Corrosion of Ruthenium Dioxide Hydrate by Ce^{IV} Ions and other Oxidants

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A 'test system' has been developed in order to investigate the corrosion stabilities and O₂-catalytic activities exhibited by samples of RuO₂ · xH₂O when exposed to a strong oxidant such as Ce^{IV} ions. The RuO₂ · xH₂O samples included commercial powders as well as one prepared in the laboratory. The majority of these samples, including the prepared samples, were unstable towards anodic corrosion ($\approx 86\%$ corrosion) and showed little O_2 catalytic activity (O_2 yields 8%). The small amount of O_2 evolved was believed to originate from water bound in the oxide powder. These $RuO_{a} \cdot xH_{a}O$ samples appeared, from thermogravimetric analysis (t.g.a.) and differential gravimetric analysis (d.t.g.a.) measurements, to be highly hydrated (H₂O content = 24–26%). A minority of commercial RuO₂ xH_2O powders, when analysed by t.g.a. and d.t.g.a., were found to be in a partially dehydrated form (H_2O content = 18%). These samples showed a much greater resistance towards corrosion (9-13% corrosion) and were able to mediate the oxidation of water (O_2 yield = 92 %) by Ce^{IV} ions. The corrosion of $RuO_2 \cdot xH_2O$ by other oxidants, e.g. BrO_3^- , MnO_4^- or PbO_2 , was also studied and the results are discussed. The implications of these findings are considered.

Ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) has, for several years, found frequent use as a catalyst for the oxidation of water by a strong oxidant (S⁺), *i.e.*

$$4S^{+} + 2H_{2}O \xrightarrow{\text{RuO}_{2} \cdot xH_{2}O} 4S + 4H^{+} + O_{2}$$
(1)

where $S^+ = Ce^{4+}$, $Ru(bipy)_3^{3+}$ or $Fe(bipy)_3^{3+}$. True catalysts for reaction (1) are rare, however, since most materials either (i) undergo some degree of anodic corrosion themselves when acting as a catalyst or (ii) are stable towards anodic corrosion but inactive as a catalyst. An 'O₂-catalyst' would find application in many different areas, including industrial electrochemistry and solar-energy conversion.

A major approach of solar-energy conversion is the development of a photochemical system capable of driving the cleavage of water¹ into H_2 and O_2 , *i.e.*

$$2H_2O \xrightarrow[\text{sunlight}]{\text{photochemical system}} 2H_2 + O_2.$$
(2)

An integral part of an efficient photochemical system for reaction (2) would be a stable, fast-acting and specific O_2 -catalyst.¹⁻³ The recent use¹⁻⁸ of $RuO_2 \cdot xH_2O$ in this role seems to be due to a misplaced trust in its high corrosion stability and catalytic activity, and this trust appears to arise from two major sources.

The first source is the false association⁴⁻⁹ of $\operatorname{RuO}_2 \cdot xH_2O$ with the largely dehydrated ruthenium dioxide (RuO_2) used extensively in the chlor-alkali industry to mediate the oxidation of brine to chlorine.¹⁰ The electrochemical properties of this latter oxide (RuO_2) have been well studied and, in both the oxidation of brine and water, it exhibits

a low overpotential towards the desired reactions and a high stability towards anodic corrosion.¹⁰ In complete contrast, electrochemical studies using $RuO_2 \cdot xH_2O$ as an anode to mediate the oxidation of water have revealed a very poor stability towards anodic corrosion,¹¹ the product of this corrosion in acid being ruthenium tetroxide (RuO₄).^{11,12}

The second source is the early work of Grätzel and co-workers on the oxidation of water by Ce^{IV} ions using RuO₂·xH₂O (supplied by Alfa) as an oxygen catalyst,^{4,9} in which 'stoichiometric' (*i.e.* 100%) yields of O₂ were claimed, implying no anodic corrosion. However, O₂ yields of 80%¹³ and then 73%¹⁴ have been reported in subsequent papers by the same group, implying some degree of corrosion.

There is a clear need to establish whether or not $RuO_2 \cdot xH_2O$ is able to act as an O_2 -catalyst, and we have developed a test system for this purpose. The test system has enabled us to carry out an investigation into the corrosion stabilities and O_2 -catalytic activities exhibited by samples of $RuO_2 \cdot xH_2O$ from a number of sources, including one prepared in the laboratory. The results of this investigation are reported below.

Experimental

Materials

The laboratory sample of $\operatorname{RuO}_2 \cdot xH_2O$ was prepared as follows: 100 mg of $\operatorname{RuCl_3} \cdot nH_2O$ (Johnson Matthey) were dissolved in 25 cm³ of water and the pH of the resulting brown solution was adjusted to 7, using a 2 mol dm⁻³ NaOH solution. In order to complete the process of alkaline hydrolysis and oxidation, the solution was heated to *ca*. 90 °C for 10 min. At this stage a black precipitate of $\operatorname{RuO}_2 \cdot xH_2O$ had formed, leaving a clear, colourless liquid phase. The $\operatorname{RuO}_2 \cdot xH_2O$ was then collected by filtration, washed thoroughly with water (*ca*. 200 cm³) and dried in air. Other samples of $\operatorname{RuO}_2 \cdot xH_2O$ were obtained from the following suppliers: Johnson Matthey, Aldrich, Strem, Fluka, Engelhard and Alfa Chemicals.

All Ce^{IV} solutions were prepared from an analytical volumetric solution (AVS) of 0.1 mol dm⁻³ Ce^{IV} sulphate (B.D.H.) using 0.5 mol dm⁻³ H₂SO₄ as the diluent. The sodium hypochlorite was obtained as a 1 mol dm⁻³ solution in 0.1 mol dm⁻³ NaOH from B.D.H.

The MnO₂ (activated) was supplied by Fluka AG. The Ru(bipy)³⁺₃ solution used was prepared by oxidation of a solution of the hydrated chloride salt of Ru(bipy)²⁺₃ (3.6×10^{-3} mol dm⁻³ in 0.5 mol dm⁻³ H₂SO₄, obtained from Strem Chemicals), using Ce^{IV} as the oxidant. In order to ensure that no Ce^{IV} remained after oxidation, only sufficient was added to oxidise 90% of the Ru(bipy)²⁺₃ present to Ru(bipy)³⁺₃. All other oxidants were obtained in the purest form available from B.D.H.

In all this work the water used was doubly distilled and deionised.

Methods

Thermogravimetric analysis (t.g.a.) and differential gravimetric analysis (d.t.g.a.) were performed using a Stanton Redcroft TG-750 instrument coupled to a Linseis chart recorder (type LS4). In this work the sample (*ca.* 6–9 mg) was heated from ambient temperature (typically *ca.* 22 °C) to 900 °C at a rate of 20 °C min⁻¹ and the percentage weight loss was recorded as a function of time using the x/t chart recorder. In all cases N₂ was flowing at a rate of 25 cm³ min⁻¹.

X-Ray powder diffraction studies were carried out using a Philips PW 1130 generator using Cu $K_{\alpha 1\alpha 2}$ radiation, a vertical goniometer (PW 1050) and a Xe gas-filled proportional counter detector (PW 1965/20).

Transmission electron micrographs of the $RuO_2 \cdot xH_2O$ samples were recorded using a transmission electron microscope (120C TEM-SCAN) manufactured by Jeol Ltd.

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Fig. 1. Schematic illustration of the 'flow system' described in the experimental section of the text. The components are (1) N₂ cylinder, (2) flow meter, (3) reaction vessel, (4) rubber septum, (5) 'RuO₄ trap' and (6) O₂-MPD. The reaction vessel (3) usually contained 100 cm³ of a 3.6×10^{-3} mol dm⁻³ Ce^{IV} solution in 0.5 mol dm⁻³ H₂SO₄. The 'RuO₄ trap' (5) contained 100 cm³ of a (0.1 mol dm⁻³ NaOCl+1 mol dm⁻³ NaOH) solution.

The Test System

In our study of the corrosion of RuO₂·xH₂O samples, the test system illustrated in fig. 1 was used. In this system a cylinder of N₂ (1) (white-spot, O₂-free, B.O.C.) provided a continuous flow [$f = 180 \text{ cm}^3 \text{ min}^{-1}$, as measured by the flow meter (2)] through two 125 cm³ Dreschel bottles. The first of these bottles, the reaction vessel (3), contained 100 cm³ of a stirred Ce^{1V} solution ($3.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ in } 0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) and had the additional feature of a rubber septum (4) through which samples of RuO₂·xH₂O, dispersed in 10 cm³ of 0.5 mol dm⁻³ H₂ SO₄ via sonication for 5 min, could be injected. The second Dreschel bottle, the RuO₄ trap (5), contained 100 cm³ of a 0.1 mol dm⁻³ NaOCl solution in 1 mol dm⁻³ NaOH which was used to collect, in the form of perruthenate ions (RuO₄⁻), any RuO₄ carried over by the N₂ stream from (3).¹⁵ The number of moles of RuO₄⁻ collected in (5) was determined spectrophotometrically, using $\lambda_{max} =$ 385 nm and $\varepsilon_{385} = 2162 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for the RuO₄ species.¹⁶ This analysis had to be performed *ca.* 12 h after injection of an RuO₂·xH₂O sample into the reaction vessel (3) in order to ensure that all the RuO₄ produced in (3) was swept out by the N₂ stream. The percentage corrosion was calculated using the equation

% corrosion =
$$[N(\text{RuO}_4^-)/N(\text{RuO}_2 \cdot xH_2O)] \times 100$$
 (3)

where $N(\text{RuO}_4^-)$ is the no. of moles of RuO_4^- found in the trap and $N(\text{RuO}_2 \cdot xH_2O)$ is the no. of moles of $\text{RuO}_2 \cdot xH_2O$ injected into the reaction vessel.

Any oxygen produced as a result of reactions in (3) was detected quantitatively using an oxygen membrane polarographic detector (O_2 -MPD) (6) coupled to the second Dreschel bottle (5). A detailed description of this method of O_2 determination using an O_2 -MPD in a flow system has been reported elsewhere.¹⁷ The percentage O_2 yield was calculated using the equation

$$O_2 \text{ yield} = [N(O_2)/N(Ce^{4+})] \times 400$$
 (4)



Fig. 2. Typical t.g.a. and d.t.g.a. curves for a highly hydrated sample of RuO₂·xH₂O (6 mg) showing, respectively, (a) percentage weight loss and (b) differential of weight loss as a function of temperature in the range 18-800 °C. Measurements were made with N₂ flowing at a rate of 25 cm³ min⁻¹ and a heating rate of 20 °C min⁻¹.

where $N(O_2)$ is the number of moles of O_2 evolved and $N(Ce^{4+})$ is the number of moles of Ce^{4+} ions consumed.

Results and Discussion

Characterisation of RuO₂·xH₂O Samples

Many of the techniques often used to characterise fine powders,¹⁸ such as X-ray diffraction and infrared spectroscopy, proved unsuitable for $\text{RuO}_2 \cdot xH_2\text{O}$. The $\text{RuO}_2 \cdot xH_2\text{O}$ samples appeared, from X-ray and electron diffraction studies, to be amorphous. In addition, the infrared spectra of the samples were featureless owing to a characteristic strong and continuous absorption band from the visible region to *ca*. 45 μ m masking out any vibrational bands.¹⁹ Transmission electron micrographs of the RuO₂ · xH₂O samples indicated that the powders were not composed of regular or well defined particles, but rather aggregates of crystallites too small (≤ 10 nm) to be readily resolved.

In contrast to the above techniques, t.g.a. and d.t.g.a. did indicate some differences between the various samples of $RuO_2 \cdot xH_2O$. The majority of samples of $RuO_2 \cdot xH_2O$ (including the prepared samples) appeared to be highly hydrated (water content = 24– 26%), and typical t.g.a. and d.t.g.a. curves are illustrated in fig. 2. However, samples of $RuO_2 \cdot xH_2O$ from Fluka and Alfa appeared to be partially dehydrated (water content = 18–19%) and, as a consequence, were studied separately, as anomalous samples of $RuO_2 \cdot xH_2O$.

Corrosion Stability and Catalytic Activity of RuO₂·xH₂O

In this work the $RuO_2 \cdot xH_2O$ used was in its highly hydrated form and the results obtained were the same for all such samples. A series of experiments were performed in

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Fig. 3. The absorption spectra, recorded using a 1 mm cell, of the Ce^{IV} solutions before (a) and 12 h after [(b)-(g)] the addition of various (0-10 mg) amounts of RuO₂·xH₂O to the reaction vessel (see fig. 1). The additions of RuO₂·xH₂O made were: (b) 0, (c) 2, (d) 4, (e) 6, (f) 6.9 and (g) 10 mg dispersions in 10 cm³ of 0.5 mol dm⁻³ H₂SO₄.

which varying amounts (0–10 mg) of $RuO_2 \cdot xH_2O$, dispersed in 10 cm³ of 0.5 mol dm⁻³ H_2SO_4 , were injected into the reaction vessel (3) of the test system, and the following observations were made.

Change in Ce^{IV} Concentration

In all cases the black colour of the $\text{RuO}_2 \cdot xH_2\text{O}$ suspension disappeared within < 5 min, implying a rapid and complete corrosion reaction. For each experiment the absorption spectrum of the Ce^{IV} solution contained in the reaction vessel (3) was recorded 12 h following injection, and these spectra have been collected together in fig. 3. From this figure it is apparent that the concentration of Ce^{IV} ions ([Ce⁴⁺]) decreases upon the addition of the RuO₂ $\cdot xH_2\text{O}$ samples, and that the decrease in [Ce⁴⁺] depends directly upon $N(\text{RuO}_2 \cdot xH_2\text{O})$, the number of moles of RuO₂ $\cdot xH_2\text{O}$ added. Indeed, the plot of the number of moles of Ce^{IV} reacted [$N(\text{Ce}^{4+})$] vs. $N(\text{RuO}_2 \cdot xH_2\text{O})$ was a straight line with a slope = 4.3 ± 0.2 . The quantity $N(\text{Ce}^{4+})$ was calculated using Beer's law and a molar absorptivity of 5580 mol⁻¹ dm³ cm⁻¹ for Ce^{IV} ions at 320 nm.²⁰

From the plot of $N(Ce^{4+}) vs$. $N(RuO_2 \cdot xH_2O)$ a value for the gradient of 4, rather than 4.3 ± 0.2 , might have been expected. The requirement of extra equivalents of Ce^{1v} implies that a second process occurs concomitant to the oxidation of $RuO_2 \cdot xH_2O$ to RuO_4 . Interestingly, Gortsema and Cobble²¹ have demonstrated that Ru^{1v} -hydrolysed polymers also require more than four equivalents of Ce^{1v} per mole of ruthenium in order to effect their oxidation to RuO_4 . They have suggested that the excess number of equivalents

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Fig. 4. A typical absorbance ($\lambda = 430 \text{ nm}$) vs. time plot for the reaction of Ce^{IV} ions (ca. $3.6 \times 10^{-3} \text{ mol dm}^{-3}$) with RuO₂ · xH₂O (ca. 70 mg dm⁻³). In this experiment, 90 mm³ of a 0.1 mol dm⁻³ Ce^{IV} solution was injected (the point of injection is denoted by the arrow) into a stirred dispersion of ca. 175 µg of RuO₂ · xH₂O in 2.5 cm³ of 0.5 mol dm⁻³ H₂SO₄.

is required to oxidise simultaneously water bound in the polymer. Evidence that this may also be the case with $RuO_2 \cdot xH_2O$ was provided by the results from the O_2 measurements (vide infra).

In fig. 4 an absorbance ($\lambda = 430 \text{ nm}$) versus time plot is illustrated in which 90 mm³ of a 0.1 mol dm⁻³ Ce^{IV} solution were injected (denoted by the arrow in the figure) into a stirred dispersion of 175 μ g of RuO₂·xH₂O in 2.5 cm³ of 0.5 mol dm⁻³ H₂SO₄. These conditions mimic those in the 'test system', and from fig. 4 it is clear that the corrosion reaction is quite fast ($t_1 \approx 17$ s).

The corrosion of a uniform distribution of spherical particles should obey an inversecubic rate law. This has been demonstrated by Segal and Williams²² in a study of the dissolution of chromium(III) oxide particles by potassium permanganate. However, in the case of $RuO_2 \cdot xH_2O$ powder the particles appear, from electron microscopy, to be non-spherical and non-uniform in size, which has so far made a detailed study of their corrosion difficult; however, work of this nature is continuing within this group.

Trapping out of RuO_4^-

Any RuO₄ generated by anodic corrosion of the injected RuO₂·xH₂O samples by the Ce^{IV} ions in the reaction vessel was subsequently swept out by the N₂ stream into the 'RuO₄ trap'. This consisted of 100 cm³ of a (0.1 mol dm⁻³ NaOCl + 1 mol dm⁻³ NaOH) solution contained in the second Dreschel bottle [(5) in fig. 1], and was based on the work of Larson and Ross.¹⁵ They established that at high (1 mol dm⁻³) NaOH concentrations and moderate (0.1 mol dm⁻³) hypochlorite concentrations, any RuO₄⁻ present is stable over a long period of time (up to several weeks). The stability of RuO₄⁻ under these conditions appears to be the result of (i) a slow rate of reduction of RuO₄⁻ to RuO₄²⁻ (ruthenate ion) by the OH⁻ present and (ii) the ability of the hypochlorite ion $[E^{\ominus}(OCl^{-}/Cl^{-}) = 0.90 \text{ Vys. NHE}]^{23}$ to oxidise any RuO₄²⁻ $[E^{\ominus}(RuO_4^{-}/RuO_4^{2-}) = 0.59 \text{ Vys.}$ NHE]²³ produced.





Fig. 5. The absorption spectra, recorded using a 0.5 cm cell, of the 'RuO₄ trap' solutions [see (5) in fig. 1] 12 h after the addition of the varying amounts (0–10 mg) of RuO₂ · xH₂O to the reaction vessel (see fig. 2). The additions of RuO₂ · xH₂O made were: (a) 0, (b) 2, (c) 4, (d) 6, (e) 6.9 and (f) 10 mg dispersions in 10 cm³ of 0.5 mol dm⁻³ H₂SO₄. The insert illustrates the straight-line relationship between $N(\text{RuO}_4)$ and $N(\text{RuO}_2 \cdot \text{xH}_2\text{O})$. The values for $N(\text{RuO}_4)$ used were calculated from the absorbances at $\lambda_{\text{max}} = 385$ nm shown on the larger diagram using $\varepsilon_{385}(\text{RuO}_4) = 2162$ dm³ mol⁻¹ cm⁻¹.

Injections of RuO_4 directly into the 'RuO₄ trap' produced negligible amounts of O₂, indicating that the initial reduction reaction of the 'RuO₄ trap' was not

$$4\operatorname{RuO}_4 + 4\operatorname{OH}^- \to 4\operatorname{RuO}_4^- + \operatorname{O}_2 + 2\operatorname{H}_2\operatorname{O}$$
(5)

for which $\Delta G^{\ominus} = 58 \text{ kJ mol}^{-1}$ of RuO_4^- but, instead, most likely

$$6RuO_4 + ClO^- + 6OH^- \to 6RuO_4^- + ClO_4^- + 3H_2O$$
(6)

for which $\Delta G^{\ominus} = -53 \text{ kJ mol}^{-1}$ of RuO_4^- .

The 'RuO₄ trap' absorption spectra recorded for all of the injected RuO₂·xH₂O samples have been collected together in fig. 5. In this figure an insert is shown of the subsequent plot of $N(\text{RuO}_{4})$ vs. $N(\text{RuO}_{2} \cdot x\text{H}_{2}\text{O})$, where $N(\text{RuO}_{4})$ has been calculated from the absorbance at $\lambda_{\text{max}} = 385$ nm for the RuO₄ species, as described earlier. The result of this plot is a straight line (correlation coefficient 0.9997) with a gradient of



Fig. 6. Typical current (*i*) vs. time traces recorded by the O₂-MPD [(6) in fig. 1] after the addition of (a) 10, (b) 4 and (c) 0 mg of $RuO_2 \cdot xH_2O$ to the reaction vessel of the flow system.



Fig. 7. Plot of the number of moles of O_2 evolved $[N(O_2)]$, as measured by the O_2 -MPD [see fig. 7 for examples] vs. the number of moles of $RuO_2 \cdot xH_2O$ added $[N(RuO_2 \cdot xH_2O)]$.

 0.86 ± 0.01 . At first this value for the gradient may appear a little disappointing, since it implies that the percentage corrosion of $\text{RuO}_2 \cdot xH_2\text{O}$ to RuO_4 is only *ca*. 86% and not, as our observations would lead us to believe, 100%. However, it must be recognised that the observed ratio $N(\text{RuO}_4^-)/N(\text{RuO}_2 \cdot xH_2\text{O})$ of 0.86 represents a minimum. This was confirmed by generating known amounts of RuO_4 in the reaction vessel and monitoring the efficiency of its transfer to the 'RuO₄ trap' by the N₂ stream. In all cases this efficiency appeared to be *ca*. 86%, indicating that the percentage corrosion of $\text{RuO}_2 \cdot xH_2\text{O}$ to RuO_4 by Ce^{IV} ions was probably closer to 100% rather than the experimentally observed value of 86%.

O_2 -Generation

Using the O_2 -MPD coupled to the 'test system' [(6) in fig. 1] it was possible to detect the number of moles of O_2 evolved, if any, upon the addition of the varying amounts of $\operatorname{Ru}O_2 \cdot xH_2O$. In fig. 6 are shown three typical current vs. time traces [(a)-(c)], recorded by the O_2 -MPD before and after the addition (at t = 0) of different amounts of $\operatorname{Ru}O_2 \cdot xH_2O$. Previous work¹⁷ had established that the area under a peak is related directly to the number of moles of $O_2 [N(O_2)]$ evolved in the reaction vessel.¹⁷

Fig. 7 shows a plot of $N(O_2)$ vs. $N(\tilde{RuO_2} \cdot x\tilde{H}_2O)$ for all additions made. The non-zero intercept of 2.8×10^{-6} mol of O_2 (see fig. 7) is due to the dissolved O_2 in the injected

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oxidising agent	standard redox potential ²³ /V vs. NHE (initial → final) oxidation state	corrosion (%)	comments
Ce ⁴⁺	$1.45 (+4 \rightarrow +3)$	86	A fast oxidation $(t_1 \approx 17 \text{ s})$ leading to some loss of yellow colour due to the reduction of Ce ^{IV} ions (see fig. 4).
BrO ₃ -	$1.44 \\ (+5 \rightarrow -1)$	82	A fast oxidation made apparent by the rapid appearance (within seconds) of a bright yellow colour due to RuO_4 formation (see fig. 6).
IO ₄	$\frac{1.65}{(+7 \to +5)^{25}}$	79	As with BrO_3^- , a fast oxidation made apparent by the rapid appearance of RuO_4 . Chemical tests for IO_3^- as a final product made using an AgNO ₃ solution proved positive.
MnO₄	1.68 (+7→+4)	87	A fast oxidation best observed spectrophotometrically. At the end of the reaction a large amount of the manganese appeared to be in the form of MnO_2 , a brown precipitate.
MnO ₂ powder	$1.21 (+4 \rightarrow +2)$	75	A slower oxidation which takes several hours. Only activated MnO_2 (Fluka AG and Aldrich) were found to be effective. Atomic absorption spectros- copy performed on the final solu- tion showed the presence of 1.16×10^{-4} mol of Mn^{2+} ions, indicating a reaction stochiometry of 2 mol of MnO_2 per mol of $RuO_2 \cdot xH_2O$, as expected.
PbO ₂ powder	1.46 (+4→+2)	83	A slow oxidation whose rate was difficult to measure. However, almost complete corrosion of the $RuO_2 \cdot xH_2O$ was effected after <i>ca</i> . 36 h (see percentage corrosion).
ClO3	$1.45 \\ (+5 \rightarrow -1)$	47	A very slow oxidation incomplete even after 10 days (the percentage corrosion given here was recorded after this time).
$S_2O_8^{2-}$	2.0	4)	
$\mathrm{Cr_2O_7^{2-}}$	(+7 - +6) 1.33 (+(-+2))	0	
Ru(bipy) ³⁺	$(+6 \rightarrow +3)$ 1.27	0	evolution by these oxidants.
IO ₃	$(+3 \rightarrow +2)$ 1.09 $(+5 \rightarrow -1)$	0	

Table 1. Corrosion of $RuO_2 \cdot xH_2O$ by a variety of oxidising agents

dispersion. (No attempt was made to purge these dispersions with N_2 , owing to the problems of powder settling.) Experiments have shown that this quantity (ca. 2.8×10^{-6} mol of O_2) is independent of the number of moles of $RuO_2 \cdot xH_2O$ present in the dispersion. From fig. 7 it would appear that the number of moles of O_2 evolved $[N(O_2)]$ is directly related to $N(RuO_2 \cdot xH_2O)$; the slope of the line was found, from a least-squares analysis, to be 0.092 ± 0.008 . In order to account for this O_2 , an extra $4 \times (0.092 \pm 0.008)$ equivalents of Ce^{IV} would be required on top of the expected 4 equivalents, to oxidise 1 mol of $RuO_2 \cdot xH_2O$ to RuO_4 . The total number of Ce^{IV} equivalents would therefore be 4.37 ± 0.03 per mol of $RuO_2 \cdot xH_2O$ added, which compares favourably with the observed value of 4.3 ± 0.2 (see previous section).

From the data contained in fig. 3 and 7 it can be shown that the percentage O_2 yield for each of the additions of $RuO_2 \cdot xH_2O$ (2–10 mg) to the Ce^{IV} solution is constant and equal to 8.5 ± 0.5 %.

The results described in the last three sections show that the corrosion of highly hydrated $RuO_2 \cdot xH_2O$ by Ce^{IV} ions is described by the equation

$$4(4+y)\operatorname{Ce}^{4+} + 4\operatorname{RuO}_{2} \cdot x\operatorname{H}_{2}O \to 4(4+y)\operatorname{Ce}^{3+} + 4\operatorname{RuO}_{4} + y\operatorname{O}_{2} + 4(4+y)\operatorname{H}^{+} + (4x-8-y)\operatorname{H}_{2}O \quad (7)$$

where $y \approx 0.26 \pm 0.03$.

 $RuO_2 \cdot xH_2O$ from most commercial sources or prepared *via* alkaline hydrolysis of $RuCl_3 \cdot nH_2O$ is in this highly hydrated form and is therefore unsuitable for use as an O_2 -catalyst.

Corrosion of RuO₂·xH₂O by Other Oxidants

The corrosion of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ by a variety of oxidants was also studied using the test system. In these experiments 10 mg of the oxide, dispersed in 10 cm³ of 0.5 mol dm⁻³ H₂SO₄, was injected into the reaction vessel containing 100 cm³ of 0.5 mol dm⁻³ H₂SO₄ and the oxidant at a concentration of 3.6×10^{-3} mol dm⁻³. As described previously, any RuO₄ produced as a result of oxidative corrosion of RuO₂ · xH₂O was subsequently trapped out as RuO₄⁻ by the hypochlorite solution in the second Dreschel bottle [(5) in fig. 1]. In table 1 the percentage corrosion found for each oxidant is listed alongside the standard redox potential of the oxidising couple believed to be in operation and any comments about the reaction. The O₂ yields observed were small (*ca.* 4–9%) for the reactions where significant corrosion (*i.e.* > 5%) occurred, and not observable for reactions where no significant corrosion occurred.

From table 1 it would appear that only the well established, strong, homogeneous oxidants, such as Ce^{4+} , BrO_3^- , IO_4^- and MnO_4^- , with standard redox potentials > 1.44 V vs. NHE, are able to oxidise rapidly (within minutes) $RuO_2 \cdot xH_2O$ to $RuO_4 [E^{\ominus}(RuO_4/RuO_2) = 1.39 V vs. NHE]$.²⁴ Oxidants such as CIO_3^- and $S_2O_8^{2-}$, although homogeneous and possessing redox potentials > 1.44 V vs. NHE, do not show a fast corrosive action; however, both often exhibit poor oxidising abilities owing to kinetic factors.^{25, 26} It is unlikely that kinetic factors are responsible for the failures of $Ru(bipy)_3^{3+}$, $Cr_2O_7^{2-}$ and IO_3^- to oxidise $RuO_2 \cdot xH_2O$, but rather thermodynamic ones, since for each reaction ΔG^{\ominus} is large and positive, *i.e.* non-spontaneous. Interestingly, for $Cr_2O_7^{2-}$, although the oxidation of $RuO_2 \cdot xH_2O$ to RuO_4 is an infeasible reaction in terms of thermodynamics, the oxidation of water is not:

$$2Cr_{2}O_{7}^{2-} + 16H^{+} \rightarrow 4Cr^{3+} + 8H_{2}O + 3O_{2}$$

$$\Delta G^{\ominus} = -116 \text{ kJ}$$
(8)

if $E^{\ominus}(\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}/\operatorname{Cr}^{3+})$ is taken as 1.33 V vs. NHE.²³ However, no O₂ evolution was observed using this oxidant.

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Both of the heterogeneous oxidants, PbO_2 and MnO_2 (activated), were able to oxidise $RuO_2 \cdot xH_2O$ to RuO_4 . It seems likely that the hydrophobic powder particles of $RuO_2 \cdot xH_2O$ form aggregates, some of which include the oxidant particles (PbO_2 , MnO_2) as well as themselves. (There is some initial evidence for this from scanning electron microscopy coupled with X.r.f. analysis.) The presence of oxidant particles in such aggregates would encourage corrosion owing to the higher local concentration ratios of [oxidant]/[$RuO_2 \cdot xH_2O$] that would then exist in these aggregates, compared to the bulk solution. This would go some way towards explaining the large percentage corrosion (*ca.* 75%) observed for MnO_2 (activated) despite the apparent thermodynamic infeasibility of the reaction as predicted from standard redox-potential data.

The results described above show that, not surprisingly, the percentage corrosion of $\operatorname{RuO}_2 \cdot x \operatorname{H}_2 O$ depends strongly upon the standard redox potential of the oxidant. (In a later paper we shall show that this is also true for the percentage O_2 yields observed when studying stable O_2 -catalysts.) Oxidants with $E^{\ominus} > ca$. 1.44 V vs. NHE can readily corrode $\operatorname{RuO}_2 \cdot x \operatorname{H}_2 O$ to RuO_4 , and the rate of this corrosion is reduced drastically if oxidants are used which possess E^{\ominus} values < ca. 1.44 V vs. NHE. No evidence could be found for a 'window potential' region for water oxidation *i.e.* a redox potential region, between the limits 1.23 < E/V vs. NHE < 1.44, where water oxidation occurs and $\operatorname{RuO}_2 \cdot x \operatorname{H}_2 O$ oxidation does not. Instead, RuO_4 formation seems to be the preferred oxidation reaction on the $\operatorname{RuO}_2 \cdot x \operatorname{H}_2 O$ surface, and attempts made to lower the standard redox potential of the oxidant to < 1.44 V vs. NHE appear only to reduce this rate of corrosion.

This point was demonstrated by varying the ratio of $[Ce^{4+}]/[Ce^{3+}]$ in the reaction vessel. Using a $[Ce^{4+}] = 3.6 \times 10^{-3} \text{ mol dm}^{-3}$, the half-lives for corrosion of an $RuO_2 \cdot xH_2O$ sample were found to be 1700, 40 and 20 s for initial concentrations of $Ce^{3+} = 3.6 \times 10^{-2}$, 3.6×10^{-3} and O mol dm⁻³, respectively. The overall percentage corrosion for all these reactions was high (> 70 %) and little O₂ evolution could be observed.

Anomalous Samples of RuO₂·xH₂O

Samples of $\text{RuO}_2 \cdot xH_2\text{O}$ from Alfa and Fluka appeared from thermogravimetric analyses to be partially dehydrated (H₂O content = 18%) and as a result were studied separately. $\text{RuO}_2 \cdot xH_2\text{O}$ in this form, when used in the 'test system', showed a much greater resistance towards corrosion (9–13%) and a high activity (O₂ yield = 92%) as a catalyst for the oxidation of water by Ce^{IV} ions, *i.e.*

$$4Ce^{4+} + 2H_2O \xrightarrow{\text{catalyst}} 4Ce^{3+} + 4H^+ + O_2.$$
(9)

It therefore appears that the water content of an $\text{RuO}_2 \cdot xH_2\text{O}$ sample may be related to its corrosion stability and O₂-catalytic activity. Subsequent work by this group has demonstrated that fully hydrated $\text{RuO}_2 \cdot xH_2\text{O}$ is stabilised towards corrosion (*i.e.* 0% corrosion) and activated as a catalyst for water oxidation (O₂ yield = 90-100%) once it has been partially dehydrated (water content = 8-9%) by annealing at *ca.* 144 °C for 5 h in air.

Conclusion

These results go far in resolving the controversy which surrounds the O₂-catalytic activity of $RuO_2 \cdot xH_2O$. Samples of $RuO_2 \cdot xH_2O$ purchased from the majority of suppliers are usually in a fully hydrated form and are therefore unstable towards anodic corrosion. However, with a minority of suppliers the $RuO_2 \cdot xH_2O$ purchased is in a partially dehydrated form and is therefore much more stable towards anodic corrosion and able to mediate the oxidation of water. The lower degree of hydration in the latter samples

may be due to the employment of a higher drying temperature in their preparation. Thus the O₂-catalytic activity of commercial samples of $RuO_2 \cdot xH_2O$ will, as has been observed, vary from manufacturer to manufacturer and may, in some cases, vary from batch to batch.

It seems likely that the anodic corrosion of any sample of $RuO_2 \cdot xH_2O$ occurs at 'kink'²² or other surface-defect sites. Such sites would be associated with a greater number of coordinated water molecules than at other surface sites. The number of these defect sites in an $RuO_2 \cdot xH_2O$ sample would be reflected by its measured, overall percentage water content.

The above assumptions provide a rationale for the observed link between the stability of a sample of $RuO_2 \cdot xH_2O$ towards anodic corrosion and its degree of hydration. Thus highly hydrated $RuO_2 \cdot xH_2O$ would be expected to have a much greater number of defect sites per gram and, as a result, would be more susceptible to anodic corrosion than partially dehydrated $RuO_2 \cdot xH_2O$.

Interestingly, on this basis it should be possible to reduce the number of surface defects in a sample of $\text{RuO}_2 \cdot xH_2O$ by annealing it. However, if the annealing temperature is too high the sample will undergo extensive crystallisation and exhibit a low specific catalytic activity (*i.e.* activity per g) for water oxidation. Alternatively, if the annealing temperature is too low, the sample will still have a number of surface defect sites and therefore undergo some anodic corrosion as well as exhibit a high specific catalytic activity.

In a second paper we report the results of a detailed investigation into the effect of annealing temperature on the stability of $RuO_2 \cdot xH_2O$ towards anodic corrosion and its O_2 -catalytic activity.

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