# Oxidation of Chloride to Chlorine by Ce<sup>IV</sup> lons mediated by Different Ru<sup>IV</sup> and Ir<sup>IV</sup>Oxide-based Catalysts

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A number of different, characterised, supported and unsupported oxides of Ru<sup>IV</sup> and Ir<sup>IV</sup> have been tested for activity as a chlorine catalyst in the oxidation of brine by Ce<sup>IV</sup> ions. All the different materials tested gave yields of chlorine of >90% and first-order kinetics for the reduction of the Ce<sup>IV</sup> ions. The samples prepared by the Adams method were the most active of the materials tested and are typified by high surface areas and appreciable activities per unit area. The kinetics of the catalysed reduction of Ce<sup>IV</sup> ions by brine were studied in detail using an Ru<sup>IV</sup> oxide prepared by the Adams method and supported on TiO<sub>2</sub> and the results were rationalised in terms of an electrochemical model in which the rate-determining step is the diffusion-controlled reduction of Ce<sup>IV</sup> ions. In support of this model the measured activation energies for the oxidation of brine by Ce<sup>IV</sup> ions, catalysed by either a supported or unsupported Adams catalyst, were both close (18–21 kJ mol<sup>-1</sup>) to that expected for a diffusion-controlled reaction (*ca*. 15 kJ mol<sup>-1</sup>).

A chlorine catalyst is a substance which can mediate the oxidation of brine to chlorine by a strong oxidant, Ox, *i.e.* 

$$2Cl^{-} + 2Ox \xrightarrow{Cl_2 \text{ catalyst}} Cl_2 + 2Red$$
(1)

provided this reaction is also thermodynamically feasible. Reaction (1) is an example of redox catalysis and from the results of numerous studies<sup>1,2</sup> of other redox catalysed reactions it appears that the redox catalyst simply provides a medium for the movement of electrons from one redox couple to another. This electrochemical model of redox catalysis has been extensively and successfully tested over many years for a large number of different redox reactions and catalysts.<sup>1,3</sup> From this model it follows that any material which is found to be a 'good' catalyst of reaction (1) may also show promise as an electrocatalyst for the oxidation of brine to chlorine in the world-wide chloralkali industry and vice versa. Thus, a reasonable, simple, first stage in the evaluation of a new material as a chlorine electrocatalyst could be a test of its activity as a  $Cl_2$  catalyst of reaction (1). Given the possible relevance of such work to the chloralkali industry it is surprising to note that very little work<sup>4,5</sup> has been carried out in the area of chlorine redox catalysis.

For reaction (1) to be thermodynamically feasible the redox potential of the Ox/Red couple must be greater than that of the  $Cl_2/Cl^-$  couple [ $E^{\circ}$  ( $Cl_2/Cl^-$ ) = 1.36 V vs. NHE]. Thus, at pH 0, a suitable choice is the Ce<sup>IV</sup>/Ce<sup>III</sup> couple in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> since its respective formal redox potential is 1.44 V vs. NHE. Previous work<sup>5</sup> has established that in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> the oxidation of brine to chlorine by Ce<sup>IV</sup> ions in homogeneous solution proceeds very slowly under ambient conditions and that a Cl<sub>2</sub> catalyst is required to promote the reaction, *i.e.* 

$$2Cl^{-} + 2Ce^{IV} \xrightarrow{Cl_2 \text{ catalyst}} Cl_2 + 2Ce^{III}$$
(2)

One of the major problems in finding suitable materials to catalyse reaction (2) is the strongly oxidising environment involved which is such that many materials are either rendered inactive (by the growth of an inert, insulating oxide surface film) or undergo anodic dissolution.

Anodes in the chloralkali industry usually comprise an  $Ru^{IV}$  and/or  $Ir^{IV}$  oxide combined intimately with  $TiO_2$  to form a 'dimensionally stable anode', *i.e.* one which is mechanically robust, readily releases chlorine and does not undergo passivation or serious dissolution with extensive

use.<sup>6</sup> It would seem likely, therefore, that an  $Ru^{IV}$  and/or  $Ir^{IV}$ oxide will act as a Cl<sub>2</sub> catalyst in reaction (2). However, it has been shown<sup>2</sup> that the two well established, extreme forms of  $Ru^{IV}$  oxide, *i.e.* highly hydrated  $RuO_2 \cdot xH_2O$  (24%  $\ge H_2O$ ) and anhydrous RuO<sub>2</sub>, behave quite differently, and not at all ideally, under strongly oxidising conditions. Thus, under acidic conditions and in the presence of a high concentration of chloride ions (2 mol dm<sup>-3</sup>)  $RuO_2 \cdot xH_2O$  undergoes partial corrosion by the Ce<sup>IV</sup> ions to form RuO<sub>4</sub> whilst mediating reaction (2), whereas anhydrous  $RuO_2$  appears largely inactive as a Cl<sub>2</sub> catalyst. Further work has shown that annealing  $RuO_2 \cdot xH_2O$  in air for 5 h at *ca.* 144 C, produces a partially dehydrated form of the oxide, which we have named thermally activated ruthenium dioxide hydrate or  $RuO_2 \cdot yH_2O^*$  for short (ca. 10% H<sub>2</sub>O).<sup>7</sup>  $RuO_2 \cdot yH_2O^*$  is much more stable than  $RuO_2 \cdot xH_2O$  towards anodic corrosion to RuO<sub>4</sub> by Ce<sup>IV</sup> ions and can act as a Cl<sub>2</sub> catalyst in reaction (2). To our knowledge this is the first reported<sup>5</sup> example of a very stable, heterogeneous Cl<sub>2</sub> catalyst.

Further work is still required to identify the combination of properties which go to make a good Cl<sub>2</sub> catalyst. Thus, in this paper we report the results of a detailed investigation of the characteristics and activities, as chlorine catalysts in reaction (2), of a series of  $Ru^{IV}$ , and some  $Ir^{IV}$ , oxide-based materials. The catalysts investigated include  $RuO_2 \cdot xH_2O$ ,  $RuO_2 \cdot yH_2O^*$ , anhydrous  $RuO_2$  and  $RuO_2$  prepared by the Adams method. In addition, the results of a kinetic study of  $Cl_2$  catalysis by  $Ru^{IV}$  and  $Ir^{IV}$  oxides prepared by either thermal activation or the Adams method, and deposited onto high surface area, inert supports, such as  $TiO_2$ ,  $SnO_2$  or  $SiO_2$ , are reported.

#### Experimental

#### Materials

The ruthenium and iridium trichloride hydrates  $(\text{RuCl}_3 \cdot n\text{H}_2\text{O} \text{ and } \text{IrCl}_3 \cdot n\text{H}_2\text{O}, \text{ respectively})$  used in the preparation of all the Ru<sup>IV</sup> and Ir<sup>IV</sup> oxide-based catalysts was supplied by Johnson Matthey. The titanium(IV) and tin(IV) oxide supports were supplied by Laporte (Tiona AG, anatase) and Alfa Ventron (batch no. 87779), respectively. All Ce<sup>IV</sup> solutions were prepared from an Analytical Volumetric Solution of 0.1 mol dm<sup>-3</sup> Ce<sup>IV</sup> sulphate in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> using 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> as the diluent. All other materials were supplied by BDH in the highest purity available. The water used was doubly distilled and deionised.

Highly hydrated ruthenium dioxide hydrate (RuO<sub>2</sub> · xH<sub>2</sub>O,  $x \ge 2.3$ ) was prepared by adding 0.1 g of RuCl<sub>3</sub> · nH<sub>2</sub>O to 100 cm<sup>3</sup> of water thermostatted at 60 °C and adjusting the pH of the solution to pH 6 using 0.1 mol dm<sup>-3</sup> NaOH solution. The resulting black suspension was stirred for several hours to ensure complete conversion of RuCl<sub>3</sub> · nH<sub>2</sub>O to RuO<sub>2</sub> · xH<sub>2</sub>O and was then filtered, washed thoroughly with water and dried in air. The conversion of RuO<sub>2</sub> · xH<sub>2</sub>O to thermally activated ruthenium dioxide hydrate (RuO<sub>2</sub> · xH<sub>2</sub>O for 5 h in air at 144 °C.

Adams  $Ru^{IV}$  oxide was prepared by grinding together a mixture of 0.1 g  $RuCl_3 \cdot nH_2O$  with 5 g of NaNO<sub>3</sub> and heating the subsequent blend for 30 min at 450 °C. The melt was then cooled in air at room temperature and the black Ru Adams (450) powder was recovered from the final cake by dissolving the NaNO<sub>3</sub> component in water. The Ru Adams (450) was filtered off, washed thoroughly with water and dried in air. A similar procedure was used to prepare another Adams-type catalyst, Ru Adams (500); although, as the name suggests, with the latter catalyst the annealing temperature was 8 min).

A series of powders was prepared in which  $\operatorname{RuO}_2 \cdot yH_2O^*$ , Ru Adams (450) or Ru Adams (500) were deposited onto a variety of different high-surface-area, inert supports, such as TiO<sub>2</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>, using the same procedures as used in the preparation of the unsupported powders but including 1 g of the support chosen in the initial reaction mixture. A few powders were also prepared in which the RuCl<sub>3</sub> ·  $nH_2O$  was partly or wholly replaced by IrCl<sub>3</sub> ·  $nH_2O$ .

#### Methods

30

20

10

0

10

0

20

wt. loss (%)

A number of different analytical techniques were used to characterise the prepared powders. Thermogravimetric analysis (TG) and differential thermal gravimetric analysis (DTG), as illustrated in Fig. 1, were performed using a Stanton Redcroft TG-760 coupled to an x/t chart recorder. For each sample the observed total weight loss was determined from its TG profile and taken as a measure of the sample's total H<sub>2</sub>O content. In this work typically 6–9 mg of the sample were heated from ambient temperature (*ca.* 22 °C) to 1000 °C at a rate of 30 °C min<sup>-1</sup>. In all cases a nitrogen flow rate of 40 cm<sup>3</sup> min<sup>-1</sup> was employed. Surface areas were determined by a single-point B.E.T. method using an instrument built to a similar design and specification as a Perkin-Elmer 212-D Sorptometer and incorporating a Gow-Mac 24-152 thermal conductivity detector. Prior to the surface

(a)

(*b*)

(d)

1000



20 *T/*°C

(c)

1000

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area measurement samples were degassed for 48 h at ambient temperature using a continuous stream of dried nitrogen.

Transmission electron microscopy was carried out using an electron microscope (Phillips EM 400T) (Fig. 2 and 3). The samples were loaded onto copper grids covered with a support film of carbon. Some of the more active of the powder dispersions were subjected to particle-size analysis by a dynamic light scattering technique using a Malvern Instruments Mastersizer model S3.01. The X-ray powder diffraction patterns for a number of the unsupported powders were recorded on film using the Guinier technique and Cu-K $\alpha_1\alpha_2$  radiation as the X-ray source.

A flow system<sup>8</sup> was used to determine the extent of corrosion undergone by each of the catalysts for reaction (2) investigated. The system comprised two Dreschel bottles coupled in series through which a continuous flow of N<sub>2</sub> was passed. The first Dreschel bottle (the reaction vessel) contained 10 mg of the sample catalyst (or 0.1 g for the supported catalysts) under test dispersed in 100 cm<sup>3</sup> of a 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> plus 2 mol dm<sup>-3</sup> NaCl solution. The second, much smaller, Dreschel bottle (the trap vessel) contained 10 cm<sup>3</sup> of a 0.1 mol dm<sup>-3</sup> NaOCl plus 1 mol dm<sup>-3</sup> NaOH solution. Reaction (2), with any accompanying corrosion of the catalyst, was initiated with the injection into the reaction vessel of 2 cm<sup>3</sup> of a 0.1 mol dm<sup>-3</sup> Ce<sup>IV</sup> stock solution in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> via a rubber septum. The degree of corrosion was determined from the amount of RuO<sub>4</sub> generated during the reaction and subsequently swept out by the N2 gas stream and trapped out as perruthenate in the second Dreschel bottle. Further details of this flow system are given elsewhere.8

A similar flow system was also used to determine the Cl<sub>2</sub> yield for each catalyst determined for reaction (2) under a set of typical reaction conditions which were also used in the subsequent kinetic study. The reaction conditions in the first Dreschel bottle were the same as for the corrosion flow system, with the exception that only 1 cm<sup>3</sup> of the Ce<sup>IV</sup> stock solution was injected. The second Dreschel bottle contained 100 cm<sup>3</sup> of an aqueous solution comprising 0.36 mol dm<sup>-3</sup> KI, 0.025 mol dm<sup>-3</sup> NaOH and 0.049 mol dm<sup>-3</sup> potassium hydrogenphthalate. Any  $Cl_2$  generated in the first Dreschel bottle following the injection of the Ce<sup>IV</sup> solution was swept out to the second Dreschel bottle where it was reduced by the iodide present to form triiodide; quantitative analysis of the latter was then carried out spectrophotometrically. Previous work<sup>9</sup> has shown that this flow system is 100% efficient for the quantitative determination of chlorine yields of 10 mm<sup>3</sup> to 10 cm<sup>3</sup>. In our work, following the injection of the Ce<sup>IV</sup> ions into the Cl<sub>2</sub> catalyst test system contained in the first Dreschel bottle, a 100% Cl<sub>2</sub> yield will correspond to the liberation of  $1.22 \text{ cm}^3$  of  $\text{Cl}_2$ .

The results arising from the characterisation studies of each of the  $Cl_2$  catalysts, using the different techniques described above, are summarised in Table 1.

The kinetics of reaction (2) were studied by monitoring spectrophotometrically ( $\lambda = 430$  nm) the decrease in the concentration of Ce<sup>IV</sup> ions as a function of time.<sup>10</sup> For each catalyst a stock dispersion was prepared, containing 7 mg (typically) of the catalyst dispersed (using 5 min of ultrasound from an ultrasound bath) in 100 cm<sup>3</sup> of a 2 mol dm<sup>-3</sup> NaCl plus 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. Each stock dispersion was then stirred continuously and used only after a minimum period of 2 h, and before 10 h, from the time it was prepared. In the study of the kinetics of reaction (2) for each catalyst an aliquot of 2.5 cm<sup>3</sup> of the stock dispersion was dispensed into a 1 cm, thermostatted (30.00 ± 0.05 °C) quartz fluorescent cell placed in the sample beam of a double-beam spectrophotometer (Perkin-Elmer Lambda 3); the dispersion was then stirred continuously (*ca.* 1000 r.p.m.). The reaction was initi-

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Fig. 2 Electron micrographs of unsupported powders tested as  $Cl_2$  catalysts: (a)  $RuO_2 \cdot yH_2O^*$ , (b)  $RuO_2$ -Adams (500), (c)  $RuO_2$  (anhyd.)

ated with the injection of 90 mm<sup>3</sup> of a 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution containing 0.1 mol dm<sup>-3</sup> Ce<sup>IV</sup> ions. The subsequent decrease in absorbance, due to the reduction of the Ce<sup>IV</sup> ions, as a function of time was recorded digitally using a microcomputer (BBC MasterClass) and stored on floppy disc. The microcomputer was also used in the subsequent analysis of the data. For kinetic runs carried out under identical experimental conditions the data were reproducible to within  $\pm$ 5%, as determined from the observed variation in first-order rate constant.

## Results

The kinetics of reaction (2) catalysed by each of the materials listed in Table 1 were studied under the typical reaction conditions described above. Fig.4A shows the observed variation in absorbance due to  $Ce^{IV}$  ions as a function of time for several  $Cl_2$  catalysts with widely differing activities. Interestingly, the observed kinetics of catalysis for these [see Fig. 4B] and all the other  $Cl_2$  catalysts tested gave an excellent fit (1  $\geq$  correlation coefficient  $\geq$  0.9995) to a first-order analysis.

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Fig. 3 Electron micrographs of supported powders tested as  $Cl_2$  catalysts: (a)  $TiO_2$ , (b)  $RuO_2 \cdot yH_2O^*$  on  $TiO_2$  (ca. 10 wt.% loading), (c)  $RuO_2$ -Adams (500) on  $TiO_2$  (ca. 10 wt.% loading)

For each catalyst, from the first-order plot of the kinetic data, the respective first-order rate constant,  $k_1$ , could be gleaned. From previous work<sup>5,10</sup> and results described later in this paper it appears that  $k_1$  is proportional to the catalyst concentration. One way in which the different catalysts may be assessed is through a comparison of the values of their specific first-order rate constants, *i.e.*  $k'_1$ , where  $k'_1 = k_1/(\text{amount} \text{ of catalyst used})$ .

With all of the catalysts studied in this work the catalytically active component is an expensive platinum-group metal (PGM), although, clearly, a desirable feature of any catalyst will be low cost. One route by which the cost of such

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Table 1 Catalyst characterisation data

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catalyst	H <sub>2</sub> O <sup>a</sup>	surface area <sup>b</sup>	corr. <sup>c</sup>	$\operatorname{Cl}_2^d$	XRD
(powder colour)	(%)	$/m^2 g^{-1}$	(%)	(%)	pattern
RuO <sub>2</sub> (anhyd.) (black)	0	7.7	< 0.05	94	Ru <sup>IV</sup> oxide (rutile) XRD pattern
$RuO_2 \cdot xH_2O$	24		$4-8^{e}$	85)	very clear with sharp mics
(black)	4.0			}	no discernible pattern
(black)	10	95	0.4	96)	
$RuO_2 \cdot yH_2O^*/TiO_2$	<1	19 (18)	0.20	98 ]	
(light grey)		10 (12)	0.05		no discernible pattern for the PGM
(grev)	<1	10 (12)	< 0.05	103	oxide (only the support)
$RuO_2 \cdot yH_2O^*/Al_2O_3$	< 1	99 (100)	0.26	96	
(grey)					
$RuO_2 \cdot yH_2O/SiO_2$	<1	201 (200)	0.37	98	no discernible pattern for the
Ru-Adams (450)	3	205	< 0.05	93	$Ru^{IV}$ oxide (rutile) XRD pattern
(black)				2	broad lines but discernible
Ru-Adams (450)/TiO <sub>2</sub>	0	19	< 0.05	95	
Ru-Adams (450)/SnO <sub>2</sub>	0	12	< 0.05	96	no discernible pattern of PGM
(grey)	-				oxide (only the support)
Ru-Adams (450)/Al <sub>2</sub> O <sub>3</sub>	0	96	< 0.05	97 )	
(grey) Ru-Adams (450)/SiO	0	105	< 0.05	95	no discernible pattern for the
(blue-grey)	0	175	< 0.05	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	PGM oxide or support
Ru-Adams (500)	6	230	< 0.05	98	Ru <sup>IV</sup> oxide (rutile) XRD pattern
(black)	0	17	.0.05	07.)	very broad lines but discernible
(grey)	0	17	< 0.05	97	no discernible pattern of PGM oxide
Ru-Adams (500)/SnO <sub>2</sub>	0	15	< 0.05	96 )	(only the support)
(grey) Ir-Adams (500)	12	182	_	101	Ir <sup>IV</sup> oxide (rutile) <b>XRD</b> pattern
(black)	12	102		101	barely discernible
Ru/Ir (1 : 1)-Adams (500)	8	209		97	Ru <sup>IV</sup> oxide (rutile) XRD pattern
$IrO_2 \cdot yH_2O^*$	4	7		95)	no discomble netters (event of
(black)				}	support)
$\frac{IrO_2 \cdot yH_2O^*/SnO_2}{(dark grey)}$	0	12	—	93)	Support

<sup>*a*</sup> Total water content as measured by the total weight loss (%) undergone by the sample upon heating it from ambient to 700 °C and determined from its TG profile. <sup>*b*</sup> Surface area measured by B.E.T. (error  $\pm$  5%), surface areas in parenthesis refer to the supports alone. <sup>*c*</sup> Degree of corrosion (%) measured using the Ce<sup>IV</sup> reaction vessel/HOCl trap flow system. <sup>*d*</sup> Cl<sub>2</sub> (%) arising from reaction (2), measured using the Ce<sup>IV</sup> reaction vessel/triiodide trap flow system (error  $\pm$  3%). <sup>*e*</sup> Estimated from the absorption spectrum of the reaction solution 24 h after the injection of the Ce<sup>IV</sup> ions; see Discussion section for further details.

catalysts may be lowered is by coating the active component onto a cheap, inert support with a high surface area, such as  $TiO_2$ ,  $SiO_2$ ,  $SnO_2$  or  $Al_2O_3$ . A catalyst which is economical with the PGM active material involved will be most readily identified by a high value for its first-order rate constant per mole of metal, *i.e.*  $k_1''$ .

For each of the  $Cl_2$  catalysts tested and  $k_1$  measured, values for  $k'_1$  and  $k''_1$  have been calculated (Table 2).

The results of a detailed study of the kinetics of reaction (2) mediated by an unsupported PGM oxide, *i.e.*  $RuO_2 \cdot yH_2O^*$ , have been reported earlier.<sup>5</sup> It is likely that the nature of the kinetics of catalysis exhibited by the other unsupported PGM oxides used in this study [*i.e.*  $RuO_2$  (anhyd.), Ru-Adams and Ir-Adams] will be similar to those of  $RuO_2 \cdot yH_2O^*$  and fit the same electrochemical model; a fundamental aspect of which, as we shall see, is a predicted first-order dependence of rate on oxidant concentration.

The kinetics of catalysis by a supported PGM oxide catalyst have not been studied in any detail before and, as a result, using one of the most active of the supported catalysts, Ru-Adams (500)/TiO<sub>2</sub>, we investigated the effect of varying [Ce<sup>IV</sup>], [Ce<sup>III</sup>], [Cl<sup>-</sup>], [cat.] and temperature on  $k_1$  (an Arrhenius plot of the data arising from the latter work is

shown in Fig. 5, from which an activation energy of  $21.4 \pm 1.3$  kJ mol<sup>-1</sup> can be calculated). The results from this detailed kinetic study are summarised in Table 3.

#### Discussion

From the results in Table 1 it appears that all the unsupported and supported PGM-based catalysts tested are able to act as efficient Cl<sub>2</sub> catalysts (Cl<sub>2</sub> yields  $\approx 95-100\%$ ) in reaction (2) and are stable (corrosion typically  $\ll 1\%$ ) towards anodic corrosion by the Ce<sup>IV</sup> ions, or the Cl<sub>2</sub> generated. RuO<sub>2</sub> · xH<sub>2</sub>O appears to be the only PGM material tested that shows some tendency towards anodic corrosion.

### **Catalyst Corrosion**

The nature of the corrosion of  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  was unusual and merits a brief discussion. The corrosion yield for  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  calculated from the  $\text{RuO}_4$  trap alone was *ca*. 0.6%. Instead the corrosion of  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  was made manifest by the gradual pale yellow-orange colouration of the reaction solution over 24 h from the time of injection of the Ce<sup>IV</sup> ions. Note that the catalysis of reaction (2) by  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  was



**Fig. 4** Kinetic study of the oxidation of brine by Ce<sup>IV</sup> ions and mediated by a series of different catalysts. The reduction of the Ce<sup>IV</sup> ions was monitored spectrophotometrically (A) and the data (typically > 200 points) were then subjected to a first-order analysis (B). The different runs illustrated correspond to: (a) no catalyst, (b) RuO<sub>2</sub> (anhyd.) (75 µg cm<sup>-3</sup>), (c) RuO<sub>2</sub> · yH<sub>2</sub>O\* (56 µg cm<sup>-3</sup>), (d) Ru-Adams (500) (77 µg cm<sup>-3</sup>), (e) Ir-Adams (500) (87 µg cm<sup>-3</sup>). In a typical run a normalised absorbance of 1 correspond to an actual absorbance of 1. The normalised absorbance refers to the actual absorbance, the absorbance due to the catalyst,  $A_{\infty}$ 

very rapid (5–10 min) and that after this reaction there was little spectrophotometric evidence of  $RuO_4$  in the reaction vessel (or, subsequently, in the  $RuO_4$  trap).

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Although RuO<sub>4</sub> is known<sup>11</sup> to be unstable in a solution containing 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 2 mol dm<sup>-3</sup> NaCl, the reaction is very slow (12–24 h) and blank experiments showed that if any (*i.e.* > 0.05%) RuO<sub>4</sub> was generated in the reaction vessel in this medium that it would be rapidly swept out by the nitrogen stream and almost quantitatively trapped as perruthenate in the second trap. Interestingly, the absorption spectrum of an RuO<sub>4</sub> solution containing 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 2 mol dm<sup>-3</sup> NaCl which has been allowed to decompose is very similar to that observed in the reaction vessel, 24 h after the injection of the Ce<sup>IV</sup> ions, when RuO<sub>2</sub> · xH<sub>2</sub>O (and no other catalyst) was used to mediate reaction (2). From these results it appears that some corrosion of the RuO<sub>2</sub> · xH<sub>2</sub>O particles takes place subsequent to catalysis of reaction (2).

Previous work<sup>12</sup> has shown that after the oxidation of water to O<sub>2</sub> by Ce<sup>IV</sup> ions, catalysed by RuO<sub>2</sub> ·  $yH_2O^*$ , the RuO<sub>2</sub> ·  $yH_2O^*$  particles are 'charged', *i.e.* they appear to possess more oxidising equivalents after catalysis compared with before. This observation is in line with the electrochemical model of redox catalysis, which predicts that prior to catalysis the powder particles must charge up the redox potential necessary for catalysis ( $E_{mix}$ ). For an Ru<sup>IV</sup> oxide catalyst the charging process will involve the creation of higher oxidation states of the metal throughout the particle and, in the case of RuO<sub>2</sub> ·  $xH_2O$ , it appears that after catalysis the 'charged' RuO<sub>2</sub> ·  $xH_2O$  particles can discharge slowly by undergoing anodic dissolution.

The product of this anodic dissolution appears to exhibit similar UV–VIS spectral characteristics to those arising from the reduction of RuO<sub>4</sub> by the 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 2 mol dm<sup>-3</sup> NaCl solution. The reduction of RuO<sub>4</sub> by HCl to form a variety of Ru<sup>IV</sup> chloro-aquo complexes, identified from their characteristic absorption spectra as Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> has been studied by several groups.<sup>13–16</sup> The spectral changes we have observed in the reaction vessel arising from the use of RuO<sub>2</sub> · xH<sub>2</sub>O as a Cl<sub>2</sub> catalyst are similar to a combined mixture of Y<sub>2</sub> and Y<sub>3</sub>, which have tentatively been assigned by others<sup>14–16</sup> to the species (H<sub>2</sub>O)Cl<sub>3</sub>Ru( $\mu$ O)<sub>2</sub>RuCl<sub>3</sub>(H<sub>2</sub>O) and (H<sub>2</sub>O)Cl<sub>4</sub>Ru-O-RuCl<sub>4</sub>(H<sub>2</sub>O), respectively. Using the reported<sup>13</sup> molar absorptivities for these species and the observed spectral changes in the reaction vessel, we estimated a maximum degree of corrosion of 4–8% for RuO<sub>2</sub> · xH<sub>2</sub>O (see Table 1).

Table 2 Catalyst rate constant data

catalyst	mass in 100 cm <sup>3</sup> H <sub>2</sub> O/mg	$/10^{-3} \mathrm{s}^{-1}$	/s <sup>-1</sup> g <sup>-1</sup>	$k_1''$ /mol <sup>-1</sup> metal s <sup>-1</sup>	$k_{1}^{'''}$ /s <sup>-1</sup> m <sup>-2</sup>
RuO, (anhyd.)	7.5	0.767	4.11	5.41	0.53
RuO, xH,O	7.3	2.73	14.9	25.8	
$RuO_{2} \cdot yH_{2}O^{*}$	5.6	2.11	15.1	22.1	0.159
$RuO_2 \cdot yH_2O^*/TiO_2$	6.4	1.41	8.80	202	0.463
$RuO_2 \cdot yH_2O^*/SnO_2$	6.7	1.41	8.42	193	0.842
$RuO_2 \cdot yH_2O^*/Al_2O_3$	6.6	1.25	7.57	179	0.076
$RuO_{2}^{*}yH_{2}^{*}O^{*}/SiO_{2}^{*}$	7.4	0.714	3.86	86.4	0.019
Ru-Adams (450)	8.1	4.38	21.6	29.3	0.106
Ru-Adams (450)/TiO <sub>2</sub>	8.8	0.990	4.50	108	0.237
Ru-Adams $(450)/SnO_2$	8.0	0.944	4.72	104	0.393
Ru-Adams $(450)/Al_2O_3$	6.7	0.544	3.25	73.6	0.034
Ru-Adams $(450)/SiO_2$	7.2	0.509	2.81	66.9	0.014
Ru-Adams (500)	7.7	5.28	27.4	38.5	0.119
Ru-Adams (500)/TiO <sub>2</sub>	7.7	2.06	10.7	255	0.628
Ru-Adams $(500)/SnO_2$	8.0	2.01	10.0	240	0.669
Ir-Adams (500)	8.7	10.0	46.0	60.9	0.252
Ru/Ir (1:1)-Adams (500)	6.7	5.78	34.5	44.7	0.165
$IrO_2 \cdot yH_2O^*$	7.2	0.415	2.30	2.8	0.328
$IrO_2 \cdot yH_2O^*/SnO_2$	6.2	0.818	5.28	45.8	0.44

 $k_1$ , first-order rate constant;  $k'_1$ , first-order rate constant per g of catalyst;  $k''_1$ , first-order rate constant per mole of PGM;  $k''_1$ , first-order rate constant per unit surface area [*i.e.* =  $k'_1/S(B.E.T.)$ ].



Fig. 5 Arrhenius plot of  $\ln(k_1)$  vs.  $T^{-1}$  for the Ru-Adams (500)/TiO<sub>2</sub> catalyst. The temperature was varied over the range 20–70 °C. All other reaction conditions were as described in the Experimental, with the exception that [cat.] = 58 µg cm<sup>-3</sup> (not 70 µg cm<sup>-3</sup>). From the gradient of this plot an activation energy of 21.4 ± 1.3 kJ mol<sup>-1</sup> was estimated

## **Catalyst Characterisation**

Characterisation of the hydrated oxides of ruthenium and iridium is a difficult task<sup>8</sup> since, invariably, these oxides exhibit a featureless IR spectrum and are amorphous to X-rays (see Table 1). One analytical technique which does yield some useful information is thermal analysis, in particular TG and its derivative form DTG. For any sample, from its TG profile the overall weight change due to loss of physically and chemically bound H<sub>2</sub>O (i.e. %H<sub>2</sub>O content) in the sample can be determined (see Table 1). Previous work<sup>7,8</sup> carried out in the absence of a high concentration of chloride ions has shown that the H<sub>2</sub>O content in a sample of RuO<sub>2</sub>·xH<sub>2</sub>O provides a good guide to its susceptibility towards anodic corrosion. Thus, samples of  $RuO_2 \cdot xH_2O$ with  $H_2O < 10\%$  are very stable towards anodic dissolution to  $RuO_4$  by  $Ce^{IV}$  ions, but unstable if the  $H_2O$ content > 23%. The rationale for these observations is that the H<sub>2</sub>O content provides a reflection of the degree of disorder within the powder microcrystallites. Thus, the greater the H<sub>2</sub>O content, the greater the disorder and, consequently the more prone the powder is to corrosion. The DTG profiles (Fig. 1) help to identify the different types of bound water associated with hydrated samples of Ru<sup>IV</sup> and Ir<sup>IV</sup> oxides. Thus, from the DTG profile for  $RuO_2 \cdot xH_2O$  it appears that there are at least three different types of water,<sup>17</sup> i.e. physical (largely removed at T > 100 °C), and two chemically bound types [T(peak) 200 °C and 450 °C, respectively].

The process of thermal activation, which converts  $RuO_2 \cdot xH_2O$  to  $RuO_2 \cdot yH_2O^*$  and markedly reduces the corrosion susceptibility exhibited by  $RuO_2 \cdot xH_2O$ , appears from the DTG data illustrated in Fig. 1 to reduce substantially the amount of the low-temperature, chemically bound  $H_2O$ . It is thought that the high susceptibility towards anodic corrosion exhibited by  $RuO_2 \cdot xH_2O$  may be due to the presence of a particular type of surface-defect site in which the ruthenium atoms are coordinated with one or more  $H_2O$  molecules. Thermal activation appears to largely remove this defect, probably through a condensation reaction between two hydroxyl groups on adjacent Ru surface atoms with the concomitant formation of an Ru—O—Ru bond. This process would lead to a less defective surface which might be expected to be less prone to corrosion.<sup>17</sup>

Unlike  $RuO_2 \cdot xH_2O$  and  $RuO_2 \cdot yH_2O^*$ , Ru-Adams (450) exhibits a clear, albeit broad, XRD pattern and, therefore, shows evidence of a moderate degree of crystallinity. It is likely, therefore, that Ru-Adams (450) will have a substantially lower number of defect sites than  $RuO_2 \cdot xH_2O$  and  $RuO_2 \cdot yH_2O^*$  and, consequently, show evidence only for a high-temperature chemically bound type  $H_2O$  in its DTG profile as appears to be the case (see Table 1).

The Adams method of preparing  $Ru^{IV}$  (and  $Ir^{IV}$ ) oxides appears to produce a material that effects an excellent compromise between the extreme forms of  $Ru^{IV}$  oxide and their favourable and unfavourable characteristics as catalysts, *i.e.*  $RuO_2 \cdot xH_2O$  with its amorphous nature [see Fig. 2(*a*)] and high surface area but certain susceptibility towards anodic corrosion and  $Ru^{IV}$  oxide (anhyd.) with its high crystallinity [see Fig. 2(*c*)] and stability towards corrosion but low surface area [due to the extensive sintering which occurs at its high temperature of formation (*ca.* 900 °C)]. Thus, Ru-Adams (450) and the slightly less crystalline form, Ru-Adams (500) [see Fig. 2(*b*)], are two of the catalysts with the highest surface areas of the materials tested and experiments show them to be very resistant indeed toward corrosion by Ce<sup>IV</sup> ions and Cl<sub>2</sub>.

#### Kinetics of Catalysis and the Electrochemical Model

In the electrochemical model of redox catalysis it is assumed<sup>1,2</sup> that the catalyst particles act simply as microelectrodes providing a medium through which electrons can flow from one redox couple to the other. At any time, t, during a redox catalysed reaction the total flow of electrons through the particles, *i.e.* the mixture current,  $i_{mix}(t)$  is related to the rate of reaction at that instant, R(t), via the expression,

$$R(t) = i_{\rm mix}(t)/F \tag{3}$$

variable <sup>b</sup>	range (units)	plot	n	m (units)	c (units)	r
[Ce <sup>IV</sup> ]	3.6-36 (10 <sup>-4</sup> mol dm <sup>-3</sup> )	$R_i^c vs. [Ce^{iv}]_0$	6	$\frac{1.21 \pm 0.04}{(10^{-3} s^{-1})}$	$-(1.4 \pm 0.9)$ $(10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1})$	0.9967
[Ce <sup>III</sup> ]	4-40 (10 <sup>-4</sup> mol dm <sup>-3</sup> )	$k_1$ vs. [Ce <sup>III</sup> ] <sub>0</sub>	6	$(10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1})$	$\frac{1.47 \pm 0.06}{(10^{-3} \text{ s}^{-1})}$	0.3078
[Cl <sup>-</sup> ] <sup>d</sup>	0.2-2 (mol dm <sup>-3</sup> )	$k_1 vs. [Cl^-]$	5	$-1.4 \pm 1.1$ (10 <sup>-4</sup> mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )	$(4.7 \pm 0.1)$ $(10^{-3} s^{-1})$	0.5306
[cat.]	7-70 (mg dm <sup>-3</sup> )	$k_1$ vs. [cat.]	6	$\frac{2.59 \pm 0.16}{(10^{-2} \text{ s}^{-1} \text{ g}^{-1} \text{ dm}^3)}$	$-2.8 \pm 4.8$ (s <sup>-1</sup> )	0.9950
Т	20–70 (°C)	$\ln(k_1/s^{-1})$ vs. $1/T$	6	$-2.57 \pm 0.16$ (10 <sup>3</sup> K)	$9.96 \pm 0.47$	0.9938

Table 3 Results of kinetic study of reaction (2) using Ru-Adams (500)/TiO<sub>2</sub> as the Cl<sub>2</sub> catalyst<sup>a</sup>

<sup>*a*</sup> Typical reaction conditions were as follows: 90 mm<sup>3</sup> of a 0.1 mol dm<sup>-3</sup> Ce<sup>IV</sup> solution were injected into 2.5 cm<sup>3</sup> of the catalyst dispersion (5.8 mg/100 cm<sup>3</sup>) containing 2 mol dm<sup>-3</sup> NaCl and 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and thermostatted at 30 °C. The decrease in absorbance due to Ce<sup>IV</sup> ions was monitored spectrophotometrically (see Experimental). <sup>*b*</sup> All other experimental conditions fixed. <sup>*c*</sup> R<sub>i</sub> or initial rate =  $k_1$ [Ce<sup>IV</sup>]<sub>0</sub>, where [Ce<sup>IV</sup>]<sub>0</sub> is the initial (*i.e.* t = 0) concentration of Ce<sup>IV</sup> ions present. <sup>*d*</sup> [cat.] = 16.4 mg/100 cm<sup>3</sup>.

Provided the redox catalyst is chemically inert under the reaction conditions employed and that the redox couples involved act independently of each other (the Wagner-Traud additivity principle) it is possible to predict, using this electrochemical model, the kinetics of catalysis from a knowledge of the current vs. voltage behaviour of the two redox couples on the redox catalyst.

A detailed investigation of the kinetics of the oxidation of water to  $O_2$  by Ce<sup>IV</sup> ions, mediated by thermally activated ruthenium dioxide hydrate (RuO<sub>2</sub> · yH<sub>2</sub>O\*), has been carried out recently.<sup>10</sup> The observed kinetics gave an excellent fit to an electrochemical model of redox catalysis in which the reduction of the Ce<sup>IV</sup> ions was considered as a Nernstian reaction and the oxidation of water to  $O_2$  as an irreversible reaction. A similar electrochemical model is likely to apply in our work on the catalysis of reaction (2) by the PGM-based materials listed in Table 1. An important consequence of this particular model is that at any time, *t*, during the redox reaction the mixture current will be given by the expression:

$$i_{\rm mix} = \frac{k_{\rm d} F A_{\rm cat}([{\rm Ce}^{4+}]_t - [{\rm Ce}^{3+}]_t \exp\{F(E_{\rm mix} - E_{\rm Ce}')/RT\})}{1 + \exp\{F(E_{\rm mix} - E_{\rm Ce}')/RT\}}$$
(4)

where  $k_d$  is the mass-transfer coefficient of the Ce<sup>IV</sup> and Ce<sup>III</sup> ions,  $A_{cat}$  is the total effective surface area of the redox catalyst particles (and is directly proportional to [RuO<sub>2</sub> · yH<sub>2</sub>O\*]),  $E_{mix, t}$  is the redox potential adopted by the particles at time, t and  $E'_{Ce}$  is the formal redox potential of the Ce<sup>IV</sup>/Ce<sup>III</sup> couple. In this model, if the following parameters are large: (i) the [Ox]/[Red] ratio, (ii) the separation between the equilibrium potentials for the  $Ce^{IV}/Ce^{III}$  and Cl<sub>2</sub>/Cl<sup>-</sup> couples and (iii) the exchange current density for the latter couple on the catalyst, then it is likely that the mixture potential adopted by the catalyst particles will be significantly different from the equilibrium potential of the Ce<sup>IV</sup>/ Ce<sup>III</sup> couple. As a result, the parameter  $(E_{mix} - E'_{Ce})$  may be sufficiently large and negative that the expression for the mixture current, i.e. eqn. (4), reduces to that for a diffusioncontrolled reaction,18 i.e.

$$i_{\rm mix} = FD[{\rm Ce}^{4+}]A_{\rm cat}/\delta \tag{5}$$

where D is the diffusion coefficient of the Ce<sup>IV</sup> ions (=  $k_d \delta$ ), and  $\delta$  is the thickness of the diffusion layer.  $\delta$  is essentially a function of the hydrodynamic flow around the microelectrode particles and in our work this was fixed by using a set stirring speed for all the kinetic runs made. Fig. 6 provides a sche-



**Fig. 6** Likely individual current vs. voltage curves for the  $Cl_2/Cl^-$  and  $Ce^{IV}/Ce^{II}$  couples on a  $Cl_2$  catalyst. In this electrochemical representation of chlorine catalysis the mixture current is diffusion-controlled and, therefore, will give rise to first-order kinetics with respect to  $[Ce^{IV}]$ 

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matic illustration of the current vs. voltage curves for a redox catalyst coupled process involving (i) the Nernstian, reduction reaction:  $Ce^{IV} \rightarrow Ce^{III}$  and (ii) the irreversible oxidation reaction:  $Cl^- \rightarrow \frac{1}{2}Cl_2$ , when the mixture current passing through the catalyst is diffusion-controlled.

If an example of catalysis of reaction (2) does fit the electrochemical model and is diffusion-controlled then, from eqn. (5), a central feature of the observed kinetics for reduction of  $Ce^{IV}$  ions will be a first-order dependence of rate upon  $[Ce^{IV}]$ . In our work the experimental conditions were such (*i.e.*  $[Ce^{III}] = 0 \mod dm^{-3}$  and  $[Cl^{-}]$  is high), that assuming the applicability of the electrochemical model, diffusioncontrolled kinetics would be most likely to be observed for each of the catalysts tested. As noted in the early part of the Results section, we found that the kinetics of  $Ce^{IV}$  reduction were near-perfect first-order for all the  $Cl_2$  catalysts tested and this observation provides support for the assumption that the electrochemical model can be used to interpret our results on  $Cl_2$  catalysis.

Table 2 lists the first-order rate constants,  $k_1$ , and the specific first-order rate constants determined for all the materials examined. From the values of  $k'_1$  listed in Table 2, the pure Ru, Ir and Ru/Ir Adams (500) catalysts appear the most active. In fact all these Adams-type catalysts appear to possess the highly desirable combination of a high surface area per g and a high specific first-order rate constant.

If the use of Adams-type catalysts as Cl<sub>2</sub> catalysts has a draw-back it is that their cost is likely to be high, given that they are examples of pure PGM oxides. However, when Ru Adams (500) is supported on an inert material, such as TiO<sub>2</sub> [see Fig. 3(c)] or SnO<sub>2</sub>, with a high surface area, the product appears appreciably superior to the other supported PGM oxide catalysts, including RuO<sub>2</sub> ·  $yH_2O^*$  [see Fig. 3(b)] and Ru-Adams (450), as can be seen from a comparison between the different values of  $k_1^{"}$  calculated for the different catalysts and listed in Table 2.

In the electrochemical model the rate of catalysis depends directly upon the effective catalytic surface area which, in turn, depends upon the true surface area, S, and the activity of the material per unit area,  $\phi$ , *i.e.* 

$$A_{\rm cat} = S\phi \tag{6}$$

the latter parameter providing a measure of the number of active sites per unit surface area. A commonly employed measure of S is the surface area per g of the powder as determined using a B.E.T. technique, S(B.E.T.), and in Table 2 the first-order rate constants per m<sup>2</sup>, *i.e.*  $k_1''' = k_1'/S(B.E.T.)$ , for all the catalysts are listed. However, previous work<sup>7</sup> in which  $RuO_2 \cdot yH_2O^*$  was used as a catalyst for the oxidation of water to  $O_2$  by Ce<sup>IV</sup> ions showed that a more appropriate estimate of S in eqn. (6) is the surface area of the aggregated particles in solution, rather than that of the powder after it has been dried and degassed, which is a necessary part of the procedure in making a surface area measurement using the B.E.T. technique. An estimate of the surface area of the aggregated particles in solution can be obtained from a particlesize analysis of the dispersion using dynamic light scattering and the expression:

$$S(\text{disp.}) = 6/(\rho d) \tag{7}$$

where  $\rho$  is the density of the catalyst in g m<sup>-3</sup> and d is the average aggregate particle size (in m). The ratio of  $k'_1/S(\text{disp.})$  we defined as  $\phi'$  since it provides a measure of  $\phi$ , the activity of the Cl<sub>2</sub> catalyst per unit area. Table 4 lists the values of S(disp.) and  $k'''_1$  determined for RuO<sub>2</sub> · yH<sub>2</sub>O\* and several RuO<sub>2</sub> · yH<sub>2</sub>O\* supported catalysts as well as the associated value of  $\phi'$  estimated as described above.

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**Table 4** S(disp.) and  $\phi'$  data

	• • •		
sample	S(disp.) /m <sup>2</sup> g <sup>-1</sup>	$/s^{-1}m^{-2}$	$(s^{-1}m^{-2})^{\phi'}$
RuO <sub>2</sub> · yH <sub>2</sub> O*	0.08	0.159	189
$RuO_{2} \cdot yH_{2}O^{*}/TiO_{2}$	2.88	0.463	3.1
$RuO_{2}^{*} \cdot yH_{2}O^{*}/SnO_{2}^{*}$	1.45	0.842	5.8
$RuO_{2} \cdot yH_{2}O^{*}/Al_{2}O_{3}$	0.63	0.076	12.0
$RuO_2 \cdot yH_2O^*/SiO_2$	0.14	0.019	27.6

S(disp.), surface area per g calculated using eqn. (6), with d = number average particle diameter in a powder dispersion as measured by light dynamic scattering.  $\phi'$ , First-order rate constant per unit area (of the powder dispersed in solution) =  $k'_1/S(\text{disp.})$ ; a 'wet' measure of the number of active sites.  $k''_1$ , First-order rate constant per unit area (of the powder dispersed in solution) =  $k'_1/S(\text{B.E.T.})$ ; a 'dry' measure of the number of active sites.

From a comparison of the values of S(disp.) in Table 4 and S(B.E.T.) in Table 1 it appears that a substantial degree of aggregation of the powder particles occurs, with a concomitant drop in effective surface area per g, upon dispersing the powders in aqueous solution. This general trend was confirmed from the results of an optical microscopy study on the same aqueous powder dispersions.

The results in Table 4 also indicate that the number of sites per unit surface area is lower on a supported, rather than unsupported, catalyst. The reason for this is apparent from the electron micrographs of the supported catalysts (see Fig. 3) which show for both  $RuO_2 \cdot yH_2O^*$  and Adams (500), that the surface coverage of the support is not even and the PGM oxides tend to form a series of catalyst islands on the surface of the support.

In theory, for a supported catalyst in which the PGM oxide uniformly and completely covered the surface of the support and retained the same morphology as the original unsupported PGM catalyst then its value for  $\phi'$  will be the same as the latter (189 s<sup>-1</sup> m<sup>-2</sup> in the case of RuO<sub>2</sub>·yH<sub>2</sub>O<sup>\*</sup>; see Table 4). From the different values for  $\phi'$  listed in Table 4 it appears that this is not the case with any of the supported catalysts. SiO<sub>2</sub>, which has a very high B.E.T. surface area (200 m<sup>2</sup> g<sup>-1</sup>), exhibits the highest coverage [*i.e.* =  $\phi'(\text{RuO}_2 \cdot \text{yH}_2\text{O}^*/\text{SiO}_2)/\phi'(\text{RuO}_2 \cdot \text{yH}_2\text{O}^*)$ ] of 14.6%. If a supported catalyst exhibited a  $\phi'$  value which was greater than that of the original PGM material then a synergistic effect due to the support would usually be invoked as the likely cause.

As noted earlier, all the catalysts exhibited first-order kinetics with respect to the concentration of Ce<sup>IV</sup> ions. This general observation is readily interpreted using the electrochemical model if the reaction is diffusion-controlled since  $i_{mix}$  (and, therefore, the rate) then depends directly upon the parameters identified in eqn. (7), one of which is [Ce<sup>IV</sup>]. A detailed study of the kinetics of an unsupported PGM catalyst of reaction (2), *i.e.*  $RuO_2 \cdot yH_2O^*$ , has been reported previously<sup>5</sup> and provides further support for the electrochemical model. The results of our kinetic study of reaction (2) mediated by a supported PGM catalyst, i.e. Ru-Adams (500), summarised in Table 3, also provide support for the electrochemical model and the applicability of eqn. (6). Thus, using Ru-Adams (500)/TiO<sub>2</sub> as the Cl<sub>2</sub> catalyst in reaction (2), the kinetics of  $Ce^{IV}$  reduction were found to be first-order not only at one typical concentration of Ce<sup>IV</sup> ions, but also over the range [Ce<sup>IV</sup>]  $(3.6-36) \times 10^{-4}$  mol dm<sup>-3</sup>. In addition the first-order rate constant  $k_1$ , where  $k_1 \equiv DA_{cat}/\delta$ , was found to be independent of [Ce<sup>III</sup>] and [Cl<sup>-</sup>], since a plot of  $k_1$  vs. [Ce<sup>III</sup>] or [Cl<sup>-1</sup>] was found to be a horizontal line (see Table 3) as indicated by the low value for the correlation coefficients and low value gradients with large errors. (Note

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that the correlation coefficient for a line approaching a perfect horizontal has a correlation coefficient and gradient both tending to zero.) In eqn. (6) the parameter,  $A_{cat}$  is proportional to the catalyst concentration, [cat.]. Thus, for Ru-Adams (500)/TiO<sub>2</sub> a plot of  $k_1$  vs. [cat.] should, according to the electrochemical model, be a good straight line with a zero intercept; this prediction appears to be confirmed by the results of such a plot, summarised in Table 3.

If reaction (2) is diffusion-controlled for Ru-Adams (500)/TiO<sub>2</sub> then the activation energy should be that for a typical<sup>19,20</sup> diffusion-controlled reaction, *i.e.* 15-19 kJ mol<sup>-1</sup>. It is possible, however, that this activation energy may be modified slightly due to temperature-induced changes in the nature of the diffusing species, which are Ce<sup>IV</sup> ions complexed with an undefined mixture of water, chloride and sulphate groups, the proportions of which may change with increasing temperature; these changes are evidenced by concomitant UV-VIS spectral changes. A measure of the activation energy for the Ce<sup>IV</sup> in the medium (*i.e.* 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> plus 2 mol dm<sup>-3</sup> NaCl) used in our catalytic study can be obtained by measuring the diffusion-controlled current, arising from the electrochemical reduction of Ce<sup>IV</sup> ions in the same medium using a gold working electrode, as a function of temperature. Fig. 7 illustrates a typical current vs. voltage profile. From this work an activation energy of  $14.8 \pm 0.5 \text{ kJ mol}^{-1}$ was calculated for the diffusion-controlled reduction of Ce<sup>IV</sup> ions on a gold cathode in 0.5 mol dm<sup>-3</sup>  $H_2SO_4$  plus 2 mol dm<sup>-3</sup> NaCl. In the study of the variation of  $k_1$  as a function of temperature for reaction (2) catalysed by Ru-Adams (500)/TiO<sub>2</sub> the activation energy was determined as  $21.4 \pm 1.3$  kJ mol<sup>-1</sup>, which compares favourably with the value found from our electrochemical studies. A similar study of  $k_1$  as a function of T, using the unsupported Ru-Adams (500) as the Cl<sub>2</sub> catalyst yielded  $18.9 \pm 1.0$  kJ mol<sup>-1</sup>, which again appears a reasonable value for a diffusion-controlled reaction.



Fig. 7 Cyclic voltammograms recorded using a gold rotating disc cathode in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 2 mol dm<sup>-3</sup> NaCl and in (a) the absence and (b) the presence of Ce<sup>IV</sup> ions ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) for a series of different temperatures. A platinum rod was used as the counter electrode and an SCE as the reference electrode; the voltage sweep rate was 3 V min<sup>-1</sup> as the rotation speed 2000 r.p.m. T = 50 °C

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