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Nonaqueous Electrocatalytic Water Oxidation by a Surface-Bound $Ru(bda)(L)_2$ Complex

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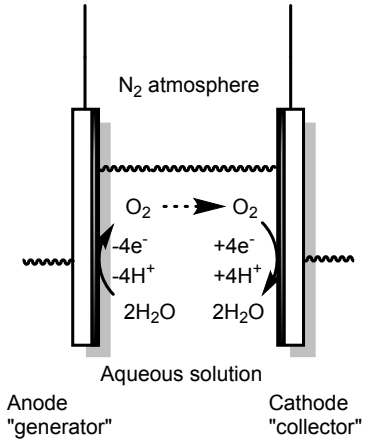
Supporting Information

Electrochemistry. Electrochemical measurements were performed with a CH Instruments 660D electrochemical workstation at room temperature. A three-electrode configuration was applied in a single compartment cell with a saturated calomel electrode (SCE, 0.24 V vs. NHE) used as reference electrodes with graphite counter electrodes. GC and BDD electrodes were polished with 1 micron MicroPolish alumina powder (Buehler, Inc.). Solutions were purged with nitrogen through a solvent bubbler filled with Milli-Q H_2O in order to exclude O_2, reduce evaporation, and to prevent catalyst decomposition. Planar fluorine- and indium-doped tin oxide (FTO or ITO) on glass (Hartford Glass; sheet resistance = 15 Ω/sq.) were also employed.

O_2 Measurements. Collector-generator cells were constructed from two FTO electrodes or with an FTO electrode with ITO-**1** electrode by first using conductive silver epoxy (Chemtronics CW2400) to attach wire leads to the top of the electrodes. Next, thinly cut pieces of microscope glass (1 mm thick, Fisher) were attached to the outer edges of a collector FTO electrode using non-conductive epoxy (Hysol E-00CL). Finally, the generator electrode was bonded to the collector FTO along the outer edges using non-conductive epoxy, with the conductive sides facing one another (care was taken to ensure the wire leads did not touch). The lateral edges of the cell were completely sealed with epoxy, leaving a void space between the two electrode faces (approximately 1mm apart) open at top and bottom; upon immersion in solution, the interior spaces fills with electrolyte by capillary action (Scheme 2). Collector efficiency for a cell of this dimension has been previously determined to be *ca.* 70%; however, the solution dynamics in the more viscous, organic solvent: propylene carbonate, did not yield the same collection efficiency.[1] The solution water oxidation catalyst (WOC) $[Ru(bda)(isoq)_2]$ was used to establish the collection efficiency here assuming a 100% Faradaic efficiency for the catalyst. This catalyst has been well-established in a previous report to have high efficiencies for water oxidation.[2] Faradaic efficiencies (FE) for ITO-**1** were determined by comparison of the charge passed at each electrode and applying the efficiency of the collector-generator cell, FE = $((Q_{Collector}/Q_{Generator})/0.25) \bullet 100\%$.

Scheme S1. Collector-generator configuration for water oxidation and O_2 detection.



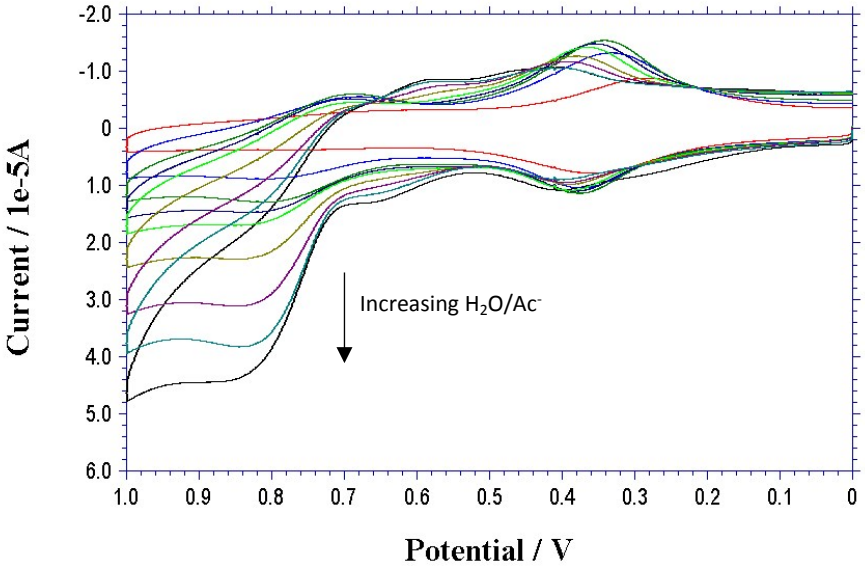


Figure S1. CVs of **1** on ITO in in PC 0.2 M in $NaClO_4$ with 1% increments of added pH 4.35 aqueous 0.2 M acetic acid/acetate buffer from 0 (red trace) to 8% added buffer solution (0.016 M in added acetate buffer; black trace), v = 0.1 V/s.

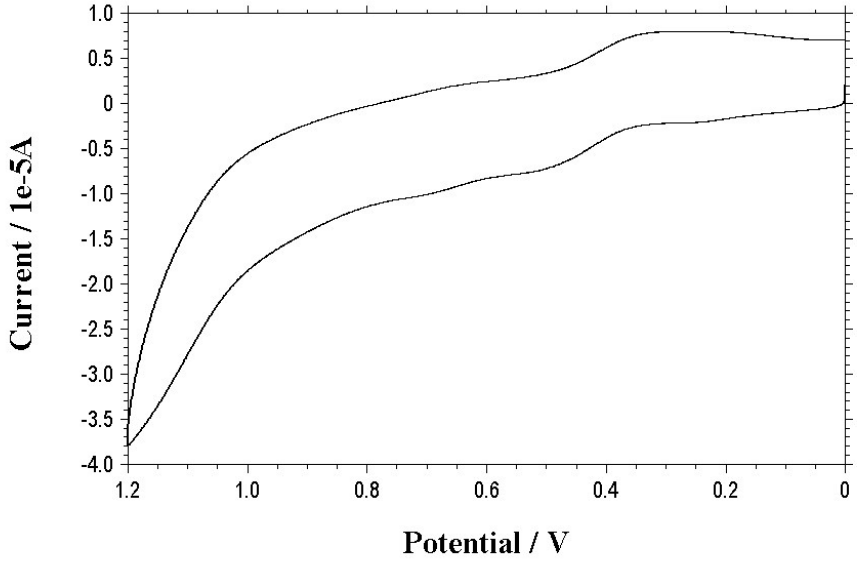


Figure S2. CV of 0.2 mM $[Ru(bda)(isoq)_2]$ in pH 4.35 solution, 0.1M acetate buffer and 0.5M $NaClO_4$ electrolyte, v = 0.1 V/s.

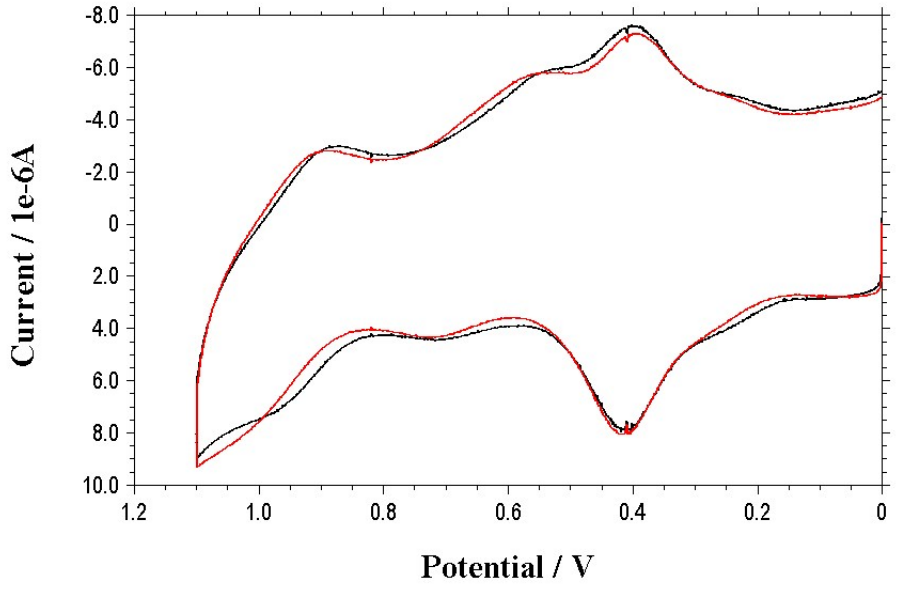


Figure S3. CVs of **1** on planarITO in pH 4.35 aqueous solution with 0.1 M acetate buffer and 0.2M $NaClO_4$ electrolyte with (red) and without (black) the addition of 20% PC, v = 0.05 V/s.

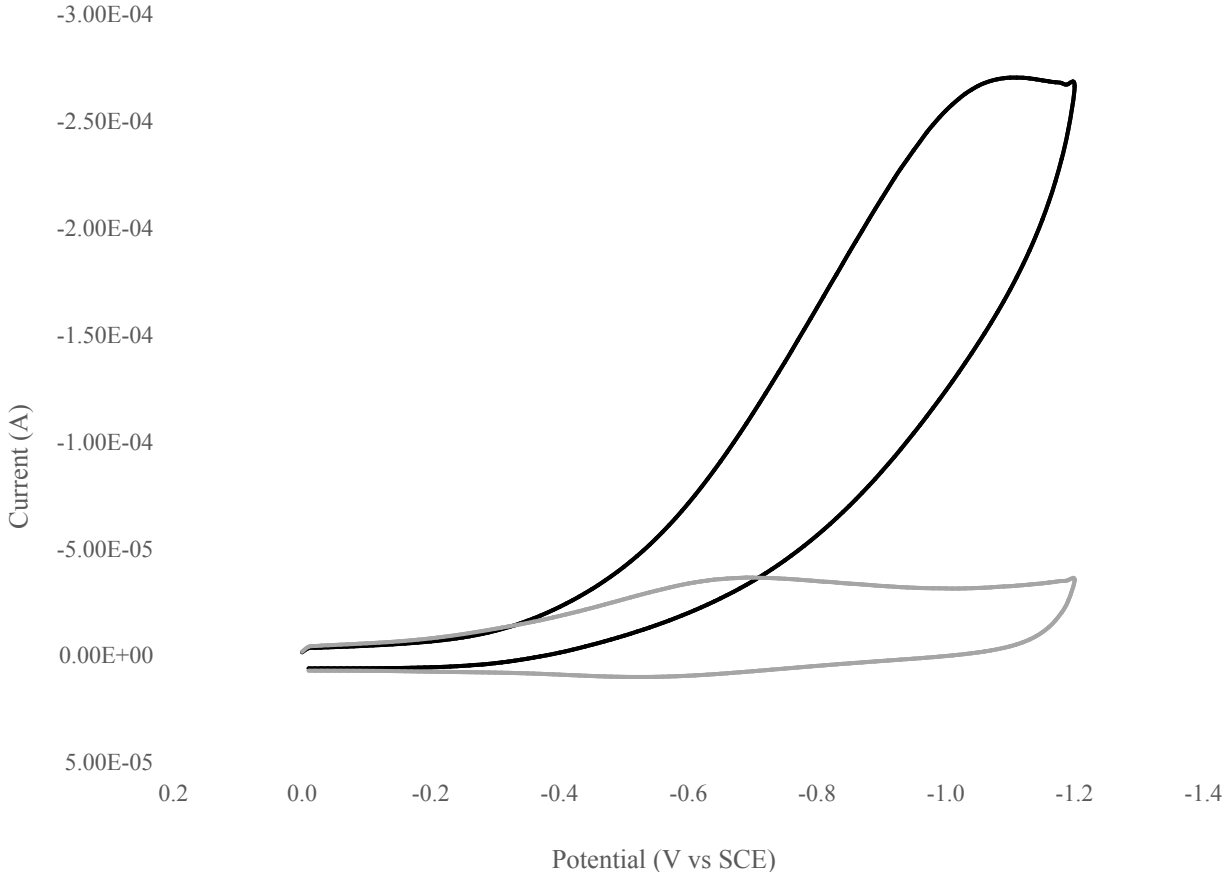


Figure S4. CVs at FTO in in PC/8% H_2O, 0.016 M in acetate, 0.2M in $NaClO_4$ in the absence (gray) and presence of air saturated solution of O_2 (black).

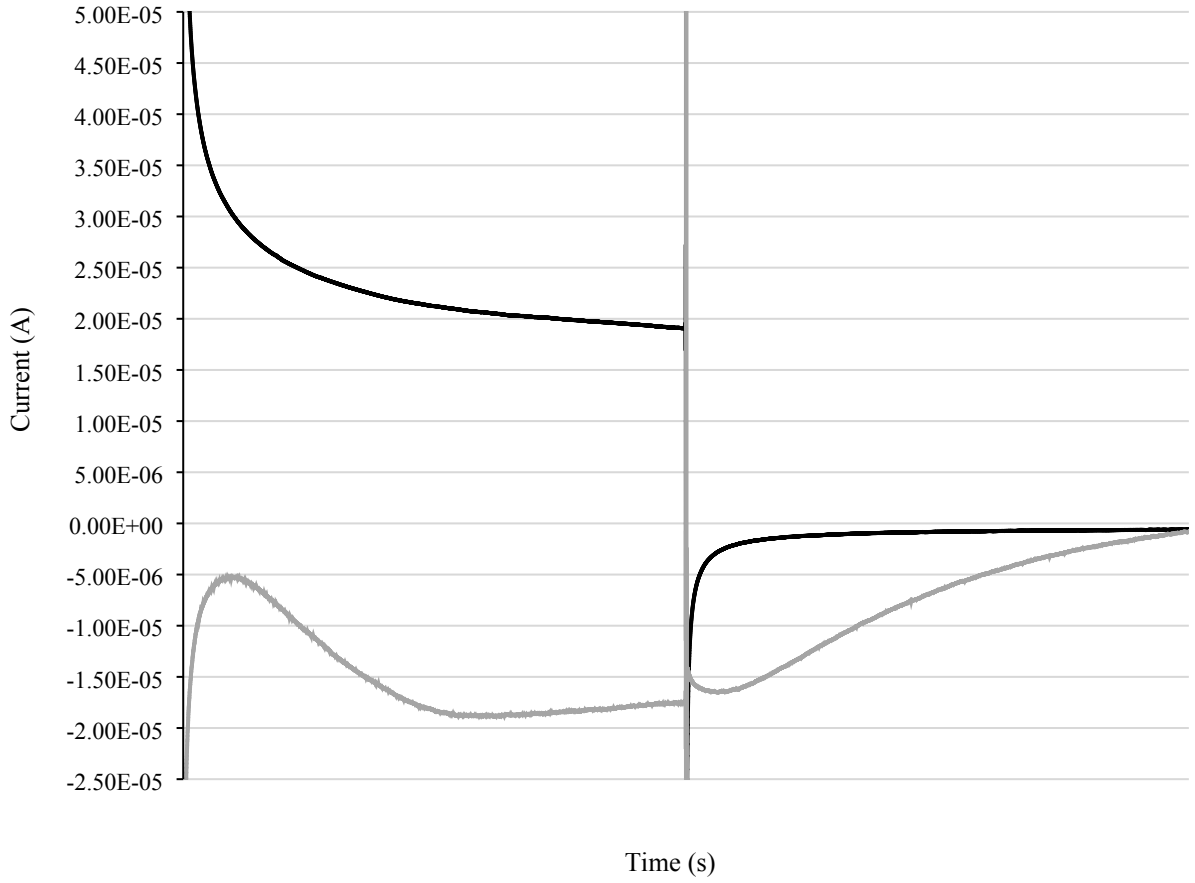


Figure S5. Current-time (i-t) traces of 0.2 mM [Ru(bda)(isoq)$_2$] electrolysis in PC/8% H_2O, 0.016 M in acetate, 0.2M in $NaClO_4$, the generator electrode is shown in the black trace poised at E_{app} = 1.2 V (t = 0 – 900 s) and E_{app} = 0.2 V (t = 901- 1800 s); at the collector electrode in the gray trace, E_{app} was -0.85 V (t = 0 – 1800 s).

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[1] D. L. Ashford, B. D. Sherman, R. A. Binstead, J. L. Templeton and T. J. Meyer, *Angew. Chem. Int. Ed.*, 2015, **54**, 4778-4781.
[2] B. D. Sherman, M. V. Sheridan, K.-R. Wee, N. Song, C. J. Dares, Z. Fang, Y.Tamaki, A. Nayak and T. J. Meyer, *Inorg. Chem.*, 2016, **55**, 512-517.