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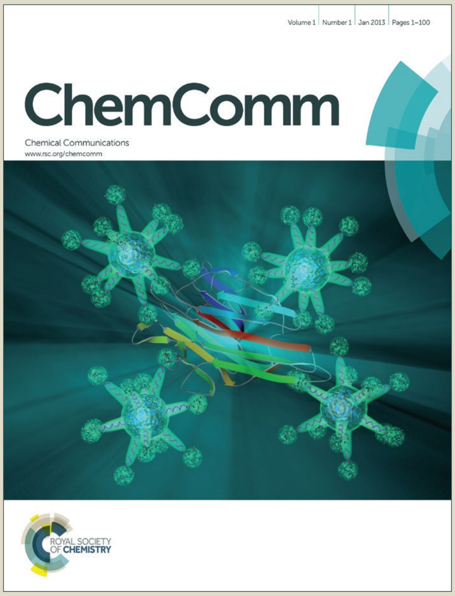

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Wireless Rotating Disk Electrode (*wRDE*) for assessing Heterogeneous Water Oxidation Catalysts (*WOCs*)

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A novel method for assessing the activity of a powdered water oxidation catalyst (*WOC*) is described, utilising an easily-prepared wireless rotating disc electrode of the *WOC*, thereby allowing its activity to be probed, via the observed kinetics of water oxidation by Ce(IV) ions, and so provide invaluable electrochemical information.

There is a great deal of interest in the development of efficient, long-lived, low-cost, solar-driven photosystems for the cleavage of water into hydrogen and oxygen[1-3]. One of the great challenges in this work is the identification of a suitable redox catalyst to mediate the oxidation of water, i.e. a water oxidation catalyst, *WOC*, by the photo-generated oxidant, *Ox*, which is usually a valance-band hole in a semiconductor photocatalyst[4,5]. The challenge arises because the oxidation of water is an electrochemically irreversible process, so that most *WOCs* require a significant overpotential, η, to drive the reaction at the current densities (ca. 20 mA cm^{-2})[4] that are possible in a very efficient, solar-driven, water-splitting cell[4]. The best WOCs are the oxides of Ru or Ir[6] but, the latter are not abundant[4] and so there has been a great deal of effort in recent years to identify new, alternative, inexpensive, i.e. Earth-abundant, highly active *WOCs*[3].

As part of this effort, many new *WOC*s are generated in powder form and then screened for activity using a simple redox reaction involving the oxidation of water, i.e. reaction (1).

$$nOx + 2H_2O \xrightarrow{WOC} nRed + 4H^+ + O_2\uparrow \qquad (1)$$

Where *Ox* is the oxidant, *Red* is the reduced form of *Ox*, and *n* is the number of equivalents necessary to consume 4 electrons from water[3,7,8]; obviously, *Ox* must have an oxidation potential greater than that of water, i.e. $E(Ox/Red) > \{E(O_2/H_2O) = 1.23 - 0.059pH\}$. In such screening studies[3,8], the powdered *WOC* is commonly dispersed in solution and, upon addition (or photochemical generation) of the oxidising chemical species, *Ox*, the rate of reaction (1) is measured, usually spectrophotometrically, via its rate of decrease in [*Ox*] with time; this rate is taken as a measure of the activity of the *WOC*[3,7-9]. A common chemical oxidant for such work is Ce(IV), since E(Ce(IV)/Ce(III)) = 1.44, 1.61 and 1.70 in 1 N H_2SO_4, HNO_3 and $HClO_4$ acid, respectively[10] (see (ESI†: S1)); and, in the absence of a *WOC*, it is very stable[7,8]. On most conducting electrode materials, the Ce(IV)/Ce(III) redox couple acts a highly reversible (i.e. Nernstian) couple[11,12], whereas that for water oxidation is highly irreversible[6].

Reaction (1) is generally used by most to provide only a crude assessment of the activity of the *WOC* under test, such as initial rate and/or turnover frequency[13,14]. Thus, in order to probe the electrocatalytic properties of a powder-based *WOC*, a knowledge of which is key if it is to be used in a final, solar-driven, water-splitting device, the powder-based *WOC* must be fabricated as an anode in what is often a poorly defined, non-trivial and time-consuming process[15]. However, the latter exercise may be unnecessary, since the kinetics of reaction (1) can allow the extraction of useful electrochemical information that relates to the electrocatalytic properties of the powder-based *WOC*. This option arises because, in most cases, the powder particles of the *WOC* act simply as micro-electrodes that couple, the electrochemical reduction of the oxidant, such as Ce(IV), with the oxidation of water[16].

In order to extract out electrochemical information *via* the kinetics of decay of *Ox*, e.g. Ce(IV)) in reaction (1), it is essential that the powder dispersion remains unchanged, i.e. doesn't corrode nor aggregate, during the course of the reaction. The latter condition is often difficult to achieve, especially with low activity *WOCs*, which exhibit a long reaction time and so provide ample opportunity for extensive aggregation (and often corrosion) to occur. Although the addition of an anti-flocculant can help reduce this effect, such additives will necessarily affect the intrinsic electrochemical characteristics of the *WOC* under test that are being probed[17].

Herein we describe a simple, quick method for fabricating a wireless, i.e. no external electrical contact, rotating disc electrode, *wRDE*, of a powdered *WOC*, here, primarily, RuO_2(Adams), which allows the electrochemical characteristics of the *WOC* to be readily probed, *via* the measured kinetics of decay of Ce(IV) in reaction (1).

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In this work, the powdered *WOC* under test was the black-coloured powder, RuO_2(Adams), the preparation of which has been described elsewhere[18]. A schematic illustration of the general method of preparation of the *wRDE* of this *WOC* is illustrated in figure 1 and full details, and photographs of the final product, are given in (ESI†: S2).

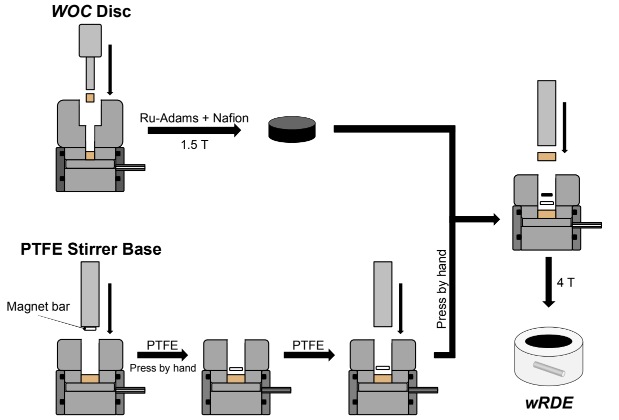

Figure 1 Schematic illustration of the preparation of a RuO_2(Adams) *wRDE*.

The electrochemical properties of the RuO_2(Adams) *wRDE* were probed by placing it in a spectrophotometer cuvette containing 1.5 ml 0.5 M H_2SO_4 solution, thermostatted at 30°C, and spinning it continuously at 1000 rpm using a magnetic stirrer. The water oxidation reaction (1) was initiated by injecting, into the solution in the cuvette, 54 μL of a 0.1 M Ce(IV) sulfate in 0.1 N H_2SO_4 (Aldrich Chemicals). The subsequent change in the absorbance, at 430 nm, of the reaction solution was measured as a function of time, using a Cary 60 spectrophotometer. A typical set of absorption spectral changes, derived from such a typical kinetic run, are illustrated in figure 2. The insert diagram shows the measured decays in absorbance, due to Ce(IV) for two serial injections of Ce(IV). The two decays are identical and near perfect 1st order with respect to Ce(IV) concentration, $[\text{Ce(IV)}]_t$, yielding a value for the first order rate constant, k_1 = 0.0149 min^{-1}, over 3 half-lives, and correlation coefficient > 0.9999. Previous work carried out using this *WOC* has established the generation of stoichiometric amounts of O_2 via reaction (1) under the same conditions[16]. In this system a value of the molar Ce:Ru ratio, θ, for just one injection of Ce(IV) 9.6×10^{-5} can be calculated[19] which suggests that it is operating under catalytic conditions. Details of this calculation can be found in (ESI†: S3).

From the identical natures of the two decay profiles illustrated in figure 2 it is clear that the rate of reaction (1) is independent of the concentration of Ce(III), i.e. $[\text{Ce(III)}]_t$, generated during the course of reaction, at reaction time *t*. This suggests that the rate is independent of the redox potential of the Ce(IV)/Ce(III) couple in solution, which, according to the Nernst equation, would change, as the $[\text{Ce(IV)}]_t$:$[\text{Ce(III)}]_t$ ratio changes, during the course of reaction (1).

Many researchers working on *WOCs* favour using cerium ammonium nitrate (CAN) as the oxidant and 1 M HNO_3 as the acid. Thus, (i) to show that such a medium is appropriate for work with a *wRDE*, (ii) provide further support for the electrochemical model presented here and (iii) to emphasise further the catalytic nature of the RuO_2(Adams), the CAN/1M HNO_3 system was used to test the RuO_2(Adams) *wRDE*. The results from this work revealed the same 1st order kinetics of Ce(IV) decay, using either 3.6×10^{-3} or 0.1 M CAN, in 1 M HNO_3, as illustrated by the decay profiles and photographs in (ESI†: S4).

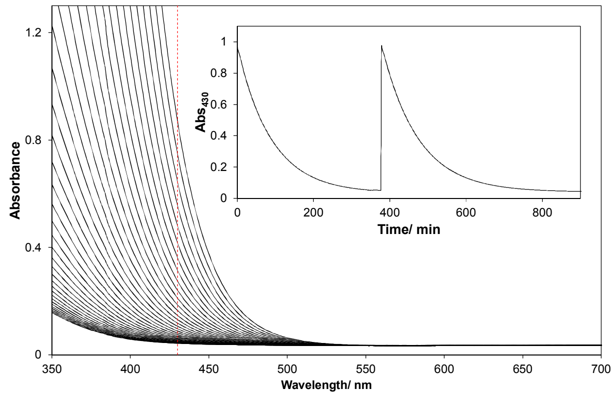

Figure 2 Change in the UV/Vis spectra upon the 1st injection of 54 μL of 0.1 M $Ce(SO_4)_2$ into 1.5 mL of 0.5 M H_2SO_4. The red broken line indicates the wavelength at which the reduction of Ce(IV) is monitored, i.e. 430 nm. The inset shows a plot of the decay of Ce(IV) over 2 serial injections. In all cases the *wRDE* rotation speed = 1000 rpm and reaction temperature = 30°C.

At a conventional, i.e. wired, *RDE*, when the rate of reduction of a oxidising species, such as Ce(IV), is independent of applied potential, the reaction is diffusion-controlled and the measure current obeys the Levich equation[11,12]:

$$i_d = 0.62.n.\mathbf{F}.A.\mathbf{D}^{2/3}\omega^{1/2}\upsilon^{-1/6}[\text{Ox}] \qquad (2)$$

where, i_d = diffusion limited current (A), *n* = number of electrons transferred during the reduction reaction, **F** = Faraday's constant (C/mol), *A* = electrode area (cm^2), **D** = diffusion coefficient for *Ox* (cm^2/s), ω = rotation speed angular rate of rotation of the electrode (rads/s), υ = kinematic viscosity (cm^2/s) and [Ox] = concentration of oxidant (mol/cm^3). The observation of excellent 1st order kinetics for the Ce(IV) reduction on the RuO_2(Adams) *wRDE*, see figure 2, suggests that in this system the rate of reaction (1), with *Ox* = Ce(IV), is diffusion-controlled and, as such, should obey the following modified version of the Levich equation:

$$\text{rate (M/s)} = k_d[\text{Ce(IV)}]_t = 0.62.A.\mathbf{D}^{2/3}\omega^{1/2}\upsilon^{-1/6}[\text{Ce(IV)}]_t/V \qquad (3)$$

where k_d is the measured value for the first order rate constant under these conditions, *V* is the reaction solution volume (cm^3). Given *A* = 0.196 cm^2, *V* = 1.554 cm^3, υ = 0.01 cm^2/s, it follows that eqn(3) predicts the following relationship between k_d (i.e. the measured value of k_1 at 30°C) and the rotation speed of the *wRDE*, ω:

$$k_d = 0.168.\mathbf{D}^{2/3}\omega^{1/2} \qquad (4)$$

In order to test this predicted relationship, the same conditions as used to generate the data in figure 2 were employed, but with the rotation speed of the *wRDE* varied systematically (100-1300 rpm) in a series otherwise identical kinetic runs involving reaction (1), with *Ox* = Ce(IV). In all cases the kinetics of Ce(IV) decay were monitored spectrophotometrically and yielded excellent 1st order plots of the decay data over 3 half-lives ($r^2 > 0.9999$).

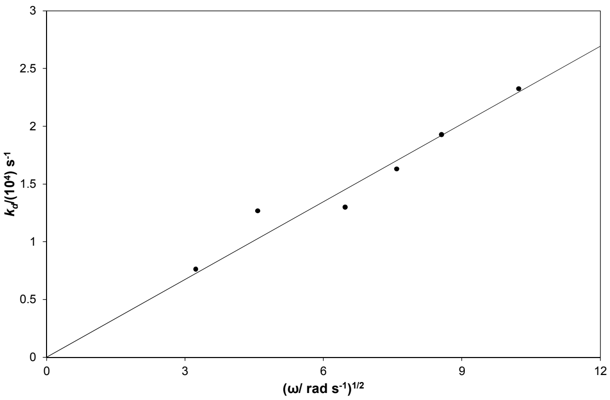

Figure 3 Plot of the 1st order rate, k_d, of reduction of Ce(IV) using the *wRDE* as a function of the square root of the rotation speed. Reaction conditions: otherwise as in figure 1.

A plot of the k_d values derived from this work versus $\omega^{1/2}$ is illustrated above in figure 3 and yields a gradient = $2.25\mathrm{x}10^{-5}$, from which a value for the diffusion coefficient, **D,** of $1.55\mathrm{x}10^{-6}$ cm^2/s was calculated using eqn (4). The latter appears low when compared to reported[11,12] values for *D* for Ce(IV) on Pt electrodes $(3.4\text{-}5)\mathrm{x}10^{-6}$ cm^2/s, although this may be because the actual value for *A* was lower than the geometric value used in the calculations. The latter situation would occur if a significant part of the *WOC* in the *wRDE* was not electro active, which would happen if, as well as naked RuO_2(Adams) particles, the surface comprised regions of pure Nafion, or Nafion-covered RuO_2, particles. Initial optical and electron micrographs of the RuO_2(Adams) *wRDE* provide some evidence for this.

Unfortunately, although the RuO_2(Adams) *wRDE* appears to obey the Levich equation, this doesn't actually probe the electrocatalytic activity of the RuO_2(Adams) as such, since the kinetics are diffusion-controlled. Instead, experimental conditions need to be used under which the kinetics is no longer purely diffusion controlled. In this work, this was simply achieved by running the same experiment as above, but at a much lower temperature, since the activation-controlled oxidation of water is much more temperature sensitive (E_a = 38-55 kJ/mol)[6] than the diffusion-controlled reduction of Ce(IV) (E_a = ca. 15 kJ/mol)[20], so that lower temperatures will favour activation-, rather than diffusion-, -controlled kinetics for reaction (1) using the RuO_2(Adams) *wRDE*.

Thus, the absorbance decay plots illustrated in figure 4, were generated for three serial injections of Ce(IV), using the same reaction conditions as used in figure 1, but with a reaction temperature of 5°C, rather than 30°C. The results show that, unlike those recorded at 30°C, at 5°C the kinetics of reaction (1) are dependent upon the amount of Ce(III) generated, i.e. the reaction slows down as the redox potential, due to the Ce(IV)/Ce(III) couple, decreases with increasing reaction time, *t*.

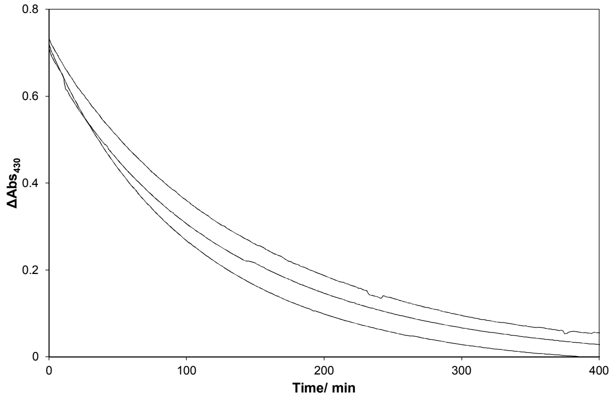

Figure 4 ΔAbs_{430} vs time upon 3 serial injections of 54 µL of 0.1 M $Ce(SO_4)_2$ into 1.5 mL of 0.5 M H_2SO_4 at 5°C. Rotation speed = 1000 rpm.

As commented earlier, in redox catalysis it is recognised[21] that the role of the catalyst is often simply that of a conductor of electrons from one redox couple – in this case *Ox/Red* in reaction (1) – to another, i.e. O_2/H_2O in reaction (1). It follows that at any time during a Ce(IV) decay, such as illustrated in figure 4, each dispersed RuO_2(Adams) *WOC* particle is poised at a mixed potential, $E_{mix,t}$, so as to allow a 'mixed' current, $i_{mix,t}$, to flow through it, with a numerical value that is the same for both the anodic and cathodic electrochemical processes that are occurring concomitantly at separate sites on the redox catalyst. The Nernstian nature of the Ce(IV)/Ce(III) electrochemical process allows the value of $E_{mix,t}$ at any time *t* during a decay, such as illustrated in figure 4, to be calculated[16] via:

$$E_{mix,t} = E'_{Ce} + (\mathbf{R}T/\mathbf{F})\ln\{[-k_d[\mathrm{Ce(IV)}]_t - r(t)]/[r(t) - k_d[\mathrm{Ce(III)}]_t]\} \qquad (5)$$

where, E'_{Ce} = 1.44 V vs NHE in 0.5 M H_2SO_4, k_d = the diffusion-controlled rate constant (s^{-1}) and $r(t)$ = the rate of Ce(IV) reduction at time t (= $d[\mathrm{Ce(IV)}]_t/dt$). Since, on any RuO_2(Adams) particle, the electrochemical reduction of Ce(IV) is coupled to the oxidation of water, it follows that the latter, irreversible process, can be related to the rate of Ce(IV) reduction by the following expression:

$$r(t) = r_w.\exp\{2.303(E_{mix,t} - E'_w)/b\} \qquad (6)$$

where, r_w = a constant that is related directly to the exchange current density for water oxidation, E'_w = the formal redox potential of the O_2/H_2O couple (here, taken as: 1.23 V vs NHE) and b = Tafel slope. It follows from eqn (6) that a plot of $E_{mix,t}$ vs $\log\{r(t)\}$ should yield a straight line with a gradient, b. At any reaction time t, for any of the decay curves illustrated in figure 4, it is possible to calculate appropriate values for: $r(t)$, $[\mathrm{Ce(IV)}]_t$, $[\mathrm{Ce(III)}]_t$ and so a value for $E_{mix,t,}$ using eqn (5). The results of this type of analysis of all the decay data illustrated in figure 4 are illustrated in figure 5 and reveal an approximate Tafel slope of 54 ± 2 mV/decade and an extrapolated value for $r(t)$ = $1.04\mathrm{x}10^{-8}$ M/min at $E_{mix,t,}$ = 1.23 V.

For RuO_2, the reported Tafel slope for oxygen evolution varies between 40 and 120 mV, depending how it is prepared[6]. A value of 65 mV/decade at 25°C in 0.5 M H_2SO_4 has been reported previously for RuO_2 films grown on Ru metal[22]. A value of 60 mV/decade at 25°C (≡ 56 mV/decade at 5°C) may be derived from theory if the deprotonation of the reaction site S-OH is the rate determining step, as proposed by Krasil'shchikov[6,23], i.e.:

$$\text{S-OH} \xrightarrow{\qquad} \text{S-O}^- + \text{H}^+ \qquad (7)$$

From the data in figure 5, given that at $E_{mix,t}$ = 1.23 V, ≡ E'_w, the value of $r(t)$, ≡ r_w in eqn(6), = 1.04×10^{-8} M/min, which in turn is ≡ 1.32 μA/cm^2, given A = 0.196 cm^2 and V = 1.554 cm^3. It follows that, in order to oxidise water to O_2 on the *wRDE* Ru(Adams) electrode at a current density = 20 mA/cm^2, an overpotential, ≡ ($E_{mix,t} - E'_w$) in eqn(6), of 226 mV will be required. This value is in reasonable agreement with the work[22] referred to earlier on RuO_2 films grown on Ru metal, for which a value of η = 270 mV can be calculated.

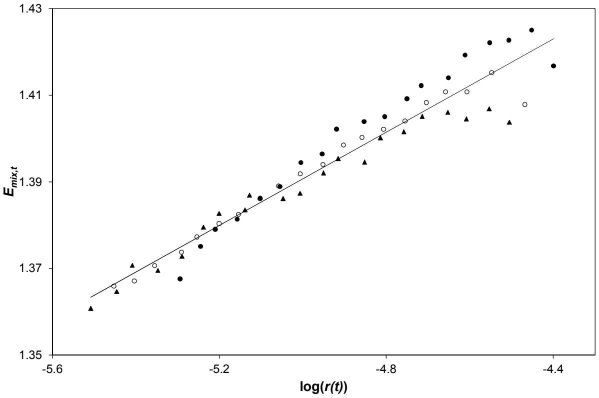

Figure 5 Tafel plot of the data in figure 5 giving a slope of 54 mV per decade and a k_d value of 0.015 min^{-1}. The units of *r(t)* here are M/min.

Table 1 List of Tafel slopes, *b*, the rate at a potential of 1.23 V, r_w, and the calculated overpotential, η (at a current density of 20 mA/cm^2), derived from the data in (ESI†: S5, figure S5).

Catalyst	*b*/ mV per decade	η/mV	r_w/ (10^9) M min^{-1}
RuO_2 (Adams)	54	226	10.4
IrO_2	58	280	2.34
PtO_2‡	125	478	23.7

‡ Run in 1 N HNO_3 at 30°C, all other wRDE's were run in 1.5 mL of 1 N H_2SO_4 at 5°C.

Other *wRDE's* were prepared using commercial forms of $IrO_2.2H_2O$ (Alfa Aesar) and PtO_2 (Sigma Aldrich) and tested using the Ce(IV) decay system yielding Tafel plots that are illustrated in (ESI†: S5), from which the values of *b* and η listed in Table 1 were derived. The difference in the η value for IrO_2, to that of RuO_2(Adams), (54 mV) is consistent with that (60 mV) reported by others recently for sputtered films of the same oxides[24]. PtO_2 has been reported previously as a *WOC* for reaction (1) in 1 N H_2SO_4, albeit of low activity[25], where *Ox* = Ce(IV), and so was studied here, as a *wRDE*, although under more oxidising conditions (i.e. in 1 M HNO_3, *vide supra*) for which E'_{Ce} is 1.61 V[10], in order to generate a more easily measured decay. The values of *b* and η derived from this work for PtO_2, see Table 1, are in reasonable agreement with those reported by others for the same material and acid (i.e. *b* = 109 mV/decade; η = 500 mV)[6].

Conclusions

In summary, the construction of a wireless rotating disc electrode, *wRDE*, of a water oxidation catalyst, in this case RuO_2(Adams), is reported. This method allows powdered materials, which might be able to act as *WOCs*, to be assessed for catalytic activity using a suitable reversible redox couple, such as Ce(IV)/Ce(III).

Acknowledgements

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