Supporting Information

Crystalline Strontium Iridate Particle Catalysts for Enhanced Oxygen Evolution in Acid

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Figure S1 XRD of IrOx after Ball Milling

XRD spectra of IrO_x as-synthesized and after ball milling for 100 cycles of 1 min at 1000 rpm. Reference spectra are shown at the bottom: Ir (00-006-0598), IrO₂ (00-015-0870), and WC (00-025-1047). Ball milling reduces crystallite size but introduces WC contamination from wear of the bowl and grinding balls. WC is inert for the OER.

In effort to reduce particle size, ball milling was performed using a Planetary Micro Mill PULVERISETTE 7 premium line (Fritsch) with 20 mL tungsten carbide (WC) grinding bowls and 80 g of 0.6 mm WC grinding balls. Due the expense of Ir, it was undesirable to synthesize the multi-gram material quantity necessary for ball milling. Instead, an inert, water soluble but isopropyl alcohol (IPA) insoluble salt was added to reach the required solid mass for milling. To reach small particle sizes, wet milling was performed with isopropyl alcohol added to reach a motor oil consistency of the catalyst/salt slurry. Approximately 200 mg of catalyst was

combined with 6 g of sodium chloride (ground with mortar and pestle to a fine powder) and 5 mL of IPA. Milling was performed with 100 cycles of 1 min of grinding at 1000 rpm followed by 9 min of rest to avoid overheating of the bowls. Additional IPA was added intermittently to maintain a motor oil slurry consistency. The catalyst material was separated from the NaCl salt by repeated sonification and centrifugation with water. Inevitable WC contamination for the milling process was introduced, however, WC oxides during OER testing and W oxide is known to be inert towards the OER.^[1]

PERCHLORIC ACID



Figure S2 XPS Surface Composition of Catalysts As-Synthesized, After Acid Leaching, and After Electrochemistry in Perchloric Acid

Surface composition represented by Sr molar percentage determined by XPS high resolution scans of strontium iridate materials as-synthesized, after 24 h acid leaching in 0.1 M HClO₄, and after quasi steady-state polarization in 0.1 M HClO₄. There is a significant decrease in surface Sr after acid leaching and even more so after electrochemistry.



Figure S3 XPS Before and After Electrochemistry in Perchloric Acid

XPS before (solid lines) and after (dashed lines) quasi steady-state polarization in 0.1 M HClO₄ shown in Figure 3. (a) Ir 4f, (b) Sr 3d, and (c) O 1s high resolution XPS spectra. IrO_x has been ball milled to decrease particle size. The Sr 3d peak positions are dependent on the material phase, with S4IrO₆, Sr₂IrO₄, and SrIrO₃ having Sr 3d peak positions in the range of 131-136 eV, 136-139 eV, and 132-134 eV, respectively. According to Ref. 2, electrons from Ir 4f and Sr 3d peaks have escape depths of approximately 1.1 and 3.5 nm, respectively.



Figure S4 ICP-MS of Ir and Sr Dissolution Over Time for Sr₂IrO₄ in Perchloric Acid

(a) Stability of Sr_2IrO_4 evaluated for 30 min, 2 h, and 6 h at 10 mA cm⁻²_{geo} in 0.1 M HClO₄. Corresponding ICP-MS measured Ir (b) and Sr (c) dissolution normalized to dissolution after 6 h.



Figure S5 Mass Loss and XRD after Acid Leaching in Perchloric Acid

(a) Total mass loss percent after acid leaching for 24 h in 0.1 M HClO₄ compared to the additive Sr and Ir mass loss percent calculated from ICP electrolyte analysis after 6 h stability testing at 10 mA cm⁻²_{geo}. XRD spectra of Sr₄IrO₆ (b), Sr₂IrO₄ (c), and SrIrO₃ (d) after 24 h acid leaching in 0.1 M HClO₄ show that bulk crystallinity is unchanged.



Figure S6 TEM After Electrochemistry in Perchloric Acid

TEM micrographs of (a, d) SrIrO₃, (b,e) Sr₂IrO₄, and (c,f) Sr₄IrO₆ after quasi steady-state polarization in 0.1 M HClO₄ shown in Figure 3. Sr₄IrO₆ was observed to change morphology under the electron beam. The well-defined lattice spacing observed for SrIrO₃ of 0.28 nm is consistent with (114) SrIrO₃. Lattice analysis of Sr₂IrO₄ is complicated due to large particle

thickness obfuscating clear lattice analysis; however, spacings of 0.23 ± 0.1 nm and 0.19 ± 0.1 nm were identified. The former is consistent with IrO₂ (200) or Sr₂IrO₄ (213) or (215) and the latter is consistent with Sr₂IrO₄ (220). Additional high-resolution analysis is necessary to definitively identify surface crystal structure after electrochemistry.



Figure S7 TEM-EDS Bulk Composition Before and After Electrochemistry

TEM-EDS of Sr iridates before (solid lines) and after quasi steady-state polarization (dashed lines) in 0.1 M HClO₄ shown in Figure 3. Ir and Sr reference peaks are shown in black and gray, respectively. Sr₂IrO₄ and Sr₄IrO₆ show significant decreases in bulk Sr content following electrochemistry, consistent with ICP-MS and XPS.



Figure S8 STEM-EDS Maps After Electrochemistry in Perchloric Acid

STEM-EDS normalized intensity maps of Sr₂IrO₄ (left), and Sr₄IrO₆ (right) after OER testing in 0.1 M HClO₄ shown in Figure 3. (a) STEM micrograph for which intensity maps were taken. (b) Overlay of Sr (red) and Ir (blue) intensity maps.

Catalyst	BET SA [m ² _{cat} g ⁻¹]	i _{1.55 V vs. RHE} [mA cm ⁻² geo]	i _{1.55 V vs. RHE} [mA cm ⁻² cat]	Tafel Slope Low ^a [mV dec ⁻¹]	Tafel Slope High ^b [mV dec ⁻¹]
Ir/C	70-200	33	0.2-0.6	60	84
Sr ₄ IrO ₆	12	22	0.7	50	134
Sr ₂ IrO ₄	2.8	31	6.1	45	73
SrIrO ₃	3.2	4.0	0.9	63	91
IrO _x -Mill		1.0		68	106

Table S1: Activity Summary in Percloric Acid

^{a)} Tafel slope fitted at low current densities (up to ~10 mA cm⁻²_{geo}). ^{b)} Tafel slope fitted at high current densities (~10-100 mA cm⁻²_{geo}).



Figure S9 Electrochemical Performance in Sulfuric Acid

(a) OER activity in 0.5 M H₂SO₄ for Sr iridates and Ir/C nanoparticles (Premetek) with loadings of 80 μ g_{Ir} cm⁻². (b) Mass activity Tafel plot. (c) Overpotential summary for materials at 10 and 20 mA cm⁻²_{geo}. (d) Galvanostatic stability test at 10 mA cm⁻²_{geo}. As was observed in perchloric electrolyte, materials degradation as the potential approaches 1.7 V vs. RHE likely due to carbon support corrosion or glassy carbon disk passivation.

Catalyst	BET SA ^a [m ² g ⁻¹]	η _{10 mA cm⁻²geo} [mV]	η _{300 A g} -1 _{Ir} [mV]	Tafel Slope Low ^b [mV dec ⁻¹]	Tafel Slope High ^c [mV dec ⁻¹]
Ir/C		305	331	63	81
Sr ₄ IrO ₆	N/A	342	370	65	83
Sr ₂ IrO ₄	N/A	291	315	40	120
SrIrO ₃	N/A	378	408	58	86
IrO _x -Mill	N/A	442	486	85	120

Table S2: Electrochemical Performance Summary of Sr Iridates in Sulfuric Acid

^{a)}BET not applicable to sulfuric acid leached particles due to insoluble SrSO₄ formation. IrO_x contains WC nanoparticles from ball milling and its surface area thus cannot be accurately determined with BET. ^{b)}Low indicates Tafel slope fitted at low current densities (up to ~10 mA cm⁻²_{geo}). ^{c)}High indicates Tafel slope fitted at high current densities (~10-100 mA cm⁻²_{geo}).



Figure S10 Activity Comparison of Perchloric and Sulfuric Acid Electrolyte

(a) Quasi steady-state OER polarization curves for Ir/C (Premetek), Sr4IrO₆, Sr₂IrO₄, SrIrO₃, and IrO_x in 0.1 M HClO₄ (solid lines) and 0.5 M H₂SO₄ (dashed lines). (b) Overpotential required to achieve 10 mA cm⁻²_{geo} for particle catalysts in 0.1 M HClO₄ (solid bars) and 0.5 M H₂SO₄ (striped bars). All catalysts show superior activity in 0.1 M HClO₄ electrolyte.



Figure S11 ICP-MS of Ir and Sr Dissolution of Sr Iridates after Stability in Sulfuric Acid

ICP-MS measured Ir (a) and Sr (b) dissolution percentage during 6 h galvanostatic stability tests of Sr₄IrO₆, Sr₂IrO₄, and SrIrO₃. The electrolyte was analyzed after stability measurements at 10 mA cm⁻²_{geo} in 0.5 M H₂SO₄. As was the case for perchloric acid, catastrophic failure during electrocatalysis does not translate to complete material dissolution as both SrIrO₃ and IrO_x show lower Ir dissolution rates than the more electrochemically stable Ir/C (Premetek).



Figure S12 ICP-MS of Ir and Sr Dissolution of Sr₂IrO₄ with Time in Sulfuric Acid

(a) Stability of Sr_2IrO_4 at 2 h, 4 h, and 6 h at 10 mA cm⁻²_{geo} in 0.5 M H₂SO₄. Corresponding ICP-MS measured Ir (b) and Sr (c) dissolution normalized to the dissolution after 6 h. After the first two hours of stability testing, 70% and 90% of the amount of Ir and Sr dissolved after 6 h, respectively, has already been dissolved. Like in perchloric acid, material loss occurs more rapidly at the beginning of testing as unstable Sr species are leached and an Ir-rich surface structure is formed.



Figure S13 TEM Micrographs of Sr Iridates after Electrochemistry in Sulfuric Acid

TEM images of (a,d) SrIrO₃, (b,e) Sr₂IrO₄, and (c,f) Sr₄IrO₆ after quasi steady-state OER polarization in 0.5 M H₂SO₄ shown in Figure S.9. Surfaces restructure but remain crystalline after electrochemistry.





STEM-EDS normalized intensity maps of SrIrO₃ (left), Sr₂IrO₄ (middle), and Sr₄IrO₆ (right) after quasi steady-state OER polarization in 0.5 M H₂SO₄ shown in Figure S.9. (a) STEM micrograph for which Sr (c) and Ir (d) intensity maps were taken. (b) Overlay of Sr and Ir intensity maps. Sr₄IrO₆ suffers from excessive SrSO₄ formation resulting in Sr-only particles.



Figure S15 XRD of Sr₂IrO₄ after Acid Leaching and Electrochemistry in Sulfuric Acid

XRD spectra of Sr₂IrO₄ after acid leaching and after quasi steady-state OER polarization in 0.5 M H₂SO₄ shown in Figure S.9. The curve for the material following electrochemistry was background subtracted and smoothed with adjacent averaging via Origin Software 9.1. Spectra match the SrSO₄ reference shown at bottom.



Figure S16 XRD of Sr Iridates after Acid Leaching in Sulfuric Acid

XRD spectra of IrO_x (a), Sr_4IrO_6 (b), Sr_2IrO_4 (c), and $SrIrO_3$ (d) after 24 h acid leaching in 0.5 M H₂SO₄. Spectra of IrO_x and $SrIrO_3$ do not change whereas Sr_4IrO_6 and Sr_2IrO_4 match $SrSO_4$ after acid leaching. The higher Sr content and leaching in Sr_4IrO_6 and Sr_2IrO_4 likely promotes $SrSO_4$ formation.



Figure S17 XPS Before and After Electrochemistry in Sulfuric Acid

XPS before (solid lines) and after (dashed lines) quasi steady-state polarization in 0.5 M H₂SO₄ shown in Figure S.9. (a) Ir 4f, (b) Sr 3d, and (c) O 1s high resolution XPS peaks. The Ir $4f_{7/2}$ binding energies of Sr₄IrO₆, Sr₂IrO₄, and SrIrO₃ (63.0, 63.1, and 63.2 eV, respectively) have converged at significantly higher energy than ball milled IrO_x (62.5 eV). The O 1s peaks are identical in location to those following perchloric acid testing (532.6 and 535.0 eV). In contrast to observations in perchloric acid, the opposite trend is observed in sulfuric acid where greater initial Sr content results in greater surface Sr following electrochemistry. Unfortunately, due to the unavoidable presence of poorly soluble SrSO₄ upon Sr dissolution in sulfuric acid, it is difficult to differentiate between Sr signal from the SrSO₄ and the active catalyst material. However, from ICP-MS and XRD studies, higher initial Sr content leads to higher Sr dissolution and increased SrSO₄ formation. Thus, increased SrSO₄ formation contributing to the XPS signal may explain the increasing Sr XPS signal with Sr content.



Figure S18 Cyclic Voltammograms of Sr Iridates in Perchloric Acid

(a, b) Cyclic voltammograms of Sr iridates in O₂-saturated 0.1 M perchloric acid at 10 mV s⁻¹ and 1600 rpm. Catalysts have loadings of 80 μ gl_r cm⁻². Sr₂IrO₄ and Sr₄IrO₆ show redox features centered around 1.15 and 1.4 V vs. RHE. These peaks have been previously observed on Iroxides and attributed to OH and O adsorption, respectively,³ or the redox transitions from Ir(III)/Ir(IV)⁴ and Ir(IV)/Ir(VI),⁵ respectively. There are no readily observable redox features for Ir/C (Premetek), ball-milled IrO_x, or SrIrO₃ potentially due to differences in the surface chemistries and geometries. Differences in capacitances are likely due to the differences in carbon loadings between the materials: 320 μ gc cm⁻², 320 μ gc cm⁻², 339 μ gc cm⁻², 612 μ gc cm⁻², 466 μ gc cm⁻², and 470 μ gc cm⁻² for Ir/C, IrO_x, Sr₄IrO₆, Sr₂IrO₄, SrIrO₃, and C, respectively. These numbers correspond to 20, 20, 40, 20, and 20 wt% metal for the respective catalyst inks. Surface areas of the catalyst materials may also play a role in the apparent capacitance of the materials (e.g. IrO_x and SrIrO₃ are expected to have lower surface areas than Ir/C (Premetek) which may result in their lower apparent capacitance). In-situ synchrotron-based techniques may help sheld light on the dependence of the redox behavior on the catalyst chemistry and should be the subject of future work.

NOTE ON SURFACE AREA NORMALIZATION

Unfortunately, in the OER catalyst literature to date, there remains no indisputable surface area normalization technique. As discussed in the main text, hydrogen underpotential deposition and CO stripping do not occur on oxidized Ir surfaces.⁶ While double layer capacitance can be used for film and unsupported catalysts, this method is not appropriate for supported particle systems as the support material significantly contributes to the measured double layer capacitance. The support contribution can be affected by the dispersion, distribution, and interaction of the particles with the support in the catalyst layer. Mercury underpotential deposition has been shown to be one of the most reliable methods of surface area determination for Ir oxide materials, however it involves toxic materials.⁶ Redox peak integration can be used for materials systems that have well-defined features of known oxidation state transitions; however, the use of this method for the Ir oxides studied here is dubious for several reasons. First, redox features are highly affected by chemical, structural, and electronic properties and are not observed for most of the catalyst systems studied here. Secondly, the origin for any redox-type features observed are unknown and would require rigorous in-situ synchrotron techniques to identify, which are out of the scope of the current study. Indeed, the only catalyst that is observed to have some redox-type features is Sr₂IrO₄ and the origin of the features is unknown and is material dependent due to differences in structural and electronic properties. This is evidenced by the fact that redox features are not even observed for the other materials

studied. Therefore, redox peak integration cannot be used to compare the surface areas of these catalyst materials with any reliability.

In this report, BET surface area was used to determine the surface area of the catalyst particles. This was chosen not as the perfect method for surface area determination, but as the most appropriate given current knowledge in the field. BET uses nitrogen adsorption to determine the surface area of powder catalysts. A previous report has found that BET surface area is well aligned with mercury underpotential deposition surface area of Ir oxide materials (BET is approximately 15-20% higher on average compared to Hg underpotential deposition). The consistency of BET surface area with an in-situ method indicates that BET can be used reliably for electrocatalyst materials. It should be noted, that BET is not a perfect method. Material changes can occur during electrochemistry that may affect surface area and reduce the reliability of BET-based measurements. Here, the catalysts were first soaked in acid for 24 h and dried prior to BET analysis to take into account roughening that might occur after Sr leaching during electrochemical testing; however, acid soaking does not perfectly mimic the electrochemical environment during OER testing and errors in surface area may result. Despite its imperfections, BET is supported by experts in the field given the current lack of a superior reliable and safe technique.⁶⁻⁸ The identification of a robust, accurate, and safe in-situ surface area determination technique is of utmost importance to the field and should be the subject of significant future effort.

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