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

Supplementary Information

S1: The formal redox potential of Ce(IV)/Ce(III) couple

The formal redox potential of the Ce(IV)/Ce(III), E'_{Ce}, couple depends upon the nature and degree of anion complexation of the Ce ions and as a consequence the value of E'_{Ce} is 1.44, 1.61 and 1.70 in 1 N H_2SO_4, HNO_3 and $HClO_4$ acid, respectively[1]; as is demonstrated later in the paper, this feature proves very useful when testing a *wRDE* with a low activity, and high overpotential (at 20 mA/cm^2), η, such as PtO_2.

1 Ionic Equilibria in Analytical Chemistry, J-L. Burgot, Springer, New York, 2012, p. 395.

S2: Preparation of a *wRDE*

A schematic illustration of the general method of preparation of the *wRDE* of this *WOC* is illustrated in figure S2a.
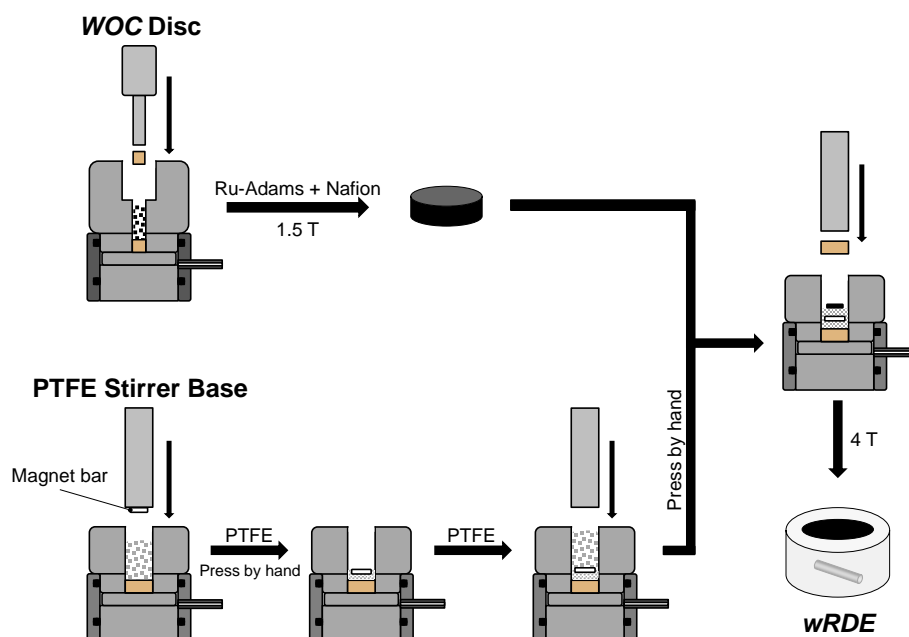

Figure S2a Schematic illustration of the preparation of a RuO_2(Adams) *wRDE*.

Thus, briefly, the RuO_2(Adams) was rendered in disc form (5 mm diameter, 1 mm thick) by mixing with Nafion powder (Ion Power, 40-60 mesh) in a 95:5 mass ratio, then pressing 50 mg of the RuO_2(Adams)/Nafion powder into a 5 mm diameter (1 mm thick) using a 5 mm IR pellet press (Specac Ltd.) with 1.5 tonne pressure for 1 min. The magnetic PTFE base of the *wRDE* was prepared separately using an 8 mm IR press (Apollo Scientific) into which were added 250 mg of PTFE powder (Aldrich Chemicals, 1 μm), compacted by hand using the IR press's steel plunger, to which was stuck (magnetically) a 6 mm long, 3 mm diameter

neodymium magnetic bar (First4magnets). Upon removal of the plunger, the magnetic bar was held firmly in place in the hand-compacted PTFE in the pellet press. A further 250 mg of PTFE were then added and, once again, compacted by hand using the plunger. At this point, the 5 mm RuO_2(Adams)/Nafion disc, prepared earlier, was then placed centrally on the compacted PTFE in the 8 mm IR press and the combination subjected to 4 tonnes pressure for 1 min to yield the final *wRDE* illustrated in figure S2b (a).

RuO_2(Adams) is known to be an excellent *WOC* for reaction (1)[2,3], where *Ox* is Ce(IV) or H_2O_2, and evidence of its activity is provided by the photographs in figure S2b (b) and S2b(c) respectively, which show O_2 bubble formation on the black RuO_2(Adams), electroactive part of the *wRDE* when exposed to a solution containing 0.1 M Ce(IV) sulfate in 0.1 N H_2SO_4 (Aldrich Chemicals), and 0.1 M H_2O_2 in water, respectively.
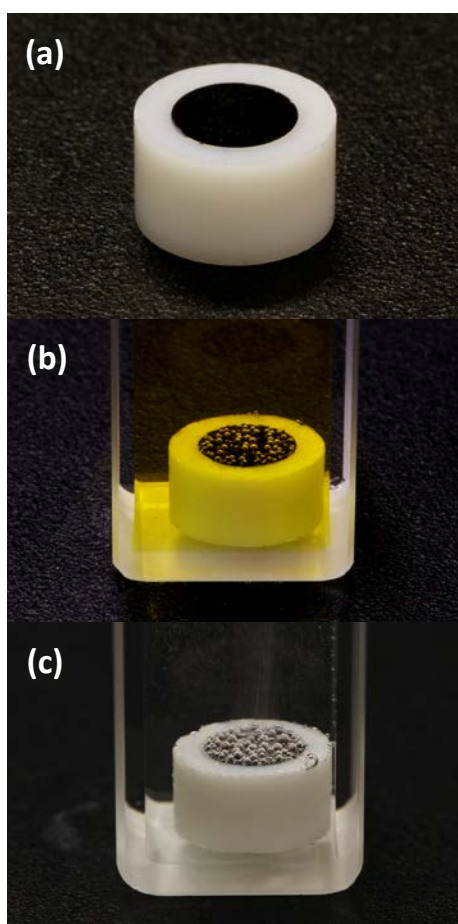

Figure S2b (a) Photograph of the 8 mm PTFE stirrer bar containing a 5 mm disk of Ru-Adams catalyst. **(b)** Oxygen bubbles produced on the surface of the Ru-Adams catalyst after 10 min in 0.1 M $Ce(SO_4)_2$ in H_2SO_4 (0.1 N). **(c)** Oxygen bubbles produced instantly upon addition of 0.1 M H_2O_2.

2   A. Mills and H. Davies, *Electrochim. Acta*, 1992, **37**, 1217–1225.
3   A. Mills, D. Hazafy, S. Elouali and C. O'Rourke, *J. Materials Chem. A*, 2016, **4**, 2863–2872.

S3: Preparation: Calculation of the Ce:Ru ratio

In this system the value of the molar Ce:Ru ratio, q, for just one injection of Ce(IV) is 70, which, at first glance, suggests the RuO_2(Adams) is not being used in catalytic quantities. However, as this method uses the *WOC* in a *wRDE*, it follows that only the exposed surface Ru sites will be engaged in mediating reaction (1). Given the average surface area of such a site is estimated[4] to be ca. 0.34 nm^2, and the surface area of the *wRDE* is 0.196 cm^2, a value for $q = 9.6 \times 10^{-5}$, can be calculated for RuO_2(Adams) *wRDE*, which suggests that it is operating under catalytic conditions.

4 R.L. Doyle, I.J. Goodwin, M.P. Brandon and M.E.G. Lyons, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13737–13783.

S4: Working with CAN

Many researchers working on *WOCs* favour using cerium ammonium nitrate (CAN) as the oxidant and 1 M HNO_2 as the acid and, in support of the electrochemical model presented here and the catalytic nature of the RuO_2(Adams), the same 1st order kinetics of Ce(IV) decay, were observed for a RuO_2(Adams) *wRDE*, using either 3.6×10^{-3} or 0.1 M CAN, in 1 M HNO_3, as illustrated by the decay profiles and photographs below (figure S4).
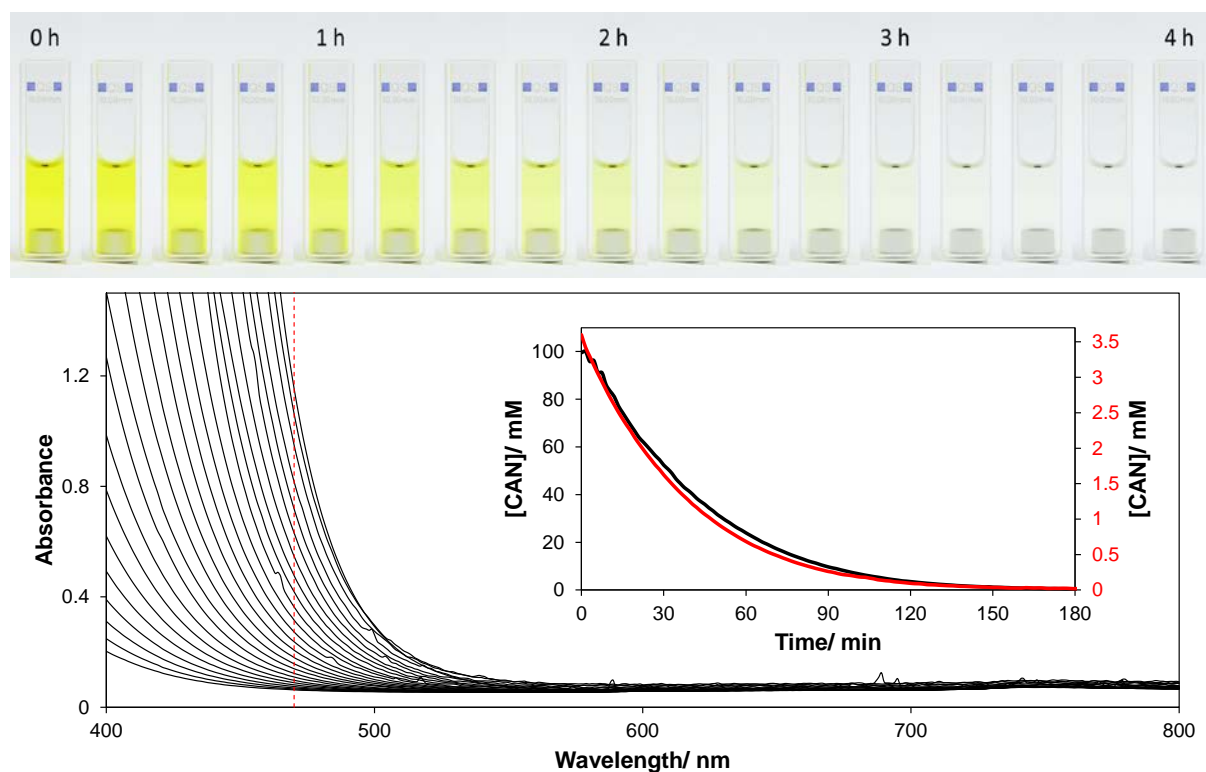

Figure S4 (top) Photographs (recorded every 15 min) showing the change in colour and (bottom) change in UV/Vis spectra (the latter recorded at 6 min intervals) of a 1.5 mL 0.1 M CAN solution in 1 N HNO_3 in a 1cm cuvette, when exposed to a RuO_2(Adams) *wRDE* spun at 1000 rpm and T = 30°C. The broken red line indicates the absorbance monitoring wavelength (470 nm) used to create the black trace in the insert diagram. The inset plot shows the measured change in concentration of CAN for an initial injection of 0.1 M (black trace), and 3.6 mM (red trace). These decay traces are first order and yield similar 1st order rate constants, k, of 0.026 min^{-1}, and 0.027 min^{-1} respectively.

S5: Tafel plots for different WOCs

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 below (figure S5) from which the values of b and η for these materials, listed in Table S5 below, were derived.
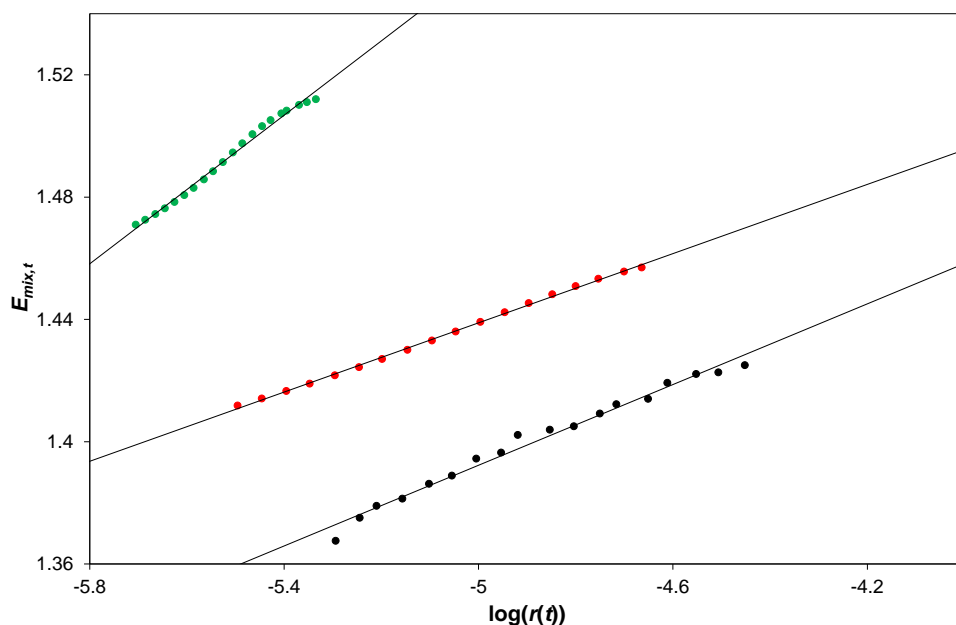

Figure S5 Tafel plots of (●) RuO_2 (Adams), (●) IrO_2, and (●) PtO_2, giving slopes, b, of 54, 58, and 125 mV per decade respectively. The units of $r(t)$ here are M/min. With the exception of PtO_2, which was run in 1 N HNO_3 at 30°C, all other wRDE's were run in 1.5 mL of 1 N H_2SO_4 at 5°C. Injection volume = 54 µL of 0.1 M $Ce(SO_4)_2$. Rotation speed = 1000 rpm.

Table S5 List of Tafel slopes, b, the rate at a potential of 1.23 V, r_w, and the overpotential, η, based on the data in figure S2.

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.