is that prolonged evolution of O_2 on Ru gives rise to a characteristic colour in the solution, as also observed by Llopis and Vazquez [17], due to dissolution of the electrode with formation of RuO_4. This is not observed with RuO_2 films. The high cathodic current observed on Ru is partly due to the reduction of species in solution derived from RuO_4. RuO_2 on the other hand is stable under prolonged oxygen evolution and, in any case, recovers the original properties.

If the potential of RuO_2 is brought abruptly from one value to another in the region between oxygen and hydrogen evolution, a high current, decreasing slowly with time, is observed. As the current falls to a few μA cm^{-2}, the needle of the ammeter oscillates around zero as though the circuit were open. This phenomenon is observed at any value of E before about 0·3 V. Between 1·35 V and 0·3 V, RuO_2 film electrodes are acting as a large capacitor. The current circulating thus may be considered as a charging current. In fact current reversal can be observed as the potential is stepped in the opposite direction. It is important to note that at any potential the electrode takes some time to reach zero current. A slow phenomenon which is not simple displacement of electrons must therefore be involved in the charging process.

The modifications occurring on RuO_2 are clearly the same as with Ru electrodes. However, although the thickness is the same for the two layers, higher currents are observed with Ru. A conclusion could be that the modifications taking place between the evolution of O_2 and H_2 in both cases involve the bulk of the electrode and not only the surface. Since these processes are quantitatively greater on Ru than on the oxide, RuO_2 films, are for some reasons more stable electrochemically than RuO_2 layers formed on Ru by anodic oxidation.

Fig. 2 shows i/E potentiostatic curves for RuO_2 obtained by starting from the rest potential and changing the potential at two different rates. At each potential, a lower current is obtained for the lower rate of stepping of the potential. If the region of H_2 discharge is reached and the direction of change in potential is reversed, the current becomes anodic for potentials about 0·3 to 0·4 V, corresponding to the limit of electrochemical stability of RuO_2 [15].

RuO_2 electrodes are mechanically more resistant to prolonged O_2 than H_2 discharges. Persistent H_2 evolution may lead to some collapse of the layer with the deposition of a black powder, presumably Ru, at the bottom of the cell. However, short H_2 discharges do not permanently modify the electrode which can entirely recover its original characteristics.

Some breakdown may be also observed during O_2 evolution. However, in this case the cause appears to be mechanical disegregation due to gas evolution in pores. In fact, only films of greater thickness than about 10 to 20 μm show such behaviour.

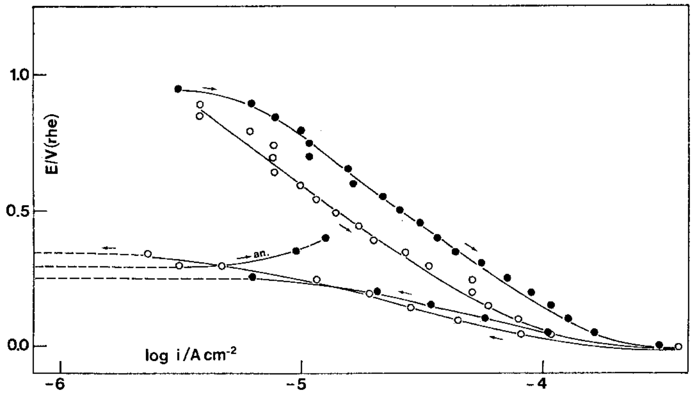

Fig. 2. Quasi-stationary potentiostatic i/E curves for RuO_2 films in 1 M $HClO_4$. Polarization time at each potential: (○) 3 min; (●) 1 min. Arrows indicate the direction of change in potential.

3.3. *Cyclic voltammetry*

A typical i/E curve for RuO_2 electrodes is shown in Fig. 3. Oxygen evolution (peak 5) starts at about 1·35 V. Two pairs of peaks are seen at about 1·1 V and 0·7 V. Peaks 2 and 3 can be attributed to the Ru_2O_3/RuO_2 couple and peaks 1 and 4 to the Ru_2O_3/Ru couple. Peak 6 is thought to be due to the solid-state reduction of RuO_2, i.e. to penetration of atomic hydrogen into the lattice. It should be noted that if the voltammetric curve is carried out between 0·4 and 1·4 V, peaks 2 and 3 remain unchanged, whereas peaks 1 and 4 are smoothed out, even though the background current is little reduced.

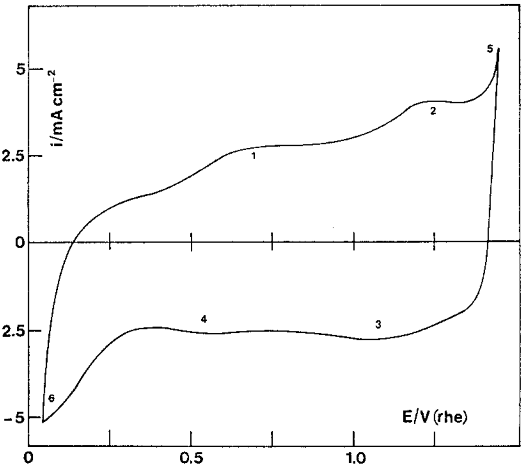

Fig. 3. Typical i/E curve for RuO_2 film electrodes in 1M $HClO_4$ at 60 mV s^{-1}.

Peaks 1 to 4 are presumably due simply to surface reactions involving all of the surface Ru atoms, whereas the magnitude of the background current can be understood only in terms of bulk modifications. These could consist in penetration of protons into the lattice. Thus, the electrode would function as a capacitor and protons would be one of the charge carriers, entering as the potential is changed to some cathodic values, and leaving as the direction of variation in E is reversed. This model could explain why, at each potential, there exists a well-defined charge which can be injected into the electrode. This would correspond to attainment of the required value of the electrochemical potential of protons in the lattice. However, the equilibrium situations at each potential would not be true electrochemical equilibria, since exchange with the solution is restricted to the surface, but rather electrostatic equilibria. This would cause the needle in the ammeter to oscillate, inasmuch as very small changes in E would produce large variations in i.

The qualitative and quantitative reproducibility of the i/E curve of RuO_2 is excellent. A periodical check of the state of the electrode can thus be made by just recording the voltammetric curve. Repeated potential cycling between O_2 and H_2 evolution do not affect the shape of the curve, no difference was observed in a series between the first and the 400th cycle. Mechanical damage is soon revealed by the voltammetric curve, the shape remaining unmodified whilst the value of the current changes.

Experiments showed that some difference exists between a 'dry' electrode (just prepared, and dipped in the electrolyte) and a 'wet' electrode (after some immersion and potential cycling). Fig. 4 shows the first curve for an electrode just dipped, compared to the curve for successive cycles. Although the two curves are similar, some quantitative differences are apparent. This suggests that the bulk of the electrode must undergo some rearrangement before the *i*/*E* curve could assume its usual shape which might be associated with hydration or protonation of the lattice.

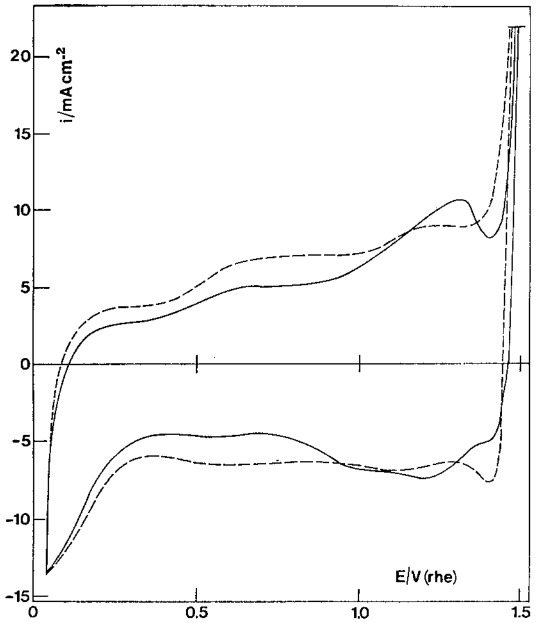

Fig. 4. *i*/*E* curves at 60 mV s^{-1} for RuO_2 in 1 M $HClO_4$. Solid curve: freshly prepared electrode, first cycle; dashed curve: usual curve.

i/*E* curves for Ru and RuO_2 are compared in Fig. 5, the two curves are qualitatively very similar. The results of Llopis and Vazquez [17] using charging curves are confirmed. The metal starts to oxidize at about 0·55 V while RuO_2 is formed at about 1 V. Similar steps can be observed on the curve for RuO_2 but the lower current suggests that only a fraction of the metal atoms is involved in solid-state reactions.

The anodic charge injected into the electrode can be obtained by integration of the *i*/*E* curve from the point at which $i = 0$. Fig. 6 shows that the charge is almost a linear function of the

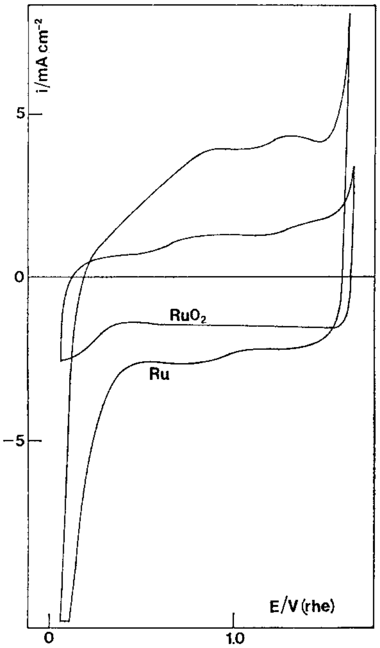

Fig. 5. *i*/*E* curves at 40 mV s^{-1} for RuO_2 films and Ru in 1 M $HClO_4$.

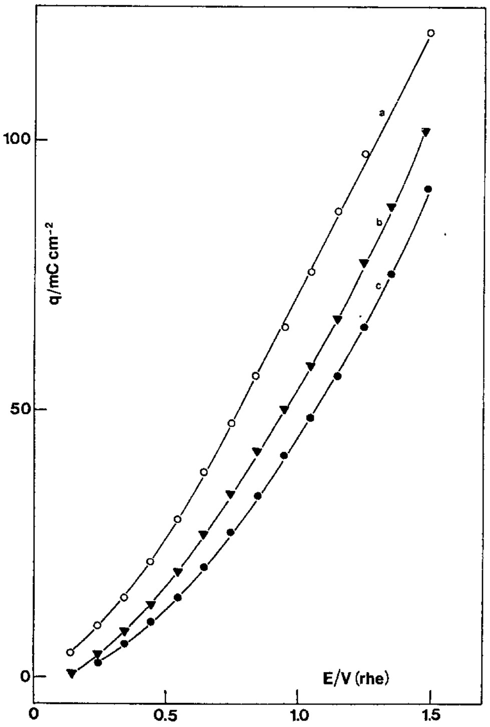

Fig. 6. Anodic charges as a function of potential as obtained by integration of *i*/*E* curves for RuO_2 films in 1 M $HClO_4$ at three different potential-sweep rates. (○) 30 mV s^{-1}. (▼) 60 mV s^{-1}. (●) 120 mV s^{-1}.

potential, precisely as in the case of a capacitor. The slope of the lines in Fig. 6 gives for the apparent capacity about 100 mF cm^{-2} which is very large compared to the double-layer capacity [18] or the capacity due to surface films [19]. As the rate of linear change in potential is increased, the integral capacity decreases, although the slope of the curves remains unaltered i.e. the differential capacity is the same. This indicates that the charging process is associated with a slow stage and is not only due to the displacement of electrons or surface species. This suggestion is supported by the results reported in Fig. 7. In fact, the charge associated with such modifications increases as the layer is made thicker. This effect could be due to surface roughness. If the layer of RuO_2 is porous, the deepness of pores could increase with thickness, thus increasing the real area. In this case, the amount of charge for double layer charging would also increase with thickness. However, the double layer charging is a fast process on rough surfaces also because it does not involve mass transfer. Thus, no dependence of charge on potential sweep rate should be observed.

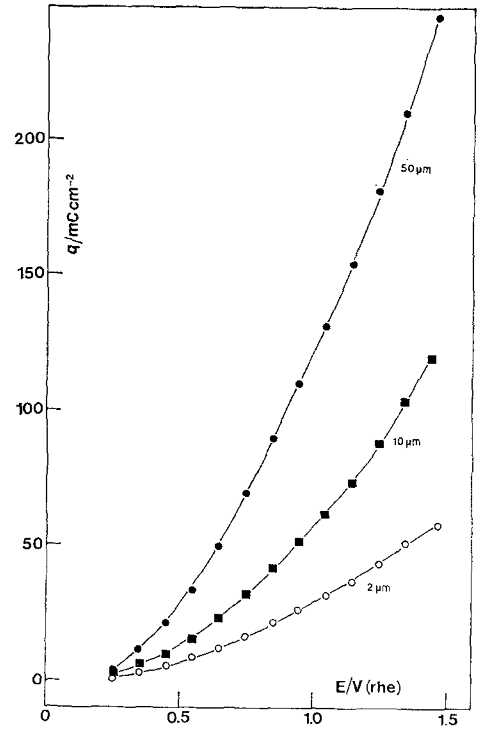

Fig. 7. Anodic charges as a function of potential as obtained by integration of i/E curves for RuO_2 films of different thickness in 1 M $HClO_4$. (○) 2µm (■) 10µm (●) 50µm.

3.4. *Charging curves*

To gain more insight into the mechanism and nature of the bulk modifications, charging curve measurements were carried out. Typical anodic and cathodic charging curves between H_2 and O_2 evolution are given in Fig. 8. The anodic curve starting from 0 V is rather monotonic, whereas the cathodic curve exhibits a

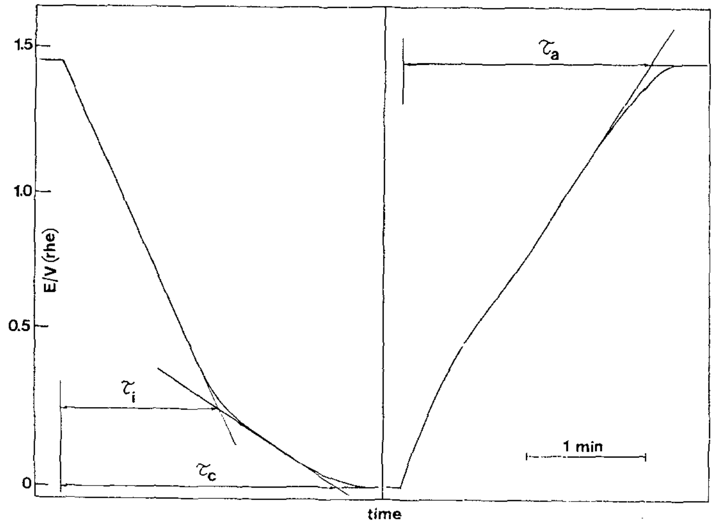

Fig. 8. Typical anodic and cathodic charging curves of RuO_2 film electrodes in 1M $HClO_4$.

characteristic inflexion at about 0·3 V. Charge as a function of current density is shown in Fig. 9.

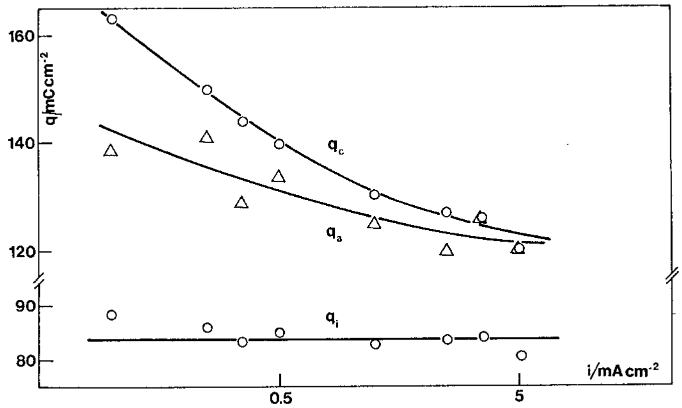

Fig. 9. Charges measured according to Fig. 8 as a function of current density.

The charge measured between 1·45 and 0 V decreases as i is increased, whereas the charge measured between 1·45 and 0·3 V is independent of current density in the range of currents examined.

The charging curves reported in Fig. 10 were obtained as follows. The electrode was kept at 1·2 V for 5 min, i.e. about the time needed for i to become negligible, then brought to 0·1 V. After a given time, t, a constant anodic current of 3·9 mA cm^{-2} was applied and the variation of E with time recorded. Charge is plotted as a function of time t in Fig. 11 for four different temperatures. The anodic charge increases with the time the electrode is held at 0·1 V. A limiting value is, on the contrary, attained for $t > 0$.

These results suggest that fast and slow modifications occur simultaneously in the electrode. Temperature has a negative effect on the stability of RuO_2 films. If the measured charge is taken as a measure of the thickness of the layer, then an increase in temperature produces a thinning of the film. Some sort of damage is also revealed by optical examination of an electrode before and after the use at relatively high temperatures. However, the effect of

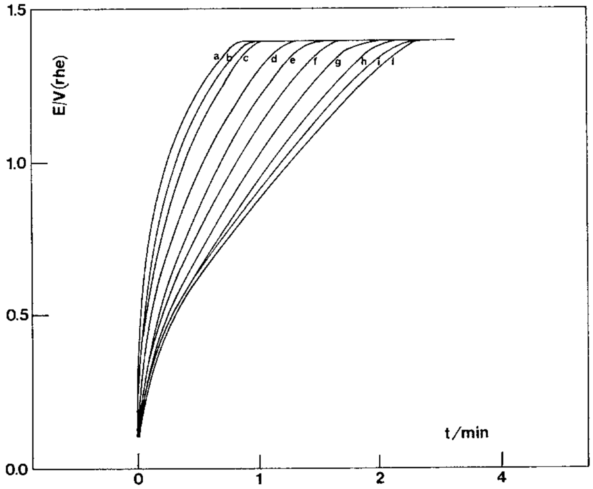

Fig. 10. Anodic charging curves of RuO_2 film electrodes in 1 M $HClO_4$ kept for different times at the starting potential of 0·1 V (rhe). From a to l, t = 2, 5, 15, 30 1, s, 2, 5, 10, 20 min respectively.

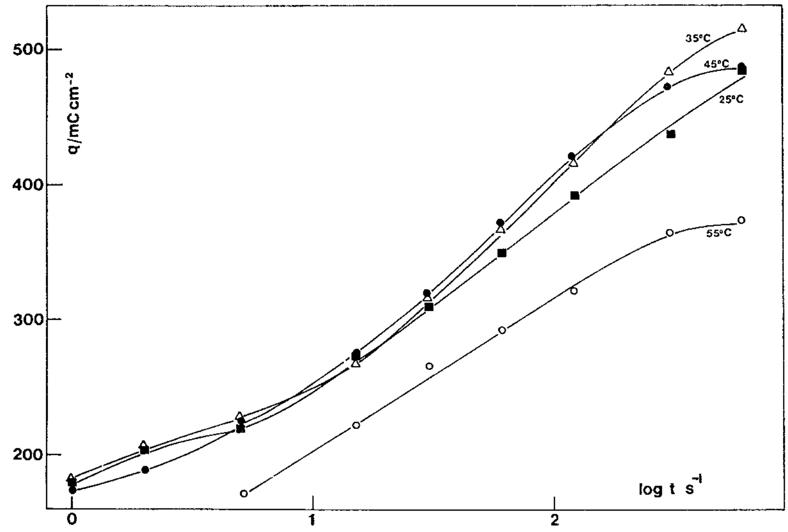

Fig. 11. Anodic charges measured according to Fig. 10 as a function of time at 0·1 V (rhe) at different temperatures.

temperature is to be considered in association with the simultaneous penetration of atomic hydrogen into the lattice. Temperature in itself is not so negative a factor.

Results shown in Fig. 12 refer to an electrode treated as above but released after a given time t at 0·1 V. The open-circuit potential tends to recover a more positive value, but the rate of rise decreases as t increases, which indicates a progressively deeper penetration of the modifications.

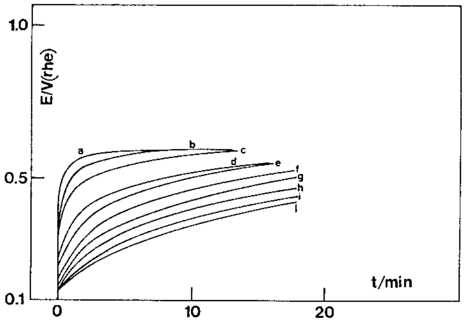

Fig. 12. Variation in potential with time for RuO_2 film electrodes kept at 0·1 V (rhe) for different times. From a to l, times as in Fig. 10.

The results in Fig. 13 corroborate these observations. The electrode was kept for 2 min at 0·1 V, then at 1·2 V for a given time t, and open-circuited. It can be seen that the electrode recovers its original properties, but the time required for recovery increases as the period at 1·2 V is decreased. A notable fact is that E versus t plots are not modified by stirring the solution. This lends further support to the view that the slow stage of the modifications is occurring within the electrode and not at the interface.

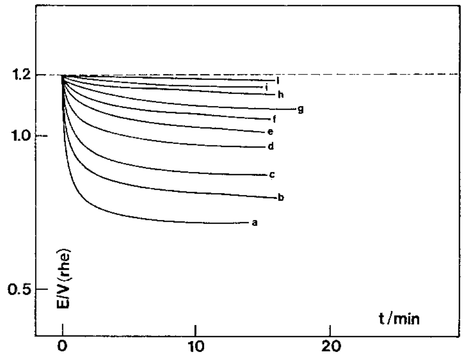

Fig. 13. Variation in potential with time for RuO_2 film electrodes kept at 0·1 V (rhe) for different times then brought to 1·2 V and released. From a to l, times as in Fig. 10.

4. Conclusions

Thermal decomposition of $RuCl_3$ leads [20, 21] to RuO_2 containing some Ru^{3+}. The amount of non-stoichiometry is not negligible as shown by chemical analysis [3]. The charge measured between 1·45 and 0·3 V may be considered as a characteristic quantity for the electrode, because it depends on the thickness and gives rise to possible chemical change or mechanical damage. This charge is thought to be associated with modifications involving the bulk of the electrode and not only its surface. Fast and slow modifications can be observed. The fast modifications, although slower than simple double-layer charging, occur between oxygen evolution, which starts at about 1·35 V, and about 0·3 V. In this range of potential, RuO_2 film electrodes behave as a very large capacitor, capable of being charged and discharged reversibly without any modification in crystal structure or properties.

Above 1·35 V, oxygen evolution occurs with overvoltages considerably lower than those on Pt. Below 0·3 V, the changes appear to be more marked and persistent. It must be recalled that the limit of thermodynamic stability [15] of RuO_2 with respect to Ru can be calculated to be at 0·43 V. Thus strong penetration of atomic hydrogen with reduction of RuO_2 to metal is expected at these potentials. If the evolution of H_2, which occurs on RuO_2 with overvoltages similar to those on Pt, is much prolonged, irreversible reduction of RuO_2 may take place and the layer of RuO_2 may disintegrate to a powder.

It is interesting to note the higher stability towards reduction of thermal RuO_2 with respect to RuO_2 formed anodically on Ru. Furthermore, the anodic stability of RuO_2 films is excellent, whereas Ru dissolves as RuO_4. The anodic stability is probably one of the most interesting aspects of this oxide. This particular behaviour may be related to the manner of preparation which probably involves a different degree of hydration of the lattice.

The charge measured between the evolution of oxygen and 0·3 V is too high to be attributed simply to surface reactions. On the (100) face of RuO_2, the atom density is [22] $1{\cdot}5 \times 10^{15}$ atoms cm^{-2}, and the average composition 1 atom of Ru and 2 atoms of O. If we assume that the surface exchanges one electron per Ru atom, the charge involved per cm^2 of real surface is 80 μCcm^{-2}. Since the charge measured experimentally is about 85 $mCcm^{-2}$ (Fig. 8), the real area of the electrode should be 1060 cm^2cm^{-2} of geometric surface. For a 2 μm thick RuO_2 film, the theoretical amount of oxide is 1·4 $mgcm^{-2}$, using a density of 6·97 gcm^{-3}. Thus, the specific surface of the RuO_2 films would be about 76 m^2g^{-1}. Sommerfield and Parravano [22] have reported a specific surface of 3·8 m^2g^{-1} for RuO_2 powder.

Calculation shows that, although the bulk of the electrode is involved, not all of the metal atoms are involved in exchange of charge. In fact the number of Ru atoms in a 2 μm film of RuO_2 is $6{\cdot}3 \times 10^{18}$ atoms cm^{-2}. The related charge, for one-electron exchange, would be about 1 Ccm^{-2}. Since 85 mC cm^{-2} are measured experimentally, it must be deduced that only about 8·5% of the Ru atoms are implicated in exchange of charge. Chemical analysis [3] reveals a non-stoichiometry of about 14% in RuO_2 powder prepared from $RuCl_3$ by decomposition in air.

From the foregoing, it is suggested that the charge involved in modifications between 1·35 and 0·3 V may reasonably be in some way related to non-stoichiometry. On the basis of this hypothesis, the following model is proposed for the behaviour of RuO_2 films in inert electrolyte solutions. Between 1·35 V and 0·3 V the electrode can be charged and discharged as an electrical condenser, and the maximum charge stored in the electrode equals one electron for Ru atom formally present as Ru^{3+}. In other words, in this range of potential the formal reaction $Ru^{4+} + e \rightarrow Ru^{3+}$ would be restricted to a number of atoms equal to the magnitude of non-stoichiometry, whereas the remaining atoms in the lattice appear to be unreactive. The above formal solid-state redox reaction should be accompanied by penetration of protons into the lattice during cathodic charging, and expulsion of protons from the bulk of the solid phase during anodic charging. The whole process is probably related to localization of charges in the lattice due to the presence of ionic defects. It may be noted that the phenomena observed here have some similarities with the processes occurring in solid state electrochemical, coulometric titrations [23, 24] which are a method for precisely changing the composition of an electrode between equilibrium measurements of the activity of a component.

The role of protons in reactions on oxides is frequently emphasized [25+29] but in this case it is also necessary to imagine the presence of a sort of 'memory' in the electrode, to understand why only a fraction of metal atoms is apparently reactive. This 'memory' is probably the reason itself for non-stoichiometry and the residual hydration of the lattice for incomplete decomposition of $RuCl_3$ should not be of secondary importance. The production of the correct physical picture of the system is obviously the most difficult task of this work and it will be further discussed in forthcoming papers.

Below 0·3 V, the entire lattice appears to become unstable with respect to reduction. Penetration of hydrogen atoms is the most probable process occurring, reduction now involving all RuO_2 atoms.

Acknowledgement

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