

Supporting Information

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In Situ Observation of Surface Species on Iridium Oxide Nanoparticles during the Oxygen Evolution Reaction**

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Supporting Information

Experimental Section

The working electrode was prepared by coating the front side of the membrane with 0.08mg/cm² Iridium (IV) Oxide nanoparticles (50-80 nm in diameter, Nanograde Inc.) through a one-step drop-casting method ²⁸ (The electrode characterization is shown in **SI 2**). The counter electrode on the back side of the membrane, where the recombination of protons and electrons into hydrogen gas takes place, consisted of platinum (Pt) nanoparticles supported on a Nafion®/carbon-black mixture. The assembled cell was introduced into the APXPS system, where saturated water vapor was introduced to the counter electrode through small tubes, while the working electrode side exposed to the gas cell was humidified via variable leak valves. The water vapor pressure was set to 10 Torr as to achieve a relative humidity of approximately 50% at room temperature and thus provide both electrolyte for electrolysis and membrane humidification for proton transport. Once the system was humidified, its electrochemical characteristics were assessed inside the APXPS chamber through voltammetry using a PineWave potentiostat, as shown in **SI 3**. All XPS and electrochemical measurements were performed at room temperature.

For the Ir 4f spectra, the XPS BE is referenced to the Fermi edge under the corresponding experimental conditions and the signal intensity is normalized to the Ir 4f_{7/2} intensity. Due to a small amount of surface charging during the acquisition of the O 1s spectra (seen in the lower BE of the gas phase water), the O1s BE is not referenced to the Fermi level but to the lower BE onset of the signal. The O1s intensity is normalized to the signal background. **Figure SI 2C** shows an overview XPS spectrum of the anode surface.

Spectral deconvolutions and background subtractions (Shirley Backgrounds) were performed using Igor-Pro software. The OCV Ir 4f spectrum was deconvoluted using Gaussian-broadened Doniach-Šunjić functions (FWHM = 1, 85% Gaussian- Lorentzian, 0.9 asymmetry). Ir spectrum recorded in OER conditions was deconvoluted using the parameters from the open circuit conditions, with a second higher binding energy component being added to produce a good fit. O 1s spectra under both open circuit and oxygen evolution conditions were deconvoluted using Voigt functions (FWHM = 2.2, 75% Gaussian- Lorentzian, 0.57asymmetry).The Inelastic Mean Free Path was calculated using the NIST Electron Inelastic-Mean-Free-Path Database: Version 1.2, using the predictive G-1 equation of Gries et al.

Cell diagram

The electrochemical cell consists of a PEEK polymer framework with two chambers separated by a PEM (see **Figure S1**). The membrane is made of Nafion® 115, coated on one side with Pt nanoparticles supported on a Nafion®/carbon-black mixture with catalyst loading of 4 mg/cm² (particle diameter 10-20 nm) from Fuel Cell Store, Inc, Boulder, CO, which serves as the counter electrode. The working electrode was coated with iridium oxide nanoparticles (particle size 50-80 nm) from Nanograde Inc through the process described in **SI 2**. The working electrode of the assembly was exposed to the APXPS gas cell, which was dosed with adjustable amounts of water vapor gas. The counter electrode, where the protons and electrons produced during the OER recombine into H₂ gas, was filled with water vapor. Both electrodes are connected to an external Pinewave potentiostat, allowing for the recording of XPS signals as a function of applied voltage (For the in-situ voltammetry under these experimental conditions, see **SI 3**).

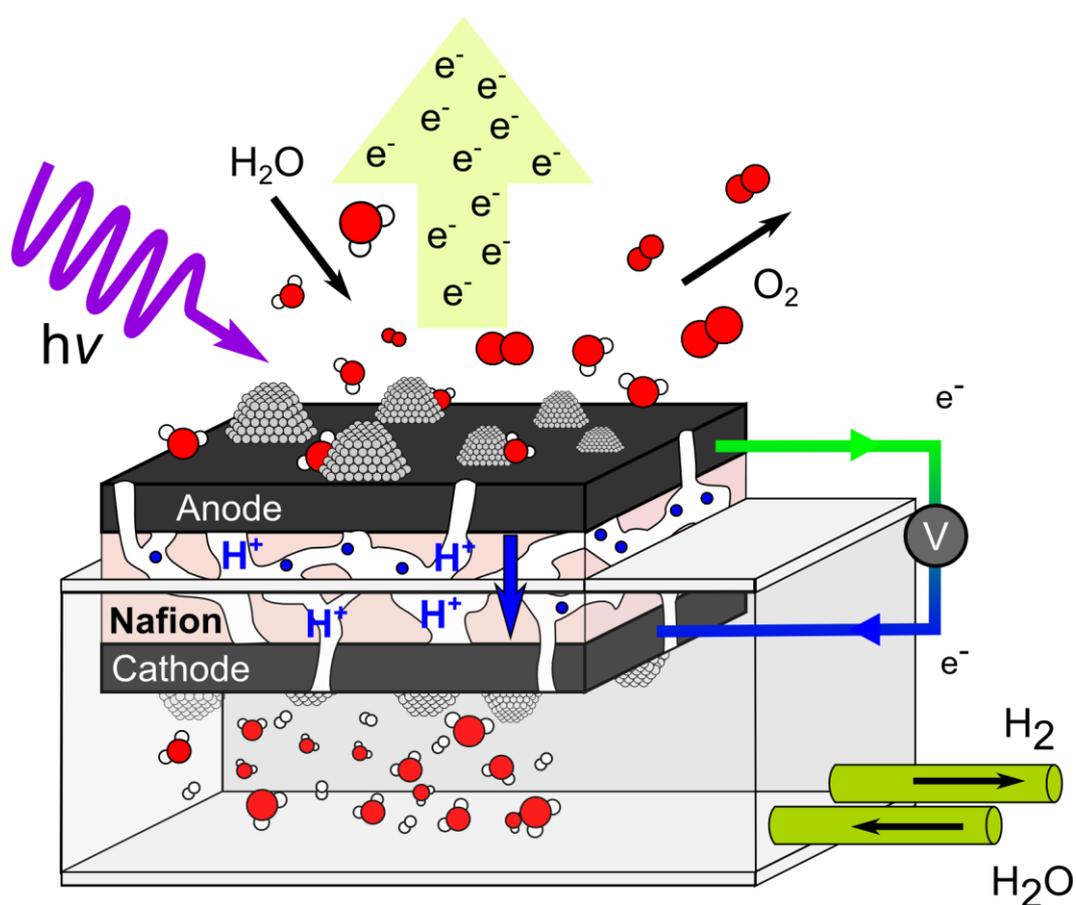


Figure S1 Schematic drawing of a PEM electrochemical cell setup for APXPS investigations: The Nafion® membrane is coated on the working electrode side with carbon-supported iridium oxide nanoparticles. The counter electrode consists of carbon-supported platinum nanoparticles. Water vapor is introduced into the system through the APXPS gas cell and the counter electrode side. Red and white circles represent oxygen and hydrogen; blue circles represent protons; grey circles represent the metallic nanoparticles.

Iridium Oxide catalyst deposition and sample characterization.

The working electrode was prepared using a one-step dropcasting method following the guidelines set by Reier et al. ²⁸ (see **Figure S2**): 0.2g XC-72 Carbon black and 0.02g Nafion were dissolved in an 6 mL isopropanol solution. 8mg of Iridium oxide nanoparticles (particle size 50-80nm), were added and suspended in the solution by means of 15 minutes of sonication. 400 μ L of the suspension were added in 50 μ L increments to the blank side of the membrane described in SI 1, resulting in a uniform carbon-nafion-catalyst coating. The resulting electrode was characterized with XPS and a 2 θ -XRD scan, exhibiting all the expected photoemission peaks and crystal indexes ²⁵.

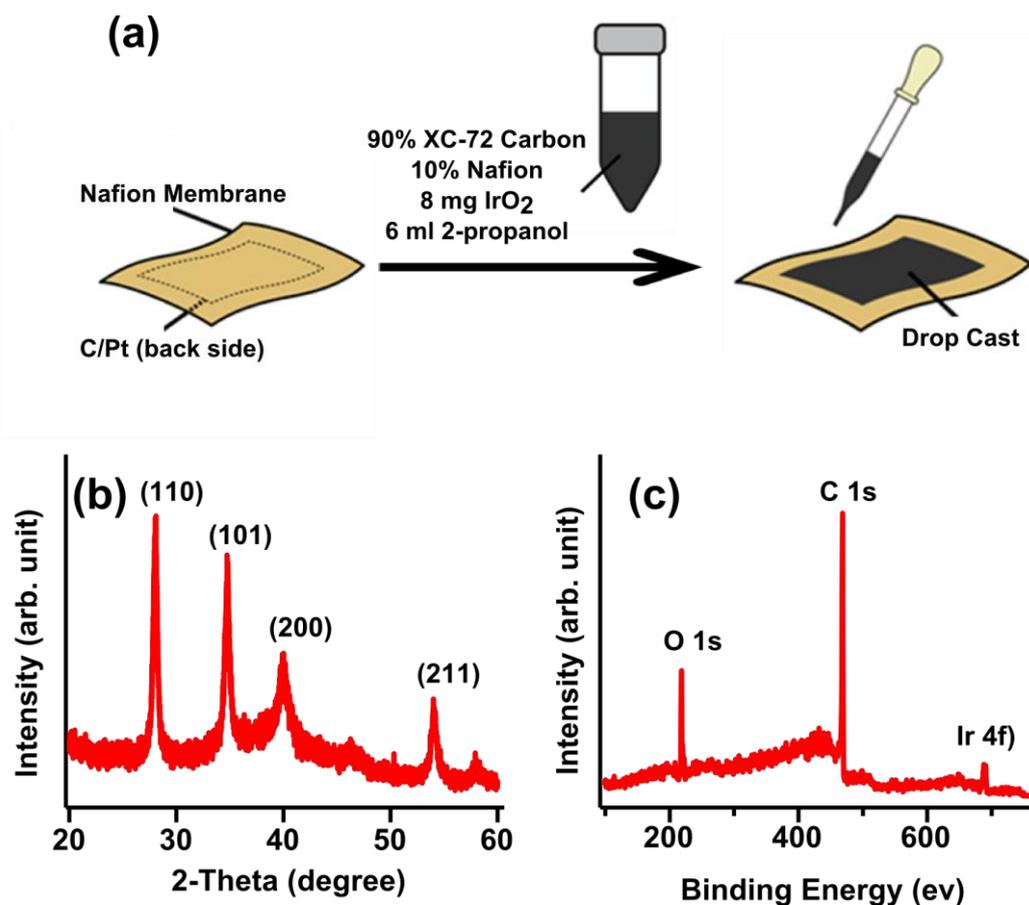


Figure S2 Electrode preparation and characterization (A) Working electrode is prepared by coating the blank side of the Nafion membrane with a suspension of carbon-Nafion-iridium oxide (B) 2 θ -XRD scan of the iridium coated polymer membrane, with crystal indices of iridium oxide assigned to all strong reflections. (C) Overview XPS spectra. Relevant photoemission peaks are labeled.

Cyclic Voltammetry

The cyclic voltammogram of the assembled electrochemical system under the experimental conditions upon which the XPS spectra were collected (10 Torr of water pressure) show all characteristic features of iridium oxide nanoparticles^{6,8,25}. In **Figure S3**, the OER onset can be seen to take place above 1.6V. For this work, the applied voltage was chosen to be 1.75 V to ensure that measurements would be performed under oxygen evolution conditions.

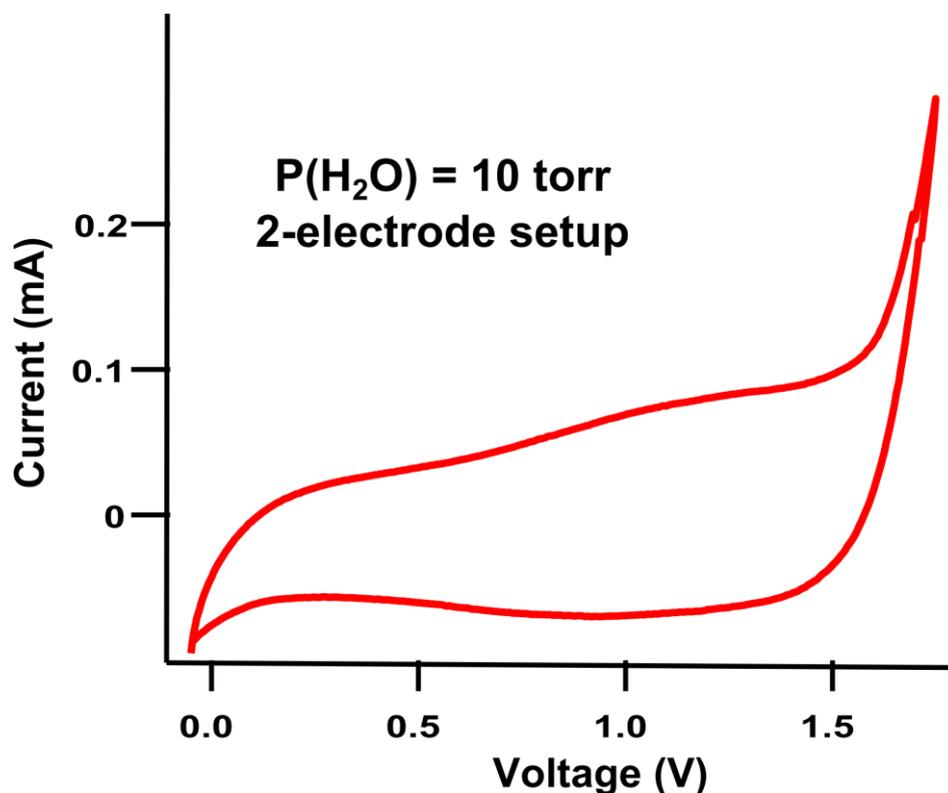


Figure S3 Voltammetry. Cyclic voltammogram of the IrO₂ electrode under the experimental conditions in which the XPS spectra in **Figures 1** and **2** were collected.”

Electrochemical reversibility

Figure S4 shows that, as the system is taken from open circuit conditions (0 V) to OER conditions (1.75 V), we see the growth of a higher binding energy phase, which disappears if the applied voltage is reduced below the onset of the oxygen evolution reaction (1 V, chosen randomly). Changes in the spectra are more subtle with respect to the main text due to the lower water vapor pressure (2 Torr), which limits the amount of available electrolyte for the OER.

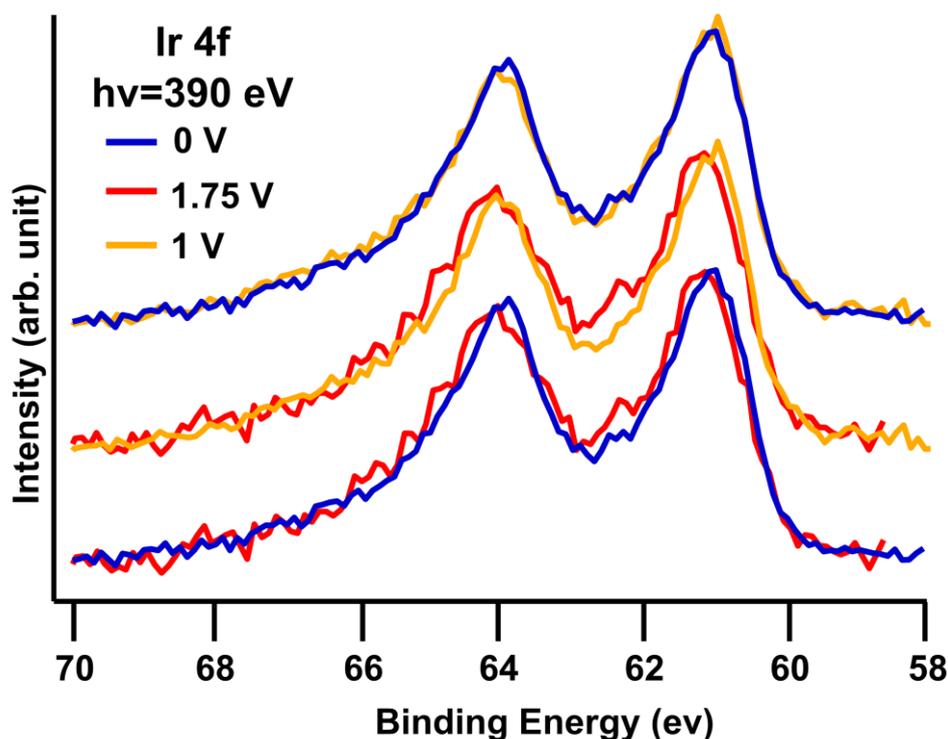


Figure S4 Electrochemical reversibility. Ir 4f XPS spectra of iridium oxide nanoparticles under 2 Torr of water under different voltage conditions. The red spectrum corresponds to the open circuit conditions, the blue spectrum to an applied voltage of 1.75 V (anodic sweep from 0 V) and the orange spectrum corresponds to an applied voltage of 1 V (cathodic sweep from 1.75 V)