Supporting Information

Anodic Deposition of a Robust Iridium-Based Water-Oxidation Catalyst from Organometallic Precursors

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Supplementary Figures

Figure S1. X-ray diffraction results. Blue line: bare FTO electrode. Red line: **BL** on FTO electrode. The contribution from **BL** (green trace) is only a broad feature at low angles, consistent with amorphous, non-crystalline material. Inset: photos of **BL** on FTO (left) and bare FTO (right).



Figure S2. Additional SEM images of BL.



 \leftarrow **BL** on FTO

← FTO slide

Figure S3. Energy dispersive X-ray spectroscopy spectrum of **BL** on ITO conducting glass. The dominant peak near 2 keV arises due to iridium.



Figure S4. Performance of **BL** at various deposition times. Electrode was held at 1.4 V for the indicated amount of time in a solution of **1**, transferred to solution of pure electrolyte, and the sustained current density determined at 1.4 V. Conditions: 0.1 M KNO₃, pH 2.9, basal plane graphite working electrode, no iR compensation, Pt counter electrode, Ag/AgCl reference. Solution was stirred during deposition.



Figure S5. Dependence of peak current on scan rate for the quasi-reversible feature of **BL**. Both the anodic and cathodic peaks show a linear dependence, confirming surface-bound nature of the catalyst material.



Figure S6. ¹⁸O isotope incorporation data. Blue data points were collected with unlabeled, natural abundance water. The red data points were collected with a sample of natural abundance water to which a small quantity of 95% H_2^{18} O had been added. The predicted change in atom percent ¹⁸O was 0.063%, and the measured change was 0.056%, confirming conversion of water into dioxygen. Colored, dotted lines near 750 indicate time when electrolysis was initiated for each experiment.



Figure S7. Long timecourse current density data. An initial drop in activity of 3.4% over 4 hours (loss of 0.85% hr⁻¹) is followed by a more stable regime in which activity drops by 0.34% hr⁻¹.



Figure S8. Sample chronoamperogram used for preparation of Tafel plot. Data shown below are for an applied voltage of 1.4 V vs. NHE.





Wavenumbers (cm-1)

Figure S9. IR spectrum. BL in KBr pellet.

Experimental Section

Compounds 1 and 2 were synthesized according to literature procedures.^{1,2}

Electrochemistry

Electrochemical measurements were made on a Princeton Applied Research Versastat 4-400 potentiostat/galvanostat using a standard three-electrode configuration.

For some experiments, a basal plane graphite electrode was used as the working electrode to reduce background current. The electrode consisted of a brass cylinder, sheathed in a teflon tube. At the tip of the brass, a two-part silver conducting epoxy (Alfa Aesar) was used to firmly attach the basal plane carbon electrode surface to the brass. Finally, the tip was sealed with the organic solvent-resistant, electrically-insulating, two-part epoxy Tra-bond 2151 (Emerson and Cuming, Canton, Mass.). Immediately prior to experiments, the working electrode was polished with 1 micron alumina paste, washed with copious amounts of water, and allowed to dry completely. Then, the surface of the working electrode was resurfaced with tape to restore the gray, basal surface.

In all experiments, a platinum wire was used as the counter electrode, and an Ag/AgCl electrode (Bioanalytical Systems, Inc.) was used as the reference electrode (NHE vs. Ag/AgCl: +197 mV). Experiments were carried out in unbuffered solutions containing 0.1 M KNO₃ (Johnson Matthey, electronics grade) as the supporting electrolyte.

For rotating disc experiments, a Princeton Applied Research Model 616 rotator with a platinum disc electrode was used. The platinum disc electrode was electrochemically cleaned prior to beginning experiments.

Where an FTO- (Hartford Glass) or ITO-coated (Delta Technologies) glass slide served as the working electrode, the surface was rinsed with water prior to use.

Electrolysis coupled to oxygen detection was carried out with a standard three-electrode configuration in a two-compartment, air-tight cell. The working and reference electrodes were in one compartment, and the counter electrode (platinum wire) was in the other compartment. Oxygen was sampled by a headspace fluorescence probe or mass spectrometry (see below).

For preparation of the Tafel plot, data were collected using a rotating disc electrode in a single-compartment cell without compensation for internal resistance. A film of **BL** was prepared *in situ* on a platinum rotating disc electrode by potentiostatic electrolysis of a solution

of **1** at 1.4 V vs. NHE for two hours without rotation. The film thickness at this time was estimated by SEM (Figure S2) to be between 1 and 2 μ m. Each point on the Tafel plot comes from a chronoamperometric (potentiostatic) experiment in which the electrode was polarized at the stated potential for five minutes in a solution of unbuffered 0.1 M KNO₃ electrolyte at pH 2.9 (adjusted with nitric acid) and held at a rotation rate of 1000 rpm. After the initial spike in current (arising from capacitance) the current reached an essentially steady value and was read from the chronoamperogram at the five-minute point. Data were collected both from low-to-high and high-to-low voltages. No marked changes were observed upon making this change.

Oxygen detection. For studies of oxygen evolution, a headspace fluorescence-probe oxygen assay was used. The apparatus (Ocean Optics, Dunedin, FL) consists of a probe (FOXY-R) and a custom glass electrochemical cell with threaded fittings for the probe, electrodes, and gas-tight septa for purging. A fluorescent dye is embedded in a sol-gel matrix in the probe tip. Upon exposure to oxygen, the quenching of the dye's fluorescence is recorded by a fluorimeter connected to the probe via a fiber-optic cable. A Stern-Volmer plot generated from standard oxygen concentrations in the cell is then used to convert the raw fluorescence lifetime data into headspace oxygen concentration. In a typical experiment, room air was purged from the electrochemical cell with pure nitrogen, and the system was allowed to equilibrate with stirring for 20 minutes. Data collection over 20 minutes showed equilibration of the system, and when a steady baseline had been achieved, electrolysis was initiated. Depending on the experimental conditions, oxygen evolution was apparent within minutes.

¹⁸O incorporation studies and H_2 detection via Stable Isotope Ratio Mass Spectrometry (SIR-MS). Analyses were performed using a Thermo-Finnigan GasBench II connected to a Thermo-Finnigan Delta^{plus} XP stable isotope ratio mass spectrometer operating in continuous-flow mode. Both the GasBench and Delta^{plus} XP were controlled by Isodat software (version 3.0). Using the GasBench II, the headspace of a two-chamber gas-tight electrochemical cell was sampled via a nested sampling needle. For the ¹⁸O incorporation studies, the headspace of the chamber containing the working and reference electrodes was sampled. Helium flows (ca. 0.5 mL min⁻¹) into the cell through an upper aperture in the needle and the resultant mixture flows back through a lower aperture and into an inner capillary. The gas mixture is then directed into a

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Nafion (DuPont) drying tube and out through a 10- μ L sampling loop in a Valco switching valve. Once the sampling loop is flushed with headspace gas, it is switched to inject the sample in the loop onto an integral gas chromatograph with a Varian CP7551 PLOT fused silica 25 m x 0.32 mm column (coating: Porabond Q) at 32°C to separate O₂ from CO₂. The separated gases are then carried through a second drying tube to an open split where a glass capillary continually draws in helium and sample gases to the mass spectrometer for analysis. In the mass spectrometer, the samples are ionized (electron ionization) and analyzed in three cups set to O₂ peaks with masses 32, 33, and 34. The relative nominal amplifications for the three cups are 1, 100, and 300. Under the conditions we used, the cell is only slightly pressurized because the sampling gas mixture from the cell was either directly vented (with the Valco valve set to "inject" mode) or was vented after going through the sampling loop (with the Valco valve set to "load" mode). This technique has been described and used previously by our group.³ The Delta^{plus} XP can also be configured to detect H₂; evolution of H₂ was detected in the electrochemical cell by sampling the headspace of the chamber containing the platinum counter electrode.

Powder X-ray diffractometry. All data were collecting using a Bruker-AXS D8-Focus with graphite monochromated Cu K_{α} radiation (1.5406 Å). The instrument was equipped with 0.6 mm slits (divergence, anti-scatter, and detector) and a NaI scintillation detector. Experiments were performed using θ -2- θ geometry, scanning from 1 – 80 ° (2 θ) at 100 s/°. The resulting photon counts for a blank FTO slide and an FTO slide with **BL** are presented in Figure S1 and are uncorrected.

IR spectroscopy. IR spectra were collected on a Nicolet 6700 FT-IR spectrometer equipped with a Smart Collector DRIFTS (diffuse reflectance) accessory. Samples for data collection were collected by scraping **BL** off of an FTO electrode and grinding with dry KBr.

SEM and EDS. Scanning electron microscopy images and EDS (energy dispersive X-ray spectroscopy) spectra were obtained with either a JEOL JXA-8530F or FEI ESEM XL-30 system. After film preparation on ITO- or FTO-coated glass, samples were rinsed and allowed

to dry. Images and data were then collected with an acceleration voltage of 10 or 15 kV, respectively for the FEI and JEOL systems.

References

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