Electronic Supplementary Information (ESI) for

An IrSi oxide film as highly active water–oxidation catalyst in acidic media

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A Table of Contents

Experimental page 1
Table S1 page 6
Fig. S1 page 7
Fig. S2 page 8
Fig. S3 page 9
Fig. S4 page 10
Fig. S5 page 11
Fig. S6 page 12
Fig. S7 page 13
Fig. S8 page 14
Fig. S9 page 15
Fig. S10 page 16
Fig. S11 page 17
Fig. S12 page 18
Fig. S13 page 19
Fig. S14 page 20
Fig. S15 page 21
Fig. S16 page 22
Fig. S17 page 23
Fig. S18 page 24
Fig. S19 page 25
Fig. S20 page 26
References page 27
Experimental

Materials and methods. All experiments were carried out under an N$_2$ atmosphere by using standard Schlenk techniques and a glovebox. [Ir$^\mathrm{V}$(η$^5$–C$_5$Me$_5$)(H)$_2$(SiEt$_3$)$_2$] (1) was prepared following literature method.$^1$ A fluorine doped tin oxide (FTO) coated glass slide (Type VU) was purchased from AGC Fabritech Co., Ltd. Distilled water was purchased from Wako Pure Chemical Industries, Ltd. H$_2^{18}$O (98 atom%) was purchased from TAIYO NIPPON SANSO CO., Ltd. All other chemicals were obtained from commercial sources and used as received.

A Si oxide–doped Ir metal film (film $A_1$) and a Si oxide–doped Ir oxide film (IrSi oxide film $A_2$) were analysed by scanning electron microscopy (SEM) using a Hitachi SU8000 and X–ray photoelectron spectroscopy (XPS) using an ULVAC PHI 5000 VersaProbe II system with an Al anode X–ray source. Binding energies were calibrated by the Sn 3d$_{5/2}$ peak of Sn oxide of FTO at 486.7 eV.$^2$ Ar ion sputtering was conducted for 45 min to etch the surface of film. Scanning transmission electron microscope (STEM) with energy dispersive X–ray spectroscopy (EDS) mappings was carried out by a JEOL JEM–ARM 200F with a silicon drift detector (SDD). X–ray diffraction (XRD) patterns were measured using an X–ray diffractometer (Rigaku SmartLab) with Cu–Kα radiation generated at 40 kV and 30 mA {scan speed: 0.01° min$^{-1}$ (2θ = 20–80°)}. Electrochemical measurements were performed using an ALS Electrochemical Analyzer Model 600D and 760DT. Gas chromatography mass spectrometry (GC–MS) was performed by using a SHIMADZU GCMS–QP 5050. Impedance spectra were recorded on a TOYO Corporation Fuel Cell Test System 890CL and Solartron Models 1287A Potentiostat/Galvanostat and 1255B Frequency Response Analyzer.

pH adjustment. The pH of 1.0 M phosphate buffer solutions were adjusted by using H$_2$SO$_4$/H$_2$O (pH 3.0–5.0), 1.0 M phosphate buffer (pH 7.0) and NaOH/H$_2$O (9.0–13.0). In the pH range of 1.0–12.0, the pH values of the solutions were determined by a pH meter (model: TOA HM20J) equipped with a pH combination electrode (model: TOA GST–5725C). Below pH 1.0 and above 12.0, pH was estimated by concentration of the solution; for example, pH values of 0.50 M H$_2$SO$_4$/H$_2$O and 0.1 M NaOH/H$_2$O were estimated to be 0.0 and 13.0, respectively.

Thermal properties of 1. Thermal properties were analysed under a flow of N$_2$ gas {flow rate: 200 standard cc min$^{-1}$ (sccm)} by thermogravimetry–differential thermal analysis (TG–DTA) using an EXSTAR TG–DTA7300 instrument. Complex 1 (5.0 mg)
was loaded in an open–type aluminium crucible. The measurement was made at atmospheric pressure with a heating rate of 2.0 °C min⁻¹.

**Preparation of the film A₁ from metal organic chemical vapour deposition (MOCVD) of 1.** Deposition of the film A₁ onto an FTO coated glass slide was conducted using a tube type MOCVD reactor (glass tube diameter: 4.0 cm). The distance between 1 and the FTO substrate was ca. 5.0 cm. Complex 1 was vaporised at ca. 95 °C under a pressure of 55–60 Pa with a flow of O₂ gas (40 sccm) as the carrier gas and the substrate was maintained at 400 °C. The deposition time was set to a period of 5 min.

**Preparation of the film A₂ from electrochemical oxidation of the film A₁.** Electrochemical treatment was conducted using the film A₁ deposited on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode at pH 0.0 in 0.50 M H₂SO₄/H₂O. The potential sweep from –0.30 to 1.5 V vs Ag/AgCl was continued until the current density at 1.5 V vs Ag/AgCl became saturated to afford the film A₂. The surface of the film A₂ was washed with distilled water and dry in air before use.

**Determination of composition of the films A₁ and A₂.** The atomic ratios of the films A₁ and A₂ were determined by EDS analysis. A₁ (atm%): Ir, 19; Si, 28; O, 53. A₂ inside (atm%): Ir, 19%; Si, 31%; O, 50%. A₂ outside (atm%): Ir, 15%; Si, 23%; O, 62%.

**Electrochemical water–oxidation by the film A₂.** The cyclic voltammograms were measured using the film A₂ deposited on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode at scan rate of 100 mV s⁻¹.

**Determination of the electroactive Ir on the film A₂.** The mol of electroactive Ir on the film A₂ on FTO coated glass slide was estimated according to the literature methods (I)³ and (II)⁴ from anodic wave of Ir³⁺/Ir⁴⁺ observed in cyclic voltammogram in 0.50 M H₂SO₄/H₂O at pH 0.0 as shown in Fig. S16 and S18. Before water–oxidation experiments, the mol of electroactive Ir was determined each time. The procedures are as follows.
Method (I)
Slope of Fig. S16b = \((n^2 \times F^2 \times A \times \Gamma) \div (4 \times R \times T)\)
where \(n\) = number of electrons, \(F\) = Faraday’s constant (C/mol), \(A\) = surface area of electrode (cm\(^2\)), \(\Gamma\) = surface concentration of Ir (mol/cm\(^2\)), \(R\) = ideal gas constant (J/mol K) and \(T\) = temperature (K).

\[3.10 \times 10^{-3} \text{ (A s/V = C/V = C}/\text{J}, \text{slope determined by Fig. S16b)}\]
\[= \{1^2 \times 96485^2 \text{ (C}^2/\text{mol}^2\} \times 1.0 \text{ (cm}^2\} \times \Gamma \text{ (mol/cm}^2\}) / \{4 \times 8.314 \text{ (J/mol K) } \times 296 \text{ (K)}\}\]
\[= \{9309355225 \text{ (C}^2 \text{ cm}^2/\text{mol}^2\} \times \Gamma \text{ (mol/cm}^2\}) / 9844 \text{ (J/mol)}\]
\[\therefore \Gamma \text{ (mol/cm}^2\} = \{3.10 \times 10^{-3} \text{ (C}/\text{J} \times 9744 \text{ (J/mol)} \} / 9309355225 \text{ (C}^2 \text{ cm}^2/\text{mol}^2\})\]
\[= 2.56 \times 10^{-9} \text{ (mol cm}^{-2}\)

Method (II)

Oxygen + n\text{e}^- \rightarrow \text{Red}

Faraday’s law: \(Q = n \times F \times A \times \Gamma\)
where \(Q\) = total charge (C), \(n\) = number of electrons, \(F\) = Faraday’s constant (C/mol), \(A\) = surface area of electrode (cm\(^2\)) and \(\Gamma\) = surface concentration of Ir (mol/cm\(^2\)).

\(Q\) corresponds to the area (integral) of anodic wave of Ir\(^{III}\)/Ir\(^{IV}\).

\(Q\) is determined as \(2.32 \times 10^{-4} \text{ C}\) by Gaussian analysis based on Fig. S18.\(^6\)

Then, \(\Gamma\) was calculated as follows.

\[
\Gamma \text{ (mol/cm}^2\} = Q / n \times F \times A
\]
\[= 2.32 \times 10^{-4} \text{ (C)} / 1 \times 96485 \text{ (C/mol)} \times 1.0 \text{ (cm}^2\)
\[= 2.40 \times 10^{-9} \text{ (mol cm}^{-2}\)

**Determination of the turnover frequency (TOF) for water oxidation by the film A\(_2\) at pH 0.0.** The electrochemical water-oxidation was conducted using the film A\(_2\) on FTO coated glass slide as a working electrode for 30 min at potentials from 1.61 to 1.91 V vs NHE (iR–free potentials of 1.46 to 1.76 V vs NHE) in 0.50 M H\(_2\)SO\(_4\)/H\(_2\)O at pH 0.0. The evolved O\(_2\) gas was collected by water displacement method. The volume of O\(_2\) was corrected by the pressure and temperature according to a combined gas law and the TOF was determined as the following equations.
Ideal gas law: $PV = nRT$

where $n = \text{mol of gas (mol)}$, $P = \text{pressure of the gas (atm)}$, $V = \text{volume of the gas (L)}$, $R = \text{gas constant (0.082 L atm/mol K)}$ and $T = \text{temperature of gas (K)}$.  

The mol of O$_2$ was determined for the case of 1.91 V vs NHE (iR–free potential of 1.76 V vs NHE).

$$
\begin{align*}
n (\text{mol}) &= \frac{P \text{ (atm)} \times V \text{ (L)}}{R \text{ (L atm/mol K)} \times T \text{ (K)}} \\
&= \frac{1.0 \times 0.80 \times 10^{-3} \text{ (L)}}{0.082 \text{ (L atm/mol K)} \times 296 \text{ (K)}} \\
&= 3.30 \times 10^{-5} \text{ (mol)}
\end{align*}
$$

Then, TOF was determined as follows.

$$
\begin{align*}
\text{TOF} &= \frac{\text{mol of O}_2 / \text{mol of Ir}}{\text{time (s)}} \\
&= \frac{3.30 \times 10^{-5} \text{ (mol)}}{2.56 \times 10^{-9} \text{ (mol/cm$^2$)} \times 1.0 \text{ (cm$^2$)}} / 1800 \text{ (s)} \\
&= 7.2 \text{ (s$^{-1}$)}
\end{align*}
$$

**Determination of the TOF for water oxidation by the film A$_2$ at pH 7.0.** The TOF for electrochemical water–oxidation by the film A$_2$ at pH 7.0 at 1.31 V vs Ag/AgCl (iR–free potential of 1.36 V vs NHE) was determined by the same procedure, method (I), as the case for film A$_2$ at pH 0.0. The TOF value was determined as 5.3 s$^{-1}$.

**Determination of the TOF for water oxidation by the film C at pH 0.0.** The film C was prepared by the literature method.$^7$ The mol of electroactive Ir on the film C ($1.85 \times 10^{-9} \text{ mol cm}^2$, Fig. S17) and the TOF for electrochemical water–oxidation by the film C at pH 0.0 at 1.71 V vs Ag/AgCl were determined by the same procedure, method (I), as the case for film A$_2$ except the film C used. The TOF value was determined as 2.5 s$^{-1}$.

**Determination of the voltammetric charges (q*) of the films A$_2$ and C.** The voltammetric charges (q*) were determined as $6.8 \times 10^{-4} \text{ C cm}^2$ for film A$_2$ and $2.3 \times 10^{-4} \text{ C cm}^2$ for film C, respectively, on the basis of the grey–shaded areas of Fig. S19.$^8$–$^{12}$

**Impedance measurement.** Impedance spectra were measured on the 3–electrode setup by connecting RE, WE and CE to Ag/AgCl reference electrode, film A$_2$ and Pt, respectively. An iR–free potential is obtained from the following equation: potential = $V - iR$, where $V$ is voltage, $i$ is current density and $R$ is Ohmic resistance that is determined by each impedance measurement at pH 0.0–13.0 as shown in Fig. S13.
**Isotope-labelling experiment for oxidation of H$_2^{18}$O by the film A$_2$.** The electrochemical water-oxidation by the film A$_2$ on FTO coated glass slide at 1.71 V vs NHE was performed in 0.50 M H$_2$SO$_4$/H$_2$O containing 5.0% H$_2^{18}$O at pH 0.0. The evolved dioxygen gases (O$_2$, $^{16}$O$_2$, $^{16}$O$_2^{18}$ and $^{18}$O$_2$) were identified by using GC–MS. The control experiment was conducted in 0.50 M H$_2$SO$_4$/H$_2$O without H$_2^{18}$O. No $^{18}$O–labelled dioxygen gas was observed.
<table>
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†: TOF for electrochemical water-oxidation. ‡: Amount of evolved O₂ from electrochemical water-oxidation. §: Current density of electrochemical water-oxidation of the films A₂, B, C, D or E divided by that of the Ir oxide. ¢: Not determined. ¶: Not reported. £: We determined the TOF of water oxidation by the film C at pH 0.0, which was prepared according to the literature method.⁷
**Fig. S1** Preparation procedures of the films $A_1$, $A_2$, $B$, $C$, $D$ and $E$.
Fig. S2 TG–DTA analysis of [IrV(η⁵–C₅Me₅)(H)(SiEt₃)₂] (1) (flow gas: N₂, flow rate: 200 sccm, heating rate: 2.0 °C min⁻¹).
**Fig. S3** Cyclic voltammograms of the film A₁ on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode at pH 0.0 in 0.50 M H₂SO₄/H₂O at 100 mV s⁻¹.
Fig. S4 XP spectra of the film A₁ on FTO coated glass slide (a) before and (b) after being etched by sputtering with Ar ions for 45 min. Magnifications of Ir 4f₇/₂ and 4f₅/₂ peaks (c) and (d) in the spectrum (a) and (b), respectively. The black and red lines correspond to XP spectra before and after Ar sputtering, respectively.
**Fig. S5** XP spectra of the film $A_2$ on FTO coated glass slide (a) before and (b) after being etched by sputtering with Ar ions for 45 min. Magnifications of Ir 4$f$, and 4$g$ peaks (c) and (d) in the spectrum (a) and (b), respectively. The black and red lines correspond to XP spectra before and after Ar sputtering, respectively.
Fig. S6 A STEM image and elemental mappings for Ir (blue), Si (orange), O (red) and Sn (green) of the film $A_1$ on FTO coated glass slide.
**Fig. S7** A STEM image and elemental mappings for Ir (blue), Si (orange), O (red) and Sn (green) of the film $A_2$ on FTO coated glass slide.
Fig. S8 (a) A STEM image of the film A₁ on FTO coated glass slide and (b) the line–profile of Ir, Si and O atoms.
Fig. S9 (a) A STEM image of the film $A_2$ on FTO coated glass slide and (b) the line-profile of Ir, Si and O atoms.
Fig. S10 SEM images of (a) the film $A_1$ on FTO coated glass slide, (b) the film $A_2$ on FTO coated glass slide and (c) FTO coated glass slide.
Fig. S11 XRD spectra of (a) FTO coated glass slide, (b) film $A_1$ on FTO coated glass slide, (c) film $A_2$ on FTO coated glass slide and (d) film $A_2$ on FTO coated glass slide heated at 600 °C for 2 h. Diffraction peaks †, ‡ and § are derived from (110), (101) and (200) of Ir oxide, respectively.
Fig. S12 (a) Cyclic voltammograms of the film A2 on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in aqueous solutions in the pH range of 0.0–13.0 at 100 mV s⁻¹. The potentials were corrected for the Ohmic drops that were determined by the impedance spectra as shown in Fig. S13. (b) Cyclic voltammograms (a) corrected for equilibrium potentials vs RHE at pH 0.0–13.0.
**Fig. S13** Impedance spectra of water oxidation by the film A₂ in aqueous solution at (a) pH 0.0, (b) pH 3.0, (c) pH 5.0, (d) pH 7.0, (e) pH 9.0 and (f) pH 13.0. These spectra were measured under open–circuit conditions by changing the frequency from 0.1 to 10000 Hz. Black solid lines are curve fittings as a following circuit. Based on these fitting results, the Ohmic resistances are determined as 14.9, 21.9, 23.8, 26.1, 24.0 and 42.4 Ω cm² for pH 0.0, 3.0, 5.0, 7.0, 9.0 and 13.0, respectively.
**Fig. S14** Positive–ion GC mass spectra obtained from the electrochemical water–oxidation by the film A\textsubscript{2} on FTO coated glass slide in 0.50 M H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O at pH 0.0 (a) without and (b) with 5% H\textsubscript{2}\textsuperscript{18}O.
Fig. S15 Tafel plots of water oxidation by the film A2 in aqueous solutions in the pH range of 0.0–13.0. The Tafel slopes were determined as 141, 176, 211, 274, 318 and 416 mV/decade for pH 0.0, 3.0, 5.0, 7.0, 9.0 and 13.0, respectively.
**Fig. S16** (a) Cyclic voltammograms of the film A₂ at different scan rates (the film A₂ on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.50 M H₂SO₄/H₂O at pH 0.0 in the range of scan rates 25–500 mV s⁻¹). (b) Dependence of peak current on different scan rates for (Ir³⁺/Ir⁴⁺) = 0.78 V. **Method (I):** Slope is $3.10 \times 10^{-3}$, and the mol of electroactive Ir site of film A₂ is estimated as $2.56 \times 10^{-9}$ mol cm⁻².
Fig. S17 (a) Cyclic voltammograms of the film C at different scan rates (the film C on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.50 M H₂SO₄/H₂O at pH 0.0 in the range of scan rates 25–500 mV s⁻¹). (b) Dependence of peak current on different scan rates for (Ir^{III}/Ir^{IV}) = 0.78 V. **Method (I)**: Slope is $1.75 \times 10^{-3}$, and the mol of electroactive Ir site of film C is estimated as $1.85 \times 10^{-9}$ mol cm⁻².
Fig. S18 Cyclic voltammograms (black lines) of (a) the film A_2 and (b) the film C with the results of Gaussian analysis (red, blue and green lines) (the film A_2 or C on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.50 M H_2SO_4/H_2O at pH 0.0 at 100 mV s\(^{-1}\)). Method (II): The areas of films A_2 and C (Ir^{III}/Ir^{IV}, red line) are 2.32 \times 10^{-4} and 1.70 \times 10^{-4} C, respectively. The mol of electroactive Ir sites of films A_2 and C are estimated as 2.40 \times 10^{-9} and 1.76 \times 10^{-9} mol cm\(^{-2}\), respectively.
Fig. S19 Cyclic voltammograms of (a) the film A₂ and (b) the film C on FTO coated glass slide as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.50 M H₂SO₄/H₂O at pH 0.0 at 100 mV s⁻¹. The grey–shaded areas show the voltammetric charges (q*) of films A₂ (6.8 \times 10^{-4} \text{ C cm}^{-2}) and C (2.3 \times 10^{-4} \text{ C cm}^{-2}).
Fig. S20 Constant chronopotentiometric stability measurement at current density of 1.0 mA cm\(^{-2}\) in 0.50 M H\(_2\)SO\(_4\)/H\(_2\)O at pH 0.0. The film A\(_2\) on FTO coated glass slide, Pt wire and Ag/AgCl are used as working, counter and reference electrodes, respectively.
References