Ruthenium Dioxide Hydrate as an Oxygen Catalyst: a Controversy Resolved?

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Fully hydrated $RuO_2.xH_2O$ undergoes mainly anodic corrosion, and demonstrates little catalytic activity toward the oxidation of water, when exposed to Ce^{4+} in solution; however, mild heat-treatment of the oxide (with an optimum at *ca.* 140 °C) *reverses* these characteristics, and so can be used to generate reproducibly an active, and stable oxygen catalyst.

In order to achieve the efficient photocleavage of water into H_2 and O_2 using solar energy, catalysts must be found which are efficient, stable, specific, and fast-acting toward the reduction and oxidation of water. A great deal of progress has been made in the area of 'H_2-catalysts', and we now have materials (such as colloidal dispersions of Pt) which are able to act in the μs time domain,[1] and so compete with the process of back electron transfer. However, the search for 'O_2-catalysts' has been far less rewarding, with many of the catalysts developed so far demonstrating a considerable variation in activity when used by different groups. Of all the catalytic material tried, none appear so variable in behaviour, and as controversial, as ruthenium dioxide hydrate ($RuO_2.xH_2O$).[2—6] Much of the controversy centres around the stability of $RuO_2.xH_2O$ toward anodic corrosion, and its catalytic activity toward the oxidation of water, when exposed to strong oxidising agents, such as Ce^{4+} and $Ru(bipy)_3{}^{3+}$ (bipy = bipyridine). For example, samples of $RuO_2.xH_2O$ supplied by Alfa Inorganic have been reported[3] to act as stable catalysts, yielding stoicheiometric amounts of O_2, for reaction (1). In contrast, other work (including a more recent study by the same group)[6] shows that $RuO_2.xH_2O$ (as supplied by Alfa Inorganic[6] and Aldrich Chemicals[2]) undergoes anodic corrosion to RuO_4 as well as,[6] or (as found in the case of $RuO_2.xH_2O$ from Aldrich Chemicals[2]) instead of, catalysing reaction (1). In this communication we outline the results of a rigorous investigation of the affect of heat-treatment on the stability and catalytic activity of $RuO_2.xH_2O$ (as supplied by Johnson Matthey, Aldrich Chemicals, and Alfa Inorganic) towards the oxidation of water by Ce^{4+}; an investigation which, we believe, resolves much of the controversy surrounding this material, and opens up the way to the production of a reproducible, active, stable O_2-catalyst.

$$4Ce^{4+} + 2H_2O \xrightarrow{RuO_2.xH_2O} 4Ce^{3+} + 4H^+ + O_2 \qquad (1)$$

Table 1. Summary of data.

	Source of $RuO_2.xH_2O$	% H_2O Content[a]	% O_2[b]	% Corrosion[b]
Before heat treatment	Johnson Matthey or Aldrich Chemicals	24	18	82
	Alfa Inorganic	19	92	15
After heat treatment at 144 °C	Johnson Matthey or Aldrich Chemicals	10	97	0
	Alfa Inorganic	7	98	0

[a] Determined by TGA. [b] Determined using the 'test system', see text.

In all our experiments, a 'test system' was used in which a N_2 cylinder provided a continuous flow (f = *ca.* 180 cm^3/min) of gas through three Dreschel bottles (each 125 cm^3), and an oxygen membrane polarographic detector (O_2-MPD), coupled in series. Of the Dreschel bottles: the first contained 100 cm^3 of 0.5 M H_2SO_4 (used to saturate the carrier gas), the second contained 100 cm^3 of a Ce^{4+} solution (always 3.6×10^{-3} M in 0.5 M H_2SO_4), and also had the additional feature of a rubber septum through which the catalyst (dispersed in 0.5 M H_2SO_4; 1 mg/ml) could be injected, and the third contained 100 cm^3 of 0.1 M NaOCl solution in 1 M NaOH [used to trap, in the form of perruthenate ($RuO_4{}^-$),[7] any RuO_4 produced]. The O_2-MPD has been described elsewhere,[8] and allowed the determination of the number of moles of O_2 produced, following catalyst injection. The % O_2 yield was calculated using equation (2), where the number of moles of Ce^{4+} consumed were determined spectrophotochemically[2] from the drop in absorbance of the Ce^{4+} solution (at $\lambda_{max.}$ = 320 nm) following injection of the catalyst. The degree of corrosion of the catalyst was taken as the ratio of the number of moles of $RuO_4{}^-$ produced (determined spectrophotochemically,[9] using $\lambda_{max.}$ = 385 nm, and ε_{385} = 2162 $dm^3 mol^{-1} cm^{-1}$) to the number of moles of $RuO_2.xH_2O$ added. This ratio represents a *minimum* value, since the RuO_4 produced also attacked the rubber septum and the glassware (as evidenced by blackening of both) before reaching the hypochlorite trap. Owing to the high solubility of RuO_4 (*ca.* 20.3 g dm^{-3}, at 20 °C),[10] a long period of time (6—8 h) was required to flush out most of the RuO_4 produced following catalyst injection.

$$\% \; O_2 \text{ yield} = \frac{\text{No. of moles of } O_2 \text{ produced}}{\text{No. of moles of } Ce^{4+} \text{ consumed}} \times 400 \qquad (2)$$

Using the 'test system' described above, and samples of $RuO_2.xH_2O$ from Johnson Matthey or Aldrich Chemicals, we found that, regardless of the amount of catalyst injected (1—10 mg), the subsequent drop in Ce^{4+} concentration (originally 3.6×10^{-3} M) was always rapid ($t_{\frac{1}{2}} < 5$ min) and corresponded to a reaction stoicheiometry of 5 Ce^{4+} ions to 1

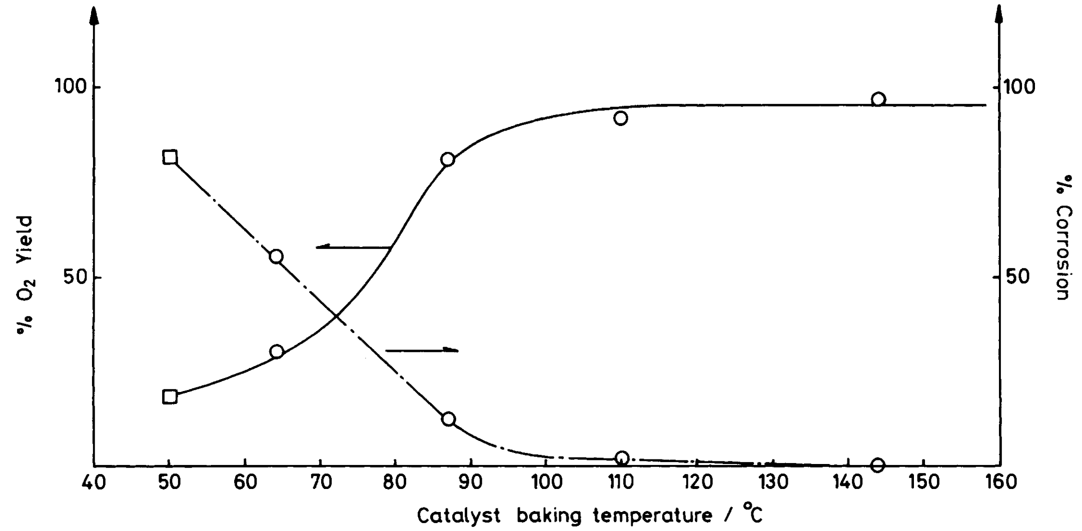

Figure 1. % O_2 Yield (——) and % corrosion observed (—·—·—) on injecting samples (7.5 mg in 7.5 ml 0.5 M H_2SO_4) of $RuO_2.xH_2O$ (Johnson Matthey) baked-out at different temperatures for 5 h, into the Ce^{4+} solution of the 'test system'. □: Commercial $RuO_2.xH_2O$ (usually dried by the manufacturer at 50 °C); ○: baked-out samples of $RuO_2.xH_2O$.

$RuO_2.xH_2O$ molecule. Although only 4 equivalents of Ce^{4+} should be necessary to oxidise a ruthenium(IV) oxide to RuO_4, the extra equivalent is believed to oxidise water bound in the original oxide.[11]

In a series of experiments, samples of $RuO_2.xH_2O$ (Johnson Matthey and Aldrich) were baked-out for 5 h over a range of temperatures (60—900 °C) (note that the commercial forms of these powders are usually dried out at *ca.* 50 °C). All samples were then tested for catalytic activity and corrosion, by injecting 7.5 mg of each into the Ce^{4+} solution of our 'test system'; some of the results are shown in Figure 1 for $RuO_2.xH_2O$ from Johnson Matthey, and a similar behaviour was observed for $RuO_2.xH_2O$ from Aldrich Chemicals. From this work it would appear that, with only a moderate increase in baking temperature (from 50—144 °C), the degree of corrosion decreases markedly (from 82 to 0%) with a concomitant increase in % O_2 yield (*ca.* 18% to 97%), see Figure 1. The '144 °C O_2-catalysts' appeared to act quite fast [$t_{\frac{1}{2}}(Ce^{4+})$ *ca.* 2.5 min], but with treatment temperatures > 144 °C, the catalytic activities of the samples decreased with increasing treatment temperature, *e.g.* with the 400 °C sample $t_{\frac{1}{2}}$ *ca.* 16 min, and with the 700 and 900 °C samples little catalytic activity was observed. This effect is probably, in part, due to a lowering in surface area with higher treatment temperature.[12,13] However, as found with the '144 °C O_2-catalyst', all samples treated at temperature >144 °C appeared to resist any corrosion to RuO_4. Samples of $RuO_2.xH_2O$ (supplied by Alfa Inorganic), when baked-out at ≥140 °C, also showed no tendency to corrode, high % O_2 yields (*ca.* 90—100%), and, with an increasing heat treatment temperature, a decreasing catalytic activity. Grätzel and his co-workers have also noted[6] this latter trend, but they claim that the decrease in catalytic activity, with increasing heat-treatment temperature, *favours* RuO_4 formation. This appears to contradict not only our own observations, but also those of many electrochemists[12,13] who have studied the anodic characteristics of $RuO_2.xH_2O$, before and after heat-treatment.

Thermal gravimetric analysis (TGA) of the commercial samples of $RuO_2.xH_2O$ used in this work, indicates a water content of *ca.* 23—24% in the Johnson Matthey and Aldrich samples, and *ca.* 19% in the Alfa Inorganic sample. However, after baking-out at 144 °C for 5 h, this water content drops to *ca.* 10% in the first two samples, and to *ca.* 7.5% in the last one. These results are of interest, particularly when taken in conjunction with those given in Figure 1, since they indicate that the instability toward anodic corrosion shown by fully hydrated $RuO_2.xH_2O$ (as supplied by Johnson Matthey and Aldrich Chemicals), and its ability to catalyse the oxidation of water, are both related to the amount of water weakly bound to the powder, and possibly involve the same reaction site. In addition, it would appear from the TGA work that the $RuO_2.xH_2O$ supplied by Alfa Inorganic is, in fact, partially dehydrated (possibly due to a higher drying temperature being employed by the manufacturer?), and, as a result, might be expected to show less tendency to corrode and a greater catalytic activity than the samples from Johnson Matthey and Aldrich Chemicals, as has been claimed by Grätzel and his co-workers.[6] This was, indeed, found to be the case, *i.e.*, when $RuO_2.xH_2O$ (7.5 mg) (Alfa Inorganic) was injected into the 'test system' (see above), it gave a high % yield of O_2 (>90%), and showed only a limited degree of corrosion (*ca.* 15%). (This tendency to corrode could be removed by heat-treatment, *e.g.* 144 °C for 5 h.) Since the partially dehydrated sample of $RuO_2.xH_2O$ (Alfa Inorganic) has a large water content (19%), compared to the stable, active '144 °C O_2-catalyst' (10%), then it is quite possible that in the former sample many of the catalytic sites are still fully hydrated (and, therefore, unstable). In addition, the few less-hydrated sites (which are stable and catalytically active) must compete very efficiently with the unstable sites for Ce^{4+} ions, to produce the observed low overall degree of corrosion, and the high % O_2 yield. Some evidence for this was found by repeated exposure of the 'Alfa' catalyst to more and more Ce^{4+}. Under these conditions all the unstable sites should be corroded, and, indeed, our experiments indicated that the unstable sites represent *ca.* 70% of this material. We have summarised some of our results in Table 1.

In conclusion, it would appear that much of the controversy surrounding $RuO_2.xH_2O$ as an O_2-catalyst may be due to a variation in its degree of hydration (see Table 1), which, in turn, depends upon how it is prepared (and, in particular, how it is dried), and, therefore, will quite likely vary from manufacturer to manufacturer, and may even vary from batch to batch. We have found that, by simply baking-out $RuO_2.xH_2O$ (as supplied by Johnson Matthey, Aldrich Chemicals, and Alfa Inorganic) for 5 h at *ca.* 140 °C an active, stable, and reproducible O_2-catalyst is produced.

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