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# **Energy and Environmental Science**

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# A Low-noble-metal $W_{1-x}Ir_xO_{3-\delta}$ Water Oxidation Electrocatalyst for Acidic Media via Rapid Plasma Synthesis

Sudesh Kumari<sup>a†</sup>, Babajide Patrick Ajayi<sup>a,b†</sup>, Bijandra Kumar<sup>a</sup>, Jacek B. Jasinski<sup>a</sup>, Mahendra K. Sunkara<sup>a,b</sup>, and Joshua M. Spurgeon<sup>a\*</sup>

#### Determination of turnover frequency

Turnover frequency (TOF) was determined as the number of OER reaction conversions occurring per catalyst active site per time. With the uncertainty in the number of metal cation sites exposed to the electrolyte and contributing to the reaction, both a lower bound and an upper bound estimate to the TOF were calculated. Due to possible sub-nm porosity from combusted organic components during the rapid plasma oxidation as well as a possible semi-permeable hydrous layer at the catalyst surface under operation, some non-surface metal sites may contribute to the reaction. The lower bound turnover frequency (TOF<sub>LB</sub>) was therefore estimated assuming all metal sites contribute to the reaction.<sup>1</sup> The upper bound turnover frequency (TOF<sub>LB</sub>), in contrast, was calculated assuming that only metal cations at the surface of the catalyst were capable of being active reaction sites.

The lower bound was calculated by:

$$TOF_{LB} = \frac{JM_{cat}}{nFl}$$

Where J is the current density at the overpotential under evaluation,  $M_{cat}$  is the molecular weight of the catalyst, n is the number of moles of electrons per mole of reaction (n = 4 for OER), F is Faraday's constant, and l is the catalyst mass loading per electrode projected area. For the catalyst  $W_{1-x}Ir_xO_{3-\delta}$ , the molecular weight was approximated by assuming charge balance with only the predominant oxidation states  $W^{6+}$ ,  $Ir^{4+}$ , and  $O^{2-}$ , which gives  $W_{1-x}Ir_xO_{3-x}$ . Thus, for the catalyst  $W_{1-x}Ir_xO_{3-x}$ x:

$$M_{cat} = 231.84 - 7.62x \ \frac{g}{mol}$$

Determining the upper bound turnover frequency required an estimate of the catalyst surface area. An electrochemically active surface area can be estimated by measuring the electrode double layer capacitance and comparing it to an estimated flat sample capacitance.<sup>2</sup> However, large experimental error and unknown capacitance values for theoretically flat catalyst materials made this an unreliable method. Instead, the upper bound was calculated using the Brunauer–Emmett–Teller (BET) gas adsorption method to measure catalyst surface area. BET analysis was performed with the Micromeritics Tristar 3000 porosimeter. Samples were carefully weighed and degassed before performing the measurements to remove any adsorbed contaminants from the surface and pores of the sample. Calculations for the BET surface area were done by using the TriStar 3000 analysis program.

The number of metal cation sites per surface area was approximated by determining the molecular volumetric concentration of the catalyst, assuming a uniform molecule distribution (i.e., roughly cubic arrangement), and relating it the molecular surface concentration. Note that this is inherently an approximation for metal cation surface concentration, since the method neglects crystal structure and surface orientation, which are not precisely known for rough polycrystalline nanoparticulates with multiple possible phases. Two different mathematical approaches were used to relate  $C_{cat,surf}$ , the catalyst molecule concentration by surface area, to  $C_{cat,vol}$ , the catalyst molecule concentration by volume, both yielding identical results. In the first method, a spherical particle of radius, R, is assumed and the number of molecules at the surface,  $N_{s}$ , is determined by integrating across the volume of a shell with width a equal to the distance between molecules:

$$N_{s} = \int_{R}^{R} 4\pi C_{cat, vol} R^{2} dR = \frac{4}{3}\pi C_{cat, vol} (3R^{2}a + 3Ra^{2} + a^{3})$$

And for the spherical particle:

$$C_{cat,surf} = \frac{N_s}{4\pi R^2} \approx a C_{cat,vol} \text{ for } R \gg a$$

Assuming uniformly distributed molecules in roughly cubic arrangement, the intermolecular distance is:  $a \approx C_{cat wal}^{-1/3}$ 

$$C_{cat,surf} \approx (C_{cat,vol})^{\frac{2}{3}}$$

Alternatively, in the second approach, a cubic particle with N molecules per side of length L is assumed:

$$C_{cat,vol} = \frac{N^3}{L^3}$$

$$N_s = N_{total} - N_{interior} = N^3 - (N-2)^3$$

$$N_s = 6\left(N^2 - 2N + \frac{4}{3}\right) \approx 6N^2 \text{ for large } N$$

$$C_{cat,surf} = \frac{N_s}{6L^2} \approx \frac{N^2}{L^2}$$

With both methods providing the same molecular surface concentration estimate of:

$$C_{cat,surf} \approx \left(C_{cat,vol}\right)^{\frac{2}{3}} \approx \left(\frac{\rho_{cat}N_A}{M_{cat}}\right)^{2/3}$$

Where  ${}^{N}{}_{A}$  is Avagadro's number, and  ${}^{\rho}{}_{cat}$  is the mass density of the catalyst.  ${}^{\rho}{}_{cat}$  was estimated assuming a linearly weighted average between the density of WO<sub>3</sub> and IrO<sub>2</sub>. For the catalyst W<sub>1-x</sub>Ir<sub>x</sub>O<sub>3-x</sub>:

$$\rho_{cat} = (1 - x)\rho_{W03} + x\rho_{Ir02} = 7.16 + 4.5x \frac{g}{cm^3}$$

The upper bound was then calculated by: IAN

$$TOF_{UB} = \frac{JAN_A}{nFC_{cat,surf}A_{BET}} = \frac{JN_A}{nF\left(\frac{\rho_{cat}N_A}{M_{cat}}\right)^2 IS_{BET}}$$

Where A is the electrode projected area,  $A_{BET}$  is the catalyst surface area as measured by BET, and  $S_{BET}$  is the BET-measured specific surface area per mass of catalyst.

WO<sub>3</sub> by itself is a very kinetically sluggish surface for OER, with a measured overpotential of 1.58 V at 10 mA cm<sup>-2</sup>. Thus in the mixed metal  $W_{1-x}Ir_xO_{3-\delta}$  catalyst, the Ir cation sites are presumed to support the large majority of oxygen evolution turnover. An Ir-specific turnover frequency was thus calculated to highlight the activity of the Ir sites accounting for their fraction of the total metal cations, assuming 100% reaction at Ir sites:

$$TOF_{LB,Ir} = \frac{TOF_{LB}}{x}$$

$$TOF_{UB,Ir} = \frac{TOF_{UE}}{x}$$

# Additional catalyst characterization data

Table S1. OER catalyst data.

	S <sub>BET</sub>	Mass Activity (A g <sup>-1</sup> )		
Catalyst [a]	(m² g⁻¹) [b]	@ η = 0.3 V [c]		
WO <sub>3</sub> (P)	3.27	0.0036		
IrO <sub>2</sub> (P)	5.89	17.4		
W <sub>0.57</sub> Ir <sub>0.43</sub> O <sub>3-δ</sub> (P)	6.57	1.46		
W <sub>0.92</sub> Ir <sub>0.08</sub> O <sub>3-δ</sub> (P)	11.37	0.077		
W <sub>0.99</sub> Ir <sub>0.01</sub> O <sub>3-δ</sub> (P)	3.68	0.220		
W <sub>0.99</sub> Ir <sub>0.01</sub> O <sub>3-δ</sub> (T)	8.66	0.014		

[a] (P) Plasma oxidized, (T) Thermally oxidized. [b] BET-measured specific surface area per mass of catalyst. [c] Current per total mass of catalyst on the electrode determined at 0.3 V of overpotential, from as-deposited catalyst without optimization for deposition method or mass loading.

# Predicted W-Ir-O phase diagram



Fig. S1 Phase diagram for the W-Ir-O system.

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The phase diagram for the combination of W, Ir, and O was generated using the online platform of the Materials Project,<sup>3, 4</sup> specifically the Phase Diagram application.<sup>5, 6</sup>

#### **Morphological differences**



**Fig. S2** (a – f) SEM and (g – j) TEM images of  $W_{1-x}Ir_xO_{3-\delta}$  catalysts prepared by plasma oxidation (P) or by thermal oxidation (T). The scale bar is 5  $\mu$ m for (a – f) and 100 nm for (g – j).

# Elemental mapping of $W_{1-x}Ir_xO_{3-\delta}$ compositions



**Fig. S3** (a - c) SEM images of the morphology and EDS elemental mapping of W and Ir for plasma-oxidized samples of (a)  $W_{0.57}Ir_{0.43}O_{3-\delta}$  and (b)  $W_{0.92}Ir_{0.08}O_{3-\delta}$  and (c) thermally oxidized  $W_{0.99}Ir_{0.01}O_{3-\delta}$ . The scale bar in (a - c) is 5  $\mu$ m.

#### **XRD Rietveld analysis**



**Fig. S4** XRD Rietveld analysis for plasma-oxidized (P) (a)  $WO_3$ , (b)  $W_{0.99}Ir_{0.01}O_{3-\delta}$ , (c)  $W_{0.92}Ir_{0.08}O_{3-\delta}$ , and (d)  $W_{0.57}Ir_{0.43}O_{3-\delta}$  and thermally oxidized (T) (e)  $W_{0.99}Ir_{0.01}O_{3-\delta}$ . Black circles mark the observed XRD intensity, the red line is the calculated intensity, the blue line is the background baseline curve, the pink line is the difference between the observed and calculated intensity, and the Bragg lines for the phases are represented by green bars for the single  $W_{1-x}Ir_xO_{3-\delta}$  phase, cyan bars for Ir, and purple bars for IrO<sub>2</sub>.

Main text Figures 2 and 5c show the X-ray diffraction (XRD) patterns and Figure S4 shows the corresponding Rietveld analysis of the iridium tungsten oxide samples prepared via plasma or thermal processes, which confirmed the formation of a triclinic phase. All the reflections in both samples were indexed based on space group  $P^{\bar{1}}$  (no. 2) and coincided with the standard values of triclinic WO<sub>3</sub> [International Center for Diffraction Data (ICDD) PDF card no. 00-020-1323]. The low reliability factor;  $R_{wp}$  (W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub>-T) = 6.2 %,  $R_{wp}$  (W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub>-P) = 7.3 %, indicated that the Rietveld refined XRD pattern fit quite well with the experimental data points in spite of the complexities and low symmetry of the triclinic structure, giving calculated cell parameters of W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub> (T) as a = 7.390(2) Å, b = 7.537(1) Å, and c = 7.703(1) Å, while the cell parameters for W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub> (P) were a = 7.329(1) Å, b = 7.518(1) Å, and c = 7.698(1) Å. The a and b lattice parameters were noticeably smaller in W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub> (P), giving it a slightly higher calculated density value of 7.259 g/cm<sup>3</sup> than the 7.180 g/cm<sup>3</sup> value for W<sub>0.99</sub>Ir<sub>0.01</sub>O<sub>3-6</sub> (T). The rest of the refined parameters are available in Table S2 below.

	<i>x</i> = 0.0(P)	<i>x</i> = 0.01(T)	x = 0.01(P)	<i>x</i> = 0.08(P)		<i>x</i> = 0.43(P)		
Phase	<sup>1</sup> WO <sub>3</sub>	WO₃	WO₃	WO₃	²lr	WO <sub>3</sub>	Ir	<sup>3</sup> IrO <sub>2</sub>
wt. fraction	1.0000	1.0000	1.0000	0.97104	0.02896	0.63986	0.22686	0.13328
Density(g/cm <sup>3</sup> )	7.260	7.180	7.259	7.258	22.537	7.262	22.512	11.661
R <sub>wp</sub>	0.092	0.0621	0.073	0.0688		0.0734		
R <sub>p</sub>	0.0674	0.0497	0.0568	0.0506		0.0524		
$R_{Bragg}$	0.0496	0.0637	0.0597	0.0402		0.1542		
a(Å)	7.315(1)	7.390(1)	7.329(1)	7.329(1)	3.841(1)	7.321(0)	3.842(0)	4.502(1)
b(Å)	7.531(1)	7.537(1)	7.518(1)	7.523(1)	3.841(1)	7.529(1)	3.842086	4.502(1)
c(Å)	7.701(1)	7.703(1)	7.698(1)	7.697(1)	3.841(1)	7.695(1)	3.842086	3.151(1)
α(°)	90.21(1)	89.38(2)	89.65(1)	89.74(1)	90	89.68(1)	90	90
β(°)	89.33(1)	89.35(1)	89.37(1)	89.35(1)	90	89.29(1)	90	90
γ(°)	90.04(2)	89.61(2)	89.91(1)	89.96(2)	90	89.95(1)	90	90
Volume(ų)	424.24(9)	428.97(15)	424.13(9)	424.36(9)	56.65(2)	424.11(7)	56.72	63.86(2)
GU	0	36.49	782.2(44)	570.6	0.00	36.49	36.49	36.49
GV	-43.2	-43.20	-43.2(6)	-41.04	-43.20	-43.20	-43.20	-43.2
GW	14.26	14.26	36.21(6)	14.26	14.26	14.26	14.26	14.26
GP	0	0.00	0.00	0	0.00	0.00	0.00	0
LX	23.47	38.94	18.38	19.01(3)	27.11(2)	13.14(2)	8.58(2)	0
LY	3.346	3.35	3.35	3.346	3.35	3.35	3.35	91.36(10)
S/L	0.02555	0.03	0.03	0.02555	0.03	0.03	0.03	0.02555
H/L	0.04787	0.05	0.05	0.04787	0.05	0.05	0.05	0.05
stec	0	8.39	0.00	0.00	0.00	0.00	0.00	0.00
L <sub>23</sub>	0	0.00	-0.27	0.00	0.00	0.00	0.00	0.00

**Table S2.** Structure parameters and R-factors of Rietveld refined samples.

 $^{1}$ Triclinic phase (Space Group P<sup>1</sup>),  $^{2}$ Cubic phase (Space Group Fd<sup>3</sup>m),  $^{3}$ Tetragonal phase (Space Group P 42/m n m).

**Note**: *a*, *b*, and *c* are the lattice constants.  $\alpha$ ,  $\beta$ , and  $\gamma$  are the unit cell angles. GU, GV and GW are the Gaussian terms for U, V and W in the Cagliotti function, GP is the Gaussian crystallite size broadening, LX is the Lorentzian isotropic crystallite size broadening while LY is the isotropic strain broadening. S/L is the axial divergence S term, H/L is the axial divergence H term, stec represents Lorentzian anisotropic strain broadening, and L<sub>23</sub> is represents the anisotropic Lorentzian microstrain.

# Ir-rich regions in $W_{1-x}Ir_xO_{3-\delta}$ catalyst particles



Fig. S5 TEM images and EDS elemental mapping for O, W and Ir for particles of (a)  $W_{0.99}Ir_{0.01}O_{3-\delta}$ , (b)  $W_{0.92}Ir_{0.08}O_{3-\delta}$ , and (c)  $W_{0.57}Ir_{0.43}O_{3-\delta}$ .

#### Analysis of precursor decomposition



**Fig. S6** TGA (blue lines) and DSC (red lines) profiles of the (a) tungsten (ammonium paratungstate hydrate, (NH<sub>4</sub>)<sub>6</sub>[W<sub>12</sub>O<sub>39</sub>]·4.8H<sub>2</sub>O, molecular weight: 3024.48 g/mol) and (b) iridium (iridium acetate, (CH<sub>3</sub>COO)<sub>4</sub>Ir, molecular weight: 428.42 g/mol) precursors used in this work.

Figure S6 shows the results of thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) measurements under a flowing air atmosphere of the tungsten and iridium precursors used to produce  $W_{1-x}Ir_xO_{3-\delta}$ . This experiment was carried out in order to elucidate the thermal events of the solid-gas interfacial reactions through thermal decomposition of catalyst sample precursors and to determine the synthesis temperature at which the speciation of the crystalline phase will occur. For the W precursor, ammonium paratungstate hydrate (Figure S6a), the results indicate that the decomposition happens in three notable steps. The first weight loss step in the TGA curve occurred from 21 - 140 °C, which is attributed to the release of water as the hydrated precursor becomes anhydrous as well as the release of some trace amounts of ammonia. The weight loss due to the ·4.8H<sub>2</sub>O hydrate should theoretically be 2.86 wt%, which agreed well with the measured 2.80 wt% loss by 140 °C according to the TGA profile. DSC indicated this drying step to anhydrous ammonium paratungstate is endothermic in nature with a negative heat flow. The second weight loss step, from 140 - 364 °C, in the TGA curve could be due to ammonia and water vapor liberation according to the equation:

$$(NH_4)_6[W_{12}O_{39}] \rightarrow 6NH_3 + 3H_2O + 12WO_3$$

The observed weight loss from the TGA in this temperature region was ~5.0 wt%, which corresponded well with a theoretical value from the above loss of ammonia and water vapor of 5.15 wt%. This step was again endothermic according to the DSC curve. The third and final weight loss step occurred from 413 - 470 °C and had a sharp exothermic peak at 443 °C as shown in the DSC profile that can be ascribed to the crystallization of the amorphous WO<sub>3</sub> phase to a crystalline WO<sub>3</sub> phase. The thermally synthesized W<sub>1</sub>.  $_{x}Ir_{x}O_{3-\delta}$  samples in this work were fabricated at well above 443 °C (processed at 500 °C), so it is expected that the crystalline phase of WO<sub>3</sub> will result under the thermal processing conditions used in this work. The theoretical ceramic yield of (NH<sub>4</sub>)<sub>6</sub>[W<sub>12</sub>O<sub>39</sub>]·4.8H<sub>2</sub>O to the remaining metal oxide as per the formula:

$$Y_{WO_3}\% = \frac{12 \times MW(WO_3)}{MW(W \ precursor)} \times 100\%$$

has a value of 92.3 wt%, which was in strong agreement with the observed yield from the TGA of 92.0 wt%.

The decomposition profile of the iridium acetate precursor showed only one main step, which occurred from 230 - 294 °C, with a sharp exothermic peak at ~263 °C as seen on the DSC curve (Figure S6b). This peak is related to complex solid-gas-solid reactions probably involving the production of metallic iridium (Ir<sup>0</sup>), iridium oxide (Ir<sup>4+</sup>) and volatile hydrocarbon products. The TGA weight fraction retained at 263 °C was 46.80 wt%, while the theoretical yield for IrO<sub>2</sub> (Ir<sup>4+</sup>) and Ir (Ir<sup>0</sup>) are 52.34 wt% and 44.90 wt%, respectively. Therefore, the TGA yield is consistent with a mixed phase of Ir and IrO<sub>2</sub>. Thus, a thermally synthesized oxide catalyst at the furnace temperature of 500 °C in this work may decompose the acetate precursor into both metallic and oxide states.

#### Full Raman spectra data



**Fig. S7** Raman spectra for each plasma-oxidized  $W_{1-x}Ir_xO_{3-\delta}$  composition.

The Raman bands for all W-containing catalyst samples displayed the characteristic peaks attributed to crystalline WO<sub>3</sub>. Pure WO<sub>3</sub> (x = 0) had four well-resolved Raman peaks that correspond to the fundamental modes of WO<sub>3</sub> at 270, 324, 711, and 808 cm<sup>-1</sup>.<sup>7, 8</sup> The bands at 711 and 808 cm<sup>-1</sup> have been assigned to the W-O-W stretching frequencies, with the band at 270 cm<sup>-1</sup> corresponding to the W-O-W bending mode. The peak at 324 cm<sup>-1</sup> has been assigned to the O-W-O bending vibration. For all mixed W<sub>1-x</sub>Ir<sub>x</sub>O<sub>3-6</sub> samples there was an additional Raman band peaking at ~960 cm<sup>-1</sup> not present in either WO<sub>3</sub> or IrO<sub>2</sub>, which the literature generally attributes to the v<sub>s</sub>(W=O terminal) symmetric stretching mode.<sup>9, 10</sup> Similar Raman features have been reported for numerous metal heteropolyoxo tungstate species.<sup>10</sup> This Raman band at ~960 cm<sup>-1</sup> thus reflects distortion among the tungsten oxide framework and further supports the presence of an iridium polytungstate phase. Also, the noticeable broadening of the Raman bands of the thermal sample relative to the plasma sample have been correlated to greater nanocrystallinity.<sup>8</sup>

### **Detailed XPS characterization**



Fig. S8 Combined XPS spectra with normalized intensity for the (a) W4f and (b) Ir4f peaks.

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**Fig. S9** XPS spectra for plasma-oxidized (a-b)  $WO_3$  (x = 0) showing the (a) O1s and (b) W4f peaks, and for (c-d)  $IrO_2$  (x = 1) showing the (c) O1s and (d) Ir4f peaks.



**Fig. S10** XPS spectra for the O1s, W4f, and Ir4f peaks for plasma-oxidized (a-c)  $W_{0.57}Ir_{0.43}O_{3-\delta}$ , (d-f)  $W_{0.92}Ir_{0.08}O_{3-\delta}$ , and (g-i)  $W_{0.99}Ir_{0.01}O_{3-\delta}$ , and (j-l) thermally oxidized  $W_{0.99}Ir_{0.01}O_{3-\delta}$ .

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