# Charging of a Redox Catalyst for O_2 Evolution

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In some recent work [1] we have shown that ruthenium dioxide hydrate powder ($RuO_2 \cdot xH_2O$) can be converted into a good redox catalyst ($RuO_2 \cdot yH_2O^*$) (by annealing $RuO_2 \cdot xH_2O$ in air at 144 °C for 5 h) for mediating the oxidation of water to O_2 by a strong oxidant, such as Ce^{4+}, BrO_3^-, MnO_4^- and IO_3^- ions. Several other groups have also demonstrated that ruthenium(IV) oxide in various forms, e.g. colloidal or supported, can act as an O_2 catalyst [2–5].

In our work on $RuO_2 \cdot yH_2O^*$ when Ce^{IV} ions are used as the oxidant, the reaction is as follows

$$4Ce^{4+} + 2H_2O \xrightarrow{RuO_2 \cdot yH_2O^*} 4Ce^{3+} + 4H^+ + O_2 \quad (1)$$
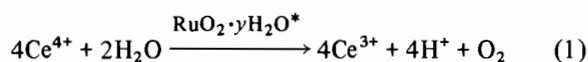
It is possible to monitor spectrophotometrically ($\lambda_{max} Ce^{IV} = 320$ nm) the change in Ce^{IV} ion concentration as a function of time and this has allowed us to carry out a detailed study of the kinetics of reaction (1) in which a number of different reaction parameters were varied, including $[Ce^{4+}]$, $[Ce^{3+}]$, [redox catalyst] and temperature [6]. We have recently demonstrated [6] that the results of this study can be readily interpreted in terms of an electrochemical model in which it is assumed that the $RuO_2 \cdot yH_2O^*$ powder particles act as microelectrodes which mediate electron transfer between a highly irreversible couple (*i.e.* O_2/H_2O) and a highly reversible couple (*i.e.* Ce^{4+}/Ce^{3+}) [7]. According to this electrochemical model, the microelectrode particles must be charged up prior to catalysis [8] and in this article we describe the results of a number of different experiments which provide strong evidence that such a step does indeed occur and, under certain circumstances, can be monitored.

Results and Discussion

In our earlier kinetic studies of reaction (1) it was found that the rate of reaction decreased as the initial concentration of Ce^{III} ions was increased [1, 6]. Indeed, at very high concentrations of Ce^{III} ions (e.g.

typically 2.65×10^{-2} mol dm^{-3}) the rate could be reduced almost to zero. However, in a recent series of experiments using low concentrations of Ce^{IV} ions (e.g. $[Ce^{4+}] = 2.7 \times 10^{-4}$ mol dm^{-3}), we have found that there is always an initial, rapid drop in Ce^{IV} concentration, which, unlike the kinetics associated with reaction (1), appears to be independent of the initial concentration of Ce^{III} ions present. This 'initial reduction step' can be seen in the Ce^{IV} absorbance *versus* time profiles illustrated in Fig. 1 which were recorded for a series of injections of the same dilute Ce^{IV} solution (70 mm^3, 0.01 mol dm^{-3}) into a H_2SO_4 solution (2.5 cm^3, 0.5 mol dm^{-3}) containing different concentrations of Ce^{III} ions (2.65×10^{-4} – 2.65×10^{-2} mol dm^{-3}) and a fixed concentration of $RuO_2 \cdot yH_2O^*$ (70 mg dm^{-3}). As shown by curves (a)–(c) in Fig. 1, this 'initial reduction step' was observed most clearly when the Ce^{III} ion concentration was high, *i.e.* when the rate of reaction (1) was negligible.

For any $RuO_2 \cdot yH_2O^*$ catalyst particle, uncharged or partly charged, the process of charging may be represented by the general equation

$$Ce^{4+} + (RuO_2 \cdot yH_2O^*)^{z+} \longrightarrow$$
$$Ce^{3+} + (RuO_2 \cdot yH_2O^*)^{(z+1)+} \quad (2)$$
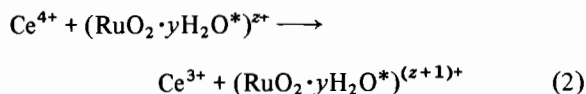
where $z+$ is the charge on the $RuO_2 \cdot yH_2O^*$ particle arising from z other previous charging reactions.
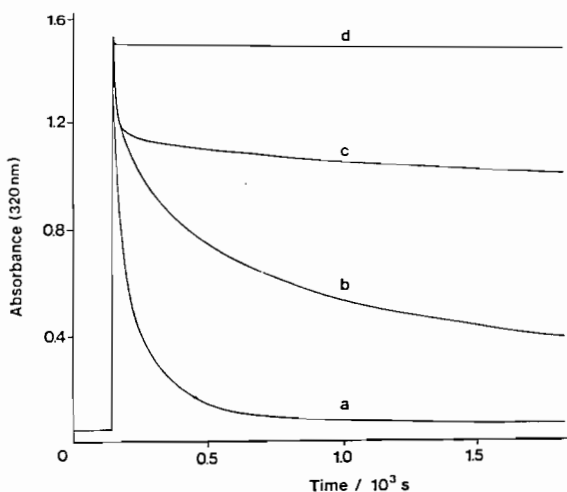

Fig. 1. Absorbance–time profiles recorded for a series of injections of a dilute Ce^{IV} solution (70 mm^3, 0.01 mol dm^{-3}) into 2.5 cm^3 of a stirred dispersion of $RuO_2 \cdot yH_2O^*$ (70 mg dm^{-3}) in 0.5 mol dm^{-3} H_2SO_4, containing different concentrations of Ce^{III} ions: (a) 2.65×10^{-4}, (b) 2.65×10^{-3}, and (c) 2.65×10^{-2} mol dm^{-3}. The absorbance–time curve (d) was recorded using the same conditions as in (c), but in the absence of the redox catalyst.

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From previous work [1, 6] we know that in the presence of a high concentration of Ce^{III} ions the catalyst particles cannot discharge via reaction (1). Thus it seems possible that the initial reduction step, illustrated by curve (c) in Fig. 1, is due to charging up of the redox catalyst particles, *i.e.* reaction (2).
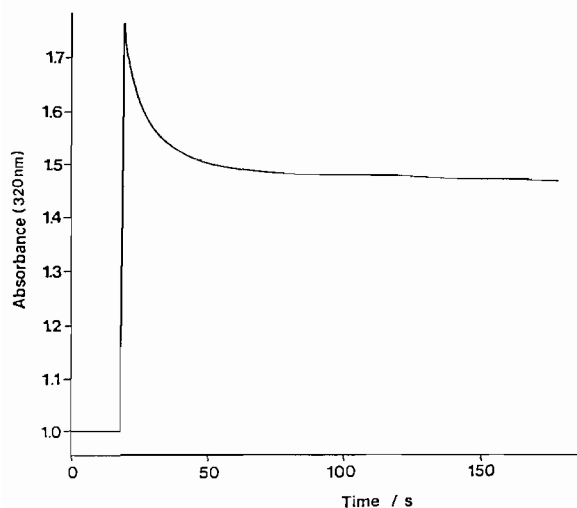

Fig. 2. Absorbance–time profile recorded for a second injection of a dilute Ce^{IV} solution (70 mm^3, 0.01 mol dm^{-3}) into the solution used to record the absorbance–time curve (c) illustrated in Fig. 1. This second injection of Ce^{IV} ions into the solution was made *ca.* 30 min after the first injection.

For any catalyst particle this process of charging will continue until its redox potential equals that of the bulk solution. If the initial reduction step is due to charging, and not an oxidisable impurity associated either with the redox catalyst or the H_2SO_4 solution containing the Ce^{III} ions, then any further increase in the redox potential of the bulk solution, brought about by a second (or third, or fourth, etc.) injection of Ce^{IV} ions for example, should cause each catalyst particle to charge up further by reducing some of the Ce^{IV} ions present until, once again, its redox potential matches that of the bulk solution; *i.e.* with each subsequent injection of Ce^{IV} ions an initial reduction step should be observed. This prediction was confirmed experimentally for a number of injections and Fig. 2 illustrates the absorbance *versus* time profile when a second injection of Ce^{IV} ions was made to the solution used to generate curve (c) in Fig. 1. Further evidence that the initial reduction step is not due to an oxidisable impurity present in the redox catalyst came from the observation of an initial reduction step, similar in every way to that illustrated in Fig. 1 curve (c), using as the redox catalyst a sample of

$RuO_2 \cdot yH_2O^*$ which had previously been used to generate, via reaction (1), 16 times more moles of O_2 than catalyst.

If the initial reduction step is due to charging and not reaction (1) then no O_2 evolution should be detected during the initial fall in $[Ce^{4+}]$. To test this prediction an oxygen membrane polarographic detector (O_2-MPD) [9] was used to monitor the concentration of dissolved O_2 when 2.5 cm^3 of a Ce^{IV} solution (6.4 $\times$ 10^{-4} mol dm^{-3}) were injected into 25 cm^3 of a $RuO_2 \cdot yH_2O^*$ dispersion (1.4 g dm^{-3}), containing a high concentration of Ce^{III} ions (2.8 $\times$ 10^{-2} mol dm^{-3}) in H_2SO_4 (0.5 mol dm^{-3}). No O_2 evolution was observed with the first, second, third or fourth injection of Ce^{IV} ions. A spectrophotometric study of the same set of experiments showed that with each injection made there was only an initial step fall in the concentration of Ce^{IV} ions. This initial reduction step typically accounted for >30% of the Ce^{IV} ions injected, thus if the step fall in Ce^{IV} concentration was associated with reaction (1), rather than reaction (2), then the concentration of O_2 generated should have been *ca.* >2% air-saturated (100% air-saturated $\equiv 2.5 \times 10^{-4}$ mol dm^{-3} O_2) which is well above the minimum detection limit of the O_2-MPD used, which was typically >0.05% air-saturated.

A kinetic study of the initial reduction step, based on the determination of the initial rate of reduction of Ce^{IV} ions as a function of a variety of reaction parameters, showed that the rate was first order with respect to both redox catalyst concentration and Ce^{IV} ion concentration, but independent of the Ce^{III} ion concentration. In addition, an Arrhenius plot of the ln(initial rate) *versus* T^{-1} gave an activation energy of 15 kJ mol^{-1}, which compares favourably with that for a diffusion-controlled reaction, *i.e.* 16 kJ mol^{-1} [10]. These findings indicate that the initial rate of the 'initial reduction step' demonstrates the same dependency upon $[Ce^{4+}]$, $[RuO_2 \cdot yH_2O^*]$, $[Ce^{3+}]$ and T as expected for the charging reaction (2).

A number of absorbance–time profiles were recorded for a series of repeat injections (50 mm^3) of Ce^{IV} ions (10^{-3} mol dm^{-3}) into a $RuO_2 \cdot yH_2O^*$ dispersion (2.5 cm^3, 70 mg dm^{-3}) containing a high concentration of Ce^{III} ions (0.1 mol dm^{-3}). By assuming that the initial reduction step observed with each injection made was due to catalyst charging, it was possible to calculate the specific capacitance of $RuO_2 \cdot yH_2O^*$ as 3.9 $\pm$ 1.1 F m^{-2}, which compares favourably with the value of 1.42 F m^{-2} reported by Burke and Healy [11] for hydrated RuO_2.

According to the electrochemical model, in the absence of a high concentration of Ce^{III} ions, when Ce^{IV} ions are added to a dispersion of $RuO_2 \cdot yH_2O^*$ in H_2SO_4, the catalyst particles are charged up to a potential sufficiently positive to oxidise water to O_2

at a rate equal to the rate of charging. Reaction (1) will stop when the $[Ce^{4+}]/[Ce^{3+}]$ ratio drops to a level at which the redox potentials of the catalyst particles will still be charged to a certain extent and, equilibrium potential of the O_2/H_2O couple. However, at this point, it is likely that the catalyst particles will still be charged to a certain extend and, therefore, more oxidising than uncharged $RuO_2 \cdot yH_2O^*$. In one set of experiments a redox indicator $(Ru(bpy)_3{}^{2+}$ or $Fe(phen)_3{}^{2+})$ was added to a dispersion of $RuO_2 \cdot yH_2O^*$ before and directly after the catalyst particles had been used to catalyse reaction (1). It was found that the catalyst was able to oxidise to a much greater extent (typically, *ca.* 5-fold) either redox indicator after use as an O_2 catalyst for reaction (1). An analysis of the liquid phase of the catalyst dispersion before and after the dispersion had been used to catalyse reaction (1) showed that the oxidising equivalents detected by either of the redox indicators were not associated with the liquid phase. These results would also appear to indicate that the $RuO_2 \cdot yH_2O^*$ particles are charged up by the Ce^{IV} ions, via reaction (2), prior to catalysis of reaction (1).

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