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Electronic Supplementary Information

Improving the Activity and Stability of Ir Catalysts for PEM Electrolyzer Anodes by SnO_2:Sb Aerogel Supports: Does V Addition play an Active Role in Electrocatalysis?

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Experimental details:

Aerogel synthesis:

SnO_2:Sb aerogels were prepared using the same method described previously.[1] A solution containing tin isopropoxide (Alfa Aesar, 99% (metals basis), 10% w/v in isopropanol) in isopropanol (iPrOH) and antimony (III) isopropoxide (Alfa Aesar, 99.9% (metals basis)) was prepared and placed under magnetic stirring to obtain a theoretical dopant rate of 10 at.%. A solution of nitric acid (HNO_3, Alfa Aesar, 2N), water and isopropanol (Acros Organics, 99.5 %) was added dropwise to the first solution; a gel formed after few minutes. Gels were aged for two days, then washed in isopropanol and dried with CO_2 at supercritical conditions (80 bars, 40 °C). As formed aerogels were thermally treated in air at 600 °C for 5 h. After calcination, the SnO_2:Sb aerogel color turned to blue.

Catalysts preparation:

The SnO_2:Sb aerogel supported iridium catalyst was synthesized via a conventional sodium borohydride reduction method at room temperature, as we reported previously.[2] In brief, 0.585 g cetyltrimethylammonium bromide (CTAB, Merck Millipore) and 0.075 g as-prepared SnO_2:Sb aerogel were dispersed in a 60 mL anhydrous ethanol solution (VWR Chemicals) and magnetically stirred for 30 minutes under an argon atmosphere. The $IrCl_3$ precursor solution composed of 0.0498 g anhydrous iridium (III) chloride ($IrCl_3$, Alfa Aesar) and 25 mL anhydrous ethanol was then transferred to a reaction suspension, maintaining magnetic stirring at room temperature with an argon flow for another 3 hours. To reduce Ir^{3+}, 0.304 g sodium borohydride ($NaBH_4$, VWR Chemicals) dissolved in 10 mL anhydrous ethanol solution was added to the reaction suspension at a rate of 2 mL min^{-1} under vigorous stirring. The reaction mixture was kept for 4 hours under the same conditions until the reduction reaction completed. Afterwards, the suspension containing Ir/SnO_2:Sb was centrifuged and rinsed with ample amounts of pure ethanol and deionized water to remove CTAB and the residual non-reduced $IrCl_3$. Finally, the synthesized catalyst was dried overnight at 40°C in air. The stoichiometric loading of Ir on SnO_2:Sb was 30 wt.%. For the V modified Ir/SnO_2:Sb-mod-V, 0.032 g ammonium metavanadate (ACS, 99.0%) was added to $IrCl_3$ precursor solution, achieving a mass ratio (vanadium to iridium) of 3:7. Unsupported IrO_x was prepared by the same route but without adding SnO_2:Sb aerogel.

X-ray Photoelectron Spectroscopy (XPS) and deconvolution:

XPS analysis was conducted using a Thermo Scientific ESCALAB 250 ultra-high vacuum (UHV) facility with a base pressure of 1×10^{-9} mbar. Al Kα radiation was used as the X-ray source (Thermo XR4). The detection spot on the sample was covered a surface area of 0.8 mm^2. The depth profiles were determined by high energy Ar^+-ion sputtering using a Thermo EX05 ion gun operated at 2 - 3 $\times10^{-8}$ mbar Ar partial pressure, 3 - 7 µA Ar^+ current with a sample area of 3×4 mm^2, 2 kV acceleration voltage and 10 mA emission current. The sputtering depths (not calibrated for the different elements) are provided as sputter time. The data were evaluated using Thermo Avantage Software and Origin 8.5.1G. To determine the atomic concentrations, the sensitivity factor database by Thermo Avandage was used. Fitting of the Ir4f detailed spectra was performed by determining the oxide species at the first sputtering level (0 s) assuming a doublet of symmetric peaks with 3 eV separation and a fixed height and width ratio and using a metallic reference with the Ir4f7/2 peak located at 60.7 eV. The resulting oxide spectrum was used to fit all other sputtering levels of the XPS depth profile and to determine the metallic:oxide ratio of the studied material.

To fit the V2p spectra, two doublets of symmetric peaks with 7.5 eV separation were used. The O1s satellite peaks that overlap with the V2p region were considered by defining two additional peaks ($O1s_{\alpha3}$ and $O1s_{\alpha4}$) shifted by -9.8 and -11.8 eV relative to the O1s signal with fixed intensity ratio of 2:1 according to the XPS handbook by Moulder et al.[3] The intensity of the fitted O1s$_{\alpha3}$ satellite peak was 6-7 % of the intensity of the measured O1s signal, which is close to the expected value of 6.4 %.[3]

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS):

Powder samples were directly deposited on adhesive conducting carbon tapes then analyzed by SEM and EDS. The morphology was observed by using secondary electron signals. The element distribution with visual color contrast was measured by using backscattered electrons. The mass percentage of the elemental composition was determined by EDS. For Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb, the experiments were carried out at DLR (Stuttgart) with a facility from Zeiss (ULTRA plus using scanning electron microscopy), equipped with an XFlash 5010 detector (Energy Resolution: 123 eV at Mn Kα; Bruker Corp.) for EDS mode. For SnO_2:Sb aerogel, the analysis was carried out in Armines by using a Supra 40 with Gemini column operated at 3.00 kV, coated with 7 nm thick platinum layer using a Quorum (Q150T) before analysis.

High-Resolution Transmission Electron Microscope (HRTEM):

HRTEM images were taken with a FEI instrument Titan 80-300 kV with image Cs-corrector at 300 kV. For sample preparation, the catalyst powders were dispersed in pure ethanol and fished with a holey carbon support film on a copper grid (Plano) afterwards. The image data processing was carried out by using both Digital Micrograph (Gatan) and ImageJ software.

Atomic Force Microscope (AFM):

Catalyst powders were dispersed in ultra-pure water by using an ultra-sonication bath and deposited on silicon wafers. To ensure electronic contact to the AFM, the samples were connected with conductive silver paste to the AFM steel disc. For AFM analysis, a Bruker Multimode 8 equipped with a Peakforce-TUNA current amplifier was used. The samples were measured in Peakforce tapping mode. The contact current used was averaged during the contact time of the AFM tip and sample by a lock-in amplifier. Pt-covered AFM tips (PPP-NCHPt, Nanosensors) were used to measure the electronic conductivity. A voltage of 25 mV was applied between the sample and the AFM tip. The current distribution was evaluated from the images using the bearing function of the AFM software. For each current value, the number of pixels falling within this current range was counted and drawn *vs.* the magnitude of current. All measurements were performed at 40-50 % RH in ambient air. For the roughness measurements, an AFM probe with a DLC spike was used (SHR150, Budgetsensors).

The results of the image evaluation are the mean values derived from several images, presented together with the standard deviation of the mean value.

Electrochemical Characterization:

1. Electrode preparation:

A glassy carbon rotating disc electrode (GC-RDE, 0.196 cm^{-2}, PINE Research Instrumentation) was used for all electrochemical characterization. Before a measurement, the GC-RDE was polished with an alumina suspension (Buehler) until a fresh GC substrate was reached, achieving a mirror-like surface. Then it was cleaned by deionized water with ultra-sonication multiple times. 10 mg of catalyst powder plus 40 µL of a Nafion resin solution (5 wt. %, Sigma Aldrich) was dispersed in 8.3 mL ultra-pure water (Alfa Aesar). Ultra-sonication in an ice bath for 0.5 h was performed to obtain a homogeneous catalytic ink. Then the 10 µL ink was dropped and coated on an as-prepared GC-RDE surface, drying in an Ar atmosphere at room temperature. Overall catalyst loading on each electrode was 60 µg cm^{-2}; therefore, the Ir loading was 60 µg cm^{-2} for unsupported IrO_x, and 17 µg cm^{-2} for Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb.

2. OER activity evaluation:

Cyclic voltammetry (CV) was carried out for electrochemical oxidation of the as-prepared catalysts and their activity evaluation. The measurements were performed at 25 °C in a three-electrode cell, in which GC-RDE was employed as a working electrode, reversible hydrogen electrode (RHE, Gaskatel) and platinum foil were used as a reference electrode and a counter electrode, respectively. N_2-saturated 0.05 M H_2SO_4 (VWR Chemicals) was used as an electrolyte. All catalyst coated electrodes were subject to the full protocol listed in Table S1. In Sequence 1, under a rotating speed of 1600 rpm, the potential was swept from 1 V to 1.6 V vs. RHE with a scanning rate of 5 mV s^{-1} for electrode activation and the OER activity pre-test. Then in Sequence 2, the potential was swept between 0 V to 1.6 V vs. RHE with a scanning rate of 20 mV s^{-1}, to electrochemically oxidize the catalysts. Sequence 3 was designed for OER activity evaluation since the electrode had achieved a steady state after Sequence 2 (EC protocol). After capacitance correction and ohmic resistance (ca. 34 Ω) correction, the first cycle of Sequence 3 was used to compare the OER activity among all of the catalysts. All the measurements were carried out by using an Autolab PGSTAT12 potentiostat except for the electrochemical impedance spectroscopy (EIS) analysis (Zahner), which was used to determine the ohmic resistance between GC-RDE and RHE.

Seq. No	**Start Potential / V vs. RHE**	**Potential range / V vs. RHE**	**Sweep rate / mV s^{-1}**	**Number of cycles**	**Purposes**
1	1.0	1.0 – 1.6	5	3	OER activity pre-test
2	OCP	0.0 – 1.6	20	10	Electrochemical Oxidation
3	1.0	1.0 – 1.6	5	3	OER activity evaluation

Table S1. Electrochemical measurement protocol.

3. Copper underpotential deposition (Cu-UPD):

The Cu-UPD experiment was carried out in two electrochemical cells, the background cell and the working cell. A reversible hydrogen electrode (RHE) was employed as a reference electrode. The background cell contained 0.5 M H_2SO_4 and was purged with N_2 gas for 20 minutes before each experiment. The working cell was filled with 5 mM $CuSO_4$ and 0.5 M H_2SO_4 where both Cu-UPD and overpotential deposition (OPD) were observed. The working cell was also degassed with N_2 flow for 20 minutes before the start of the experiment. Freshly coated electrodes were used for these measurements.

Firstly, the electrode was kept in the background cell at 0.05 V vs. RHE for 10 minutes to reduce the reversible iridium oxide species that formed during catalyst synthesis on the Ir particle surface. The electrode was then cycled in the potential window between 0.2 V to 0.72 V vs. RHE for 3 cycles with a scanning rate of 20 mV s^{-1} to obtain the background CV profiles. After that, the electrode was again held at a constant potential of 0.05 V vs. RHE for another 10 minutes to ensure that no reversible iridium oxide species existed before Cu-UPD. Secondly, the electrode was transferred to the working cell (5 mM $CuSO_4$ + 0.5 M H_2SO_4, N_2-saturated), followed directly by 3 cycles of CV from 0.2 V to 0.72 V vs. RHE with a scanning rate of 20 mV s^{-1} to obtain the copper UPD and UPD-stripping peaks.[4]

4. Stability measurements:

Chronopotentiometry was used to evaluate the stability of the catalysts. The measurements were carried out in N_2-saturated 0.05 M H_2SO_4 under a rotating speed of 1600 rpm. A fresh electrode was prepared and initially applied with the full electrochemical protocol listed in Table S1 to achieve an electrochemically oxidized electrode as well as to make sure that the target electrode could work properly. Afterwards, the galvanostatic mode was used, and the current density loaded on the electrode was set up to 1 mA cm^{-2}; in the meantime, the potential was recorded. The duration of the stability test was 15 hours, and the measurements automatically stopped when the potential on target electrode reached 2.0 V vs. RHE to protect the glassy carbon electrode.

For the purpose of further confirming catalyst stability, a “duty-cycle” protocol[5] was applied to all three catalysts, which was proposed by Strasser and co-workers to simulate the dynamic working conditions of a PEM electrolyzer. The protocol was described in detail in a previously published paper[4] and offered a harsher working environment than the normal chronopotentiometry measurement under a constant current density. Again, as-prepared fresh electrodes were used for this independent measurement and were pre-treated by the protocol listed in Table S1. Following, the first duty cycle was applied. In brief, the electrode potential was initially kept at $E^{0.5}$ (at which the current density is 0.5 mA cm^{-2} selected from the activity evaluation curve performed in advance) for 10 min; then, the potential was increased by a step of 20 mV ($E^{0.5}$+20 mV) for another 10 min, and the potential step increase was repeated 5 times until the final potential ($E^{0.5}$+100 mV) was reached. For each duty-cycle, the electrode was loaded with a varied potential for 1 h. Between every two duty-cycles, two cycles of CV were performed in the OER region to evaluate any change in activity. For each catalyst, the "duty-cycle" measurement stops when the electrode could not reach 1 mA cm^{-2} up to 2.0 V vs. RHE. The maximum applied duty cycle number was 15.

XPS analysis:

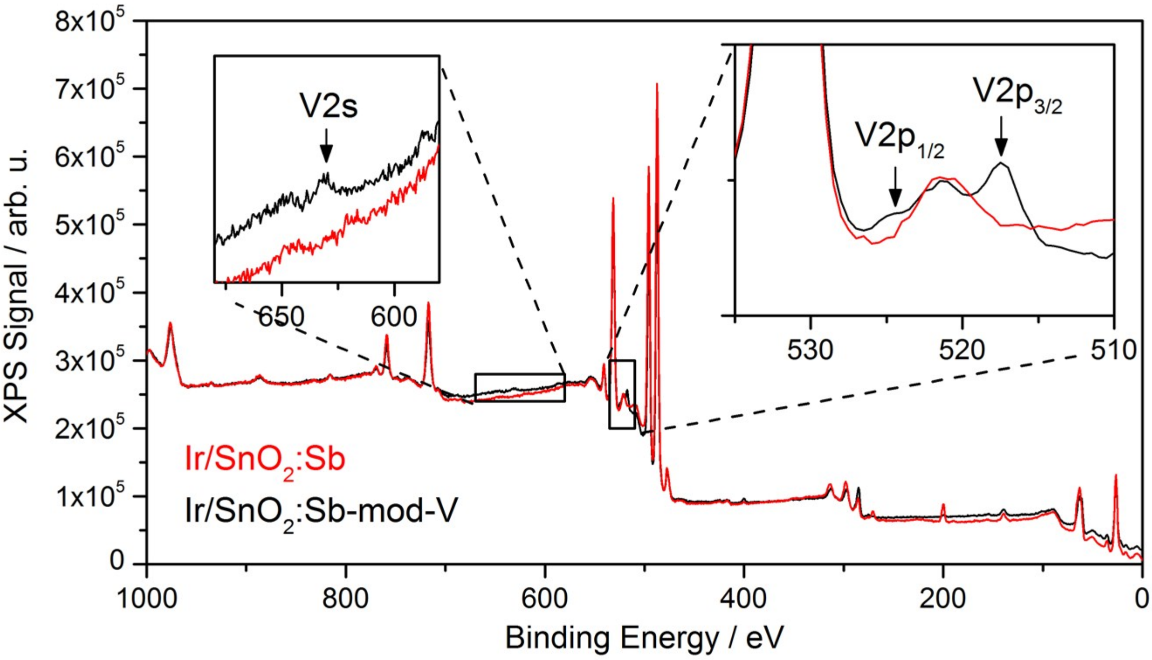

Fig. S1 XPS survey spectra of Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb demonstrating that V2p and V2s peaks were detected in Ir/SnO_2:Sb-mod-V but not in Ir/SnO_2:Sb.

The XPS survey spectra of the Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb samples clearly show that XPS signals due to vanadium were detected in the first but not in the latter sample.

SEM and EDS analysis:

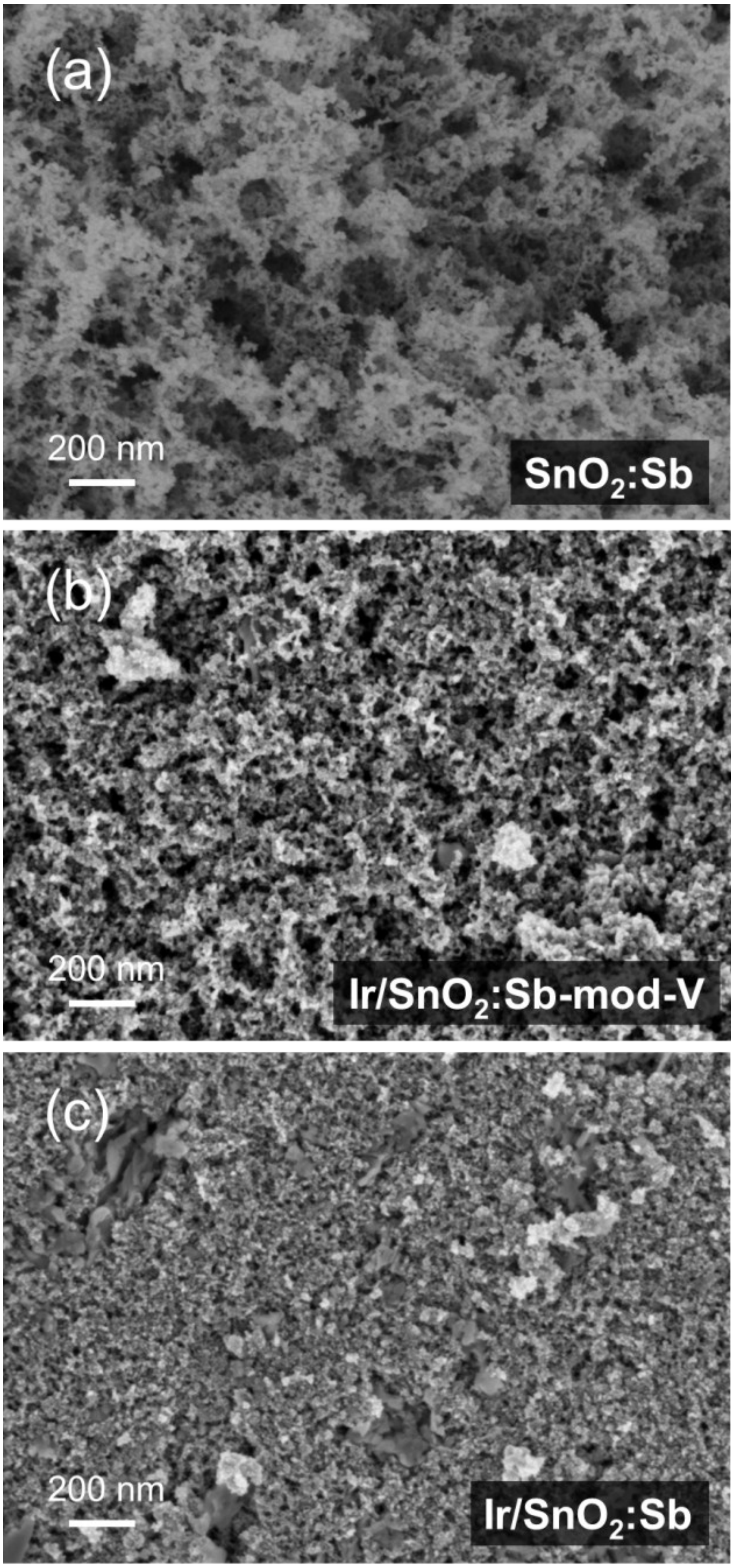

Fig. S2 SEM images showing morphology of (a) SnO$_2$:Sb aerogel, (b) Ir/SnO$_2$:Sb-mod-V and (c) Ir/SnO$_2$:Sb at high resolution.

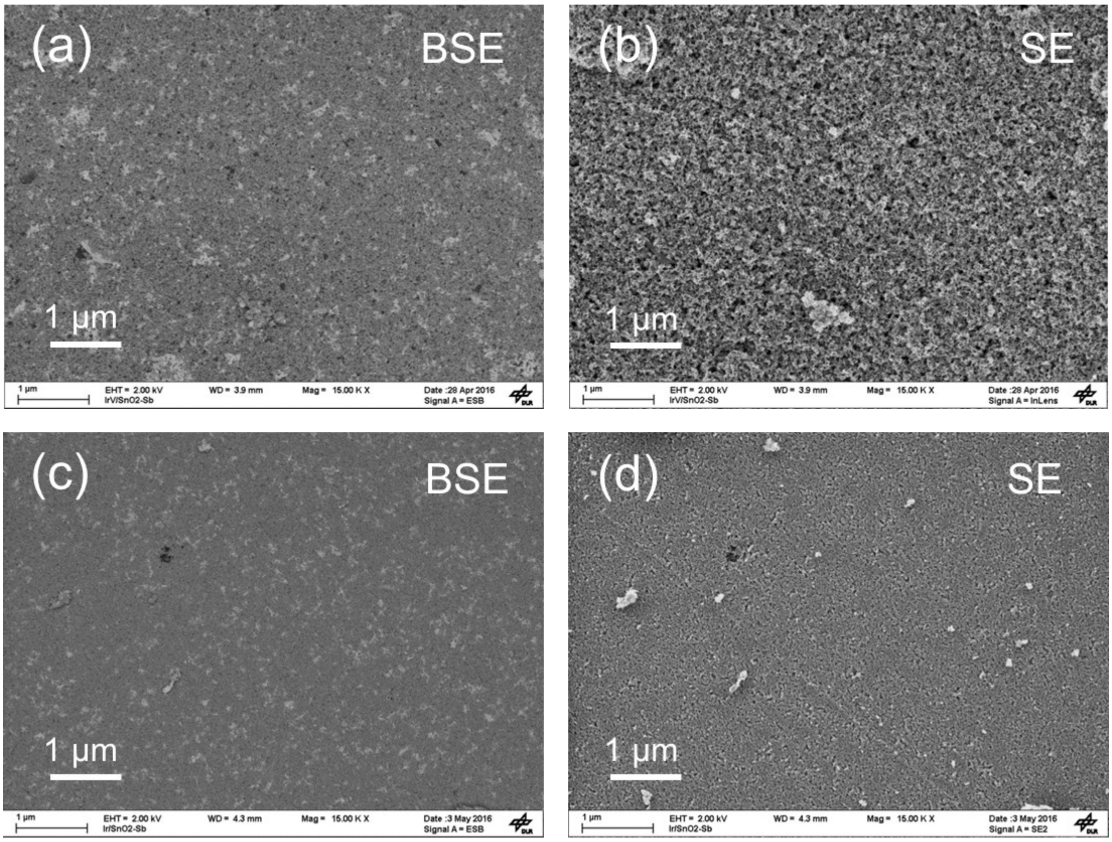

Fig. S3 SEM images of (a, b) Ir/SnO_2:Sb-mod-V and (c, d) Ir/SnO_2:Sb: panel (a) and (c) were analyzed by back-scattered electrons for the elemental distribution; panel (b) and (d) were analyzed by secondary electrons for morphology observations.

Ir/SnO$_2$:Sb-mod-V								
Analyzed Areas	C / wt.%	O / wt.%	Na / wt.%	Cl / wt.%	V / wt.%	Sn / wt.%	Sb / wt.%	Ir / wt.%
A1	8.74	15.59	0.82	0.32	3.14	39.62	4.29	27.48
A2	7.09	12.50	0.51	0.46	3.22	44.56	5.17	26.50
A3	9.05	15.98	0.88	0.35	2.90	39.52	4.01	27.31
A4	4.26	7.11	0.85	0.57	3.74	46.25	6.50	30.72
A5	5.76	10.18	1.20	0.46	3.32	45.87	5.58	27.64
A6	7.73	11.57	0.91	0.49	3.14	44.38	5.52	26.28
A7	7.34	13.49	1.25	0.32	3.72	41.04	4.42	28.41
A8	4.71	6.88	0.81	0.45	3.62	44.28	6.41	32.84
A9	9.01	17.07	0.91	0.27	3.10	39.04	3.97	26.62
A10	7.04	11.30	0.95	0.41	3.22	45.29	5.16	26.26
Average	7.703	12.167	0.909	0.41	**3.312**	42.985	5.103	**28.006**

Table S2. EDS analysis on the element ratios from selected areas of the Ir/SnO$_2$:Sb-mod-V sample.

Ir/SnO$_2$:Sb							
Analyzed Areas	C / wt.%	O / wt.%	Na / wt.%	Cl / wt.%	Sn / wt.%	Sb / wt.%	Ir / wt.%
A1	5.76	6.70	1.53	4.84	17.37	6.90	56.90
A2	4.41	9.21	1.96	1.40	46.92	19.50	16.60
A3	5.07	16.40	1.89	0.84	54.74	6.87	14.18
A4	5.95	19.81	1.64	0.77	50.05	6.07	15.71
A5	8.34	13.68	1.61	2.32	24.91	9.23	39.91
A6	5.49	13.54	2.23	1.20	41.53	16.18	19.83
A7	7.89	21.83	1.93	0.77	47.30	5.56	14.72
A8	6.87	19.66	2.08	0.96	47.12	5.49	17.82
A9	6.21	9.26	1.65	4.16	21.32	8.39	49.01
A10	5.00	8.91	1.85	2.64	30.78	12.00	38.82
Average	6.099	13.90	1.837	1.99	38.204	9.619	**28.35**

Table S3. EDS analysis on the element ratios from selected areas of the Ir/SnO$_2$:Sb sample.

HRTEM:

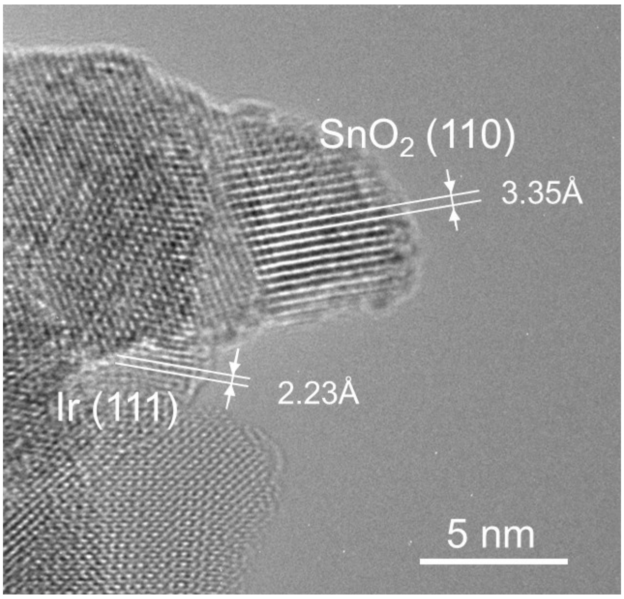

Fig. S4 HRTEM image of Ir/SnO_2:Sb-mod-V after the electrochemical oxidation (EC) protocol.

AFM results:

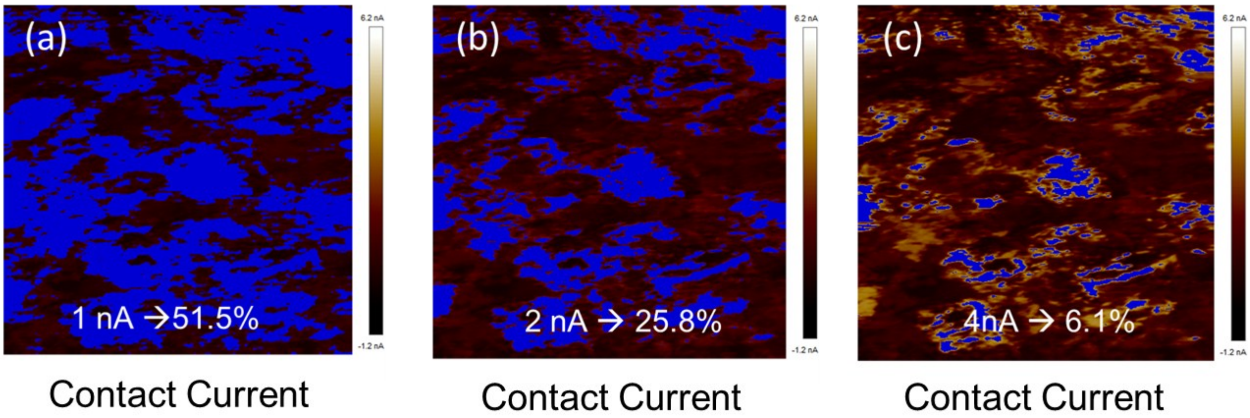

Fig. S5 Contact current of Ir/SnO_2:Sb-mod-V with different thresholds. The conductive area is marked in blue: (a) 1 nA; (b) 2 nA and (c) 4 nA.

In Fig. S5, contact current images of the Ir/SnO_2:Sb-mod-V sample are presented with different current thresholds to visualize the highly conductive spots. In Fig. S6 (a) and (b), topography images of the Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb are shown at the micrometer scale. The roughness, R_a, was determined to be 272 nm for Ir/SnO_2:Sb-mod-V and 200 nm for Ir/SnO_2:Sb.

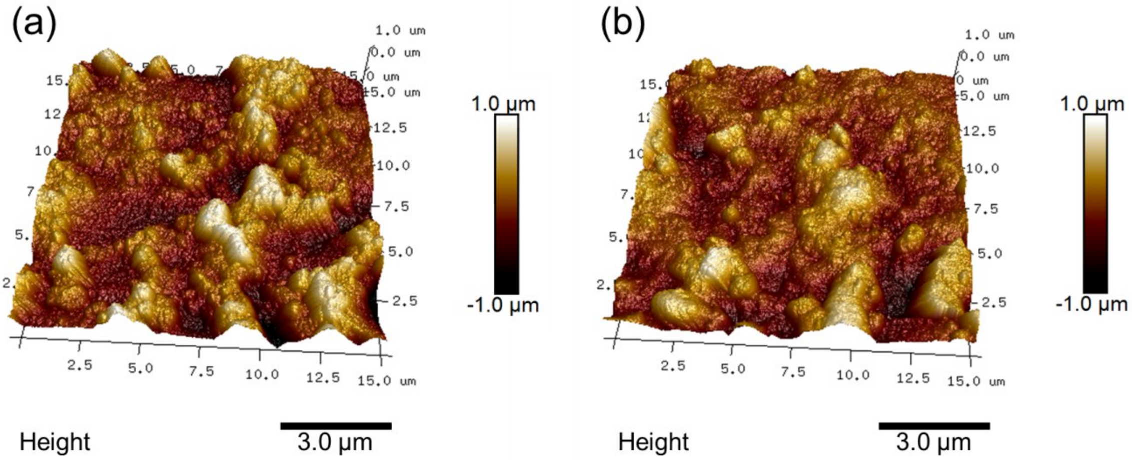

Fig. S6 3D topography (15 µm) of (a) Ir/SnO_2:Sb-mod-V and (b) Ir/SnO_2:Sb measured with AFM.

Electrochemical measurements:

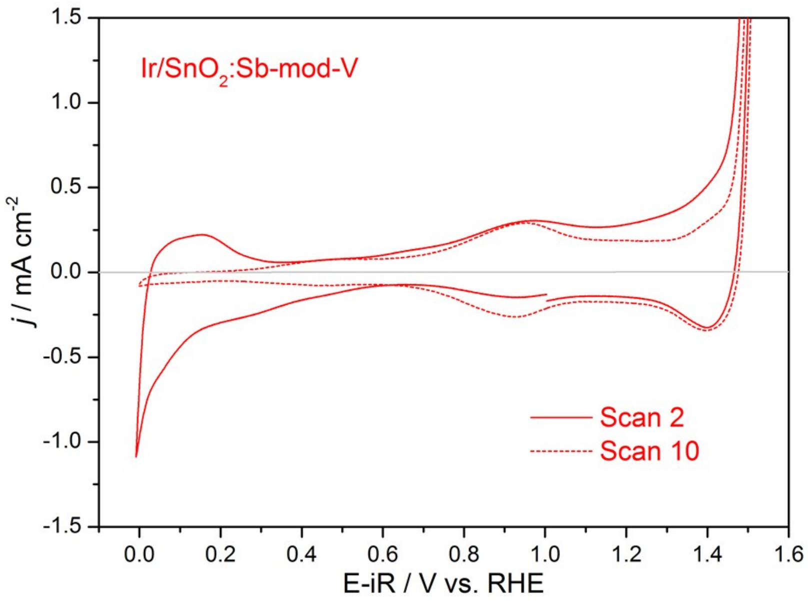

Fig. S7 Fingerprint CV profiles (cycle 2 and cycle 10) of the Ir/SnO_2:Sb-mod-V sample during the electrochemical oxidation (EC) protocol.

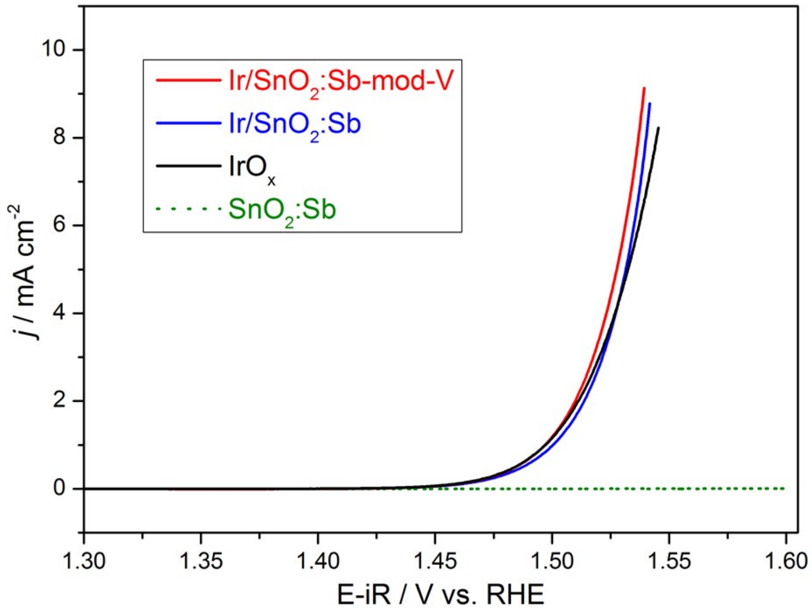

Fig. S8 Geometric OER activity comparison among Ir/SnO_2:Sb-mod-V, Ir/SnO_2:Sb, unsupported IrO_x and pure SnO_2:Sb aerogel (N_2-saturated 0.05 M H_2SO_4, 5 mV s^{-1}, 1600 rpm, 25 °C). Ir loading on GC-RDE: 17 µg cm^{-2} for Ir/SnO_2:Sb-mod-V and Ir/SnO_2:Sb, 60 µg for unsupported IrO_x.

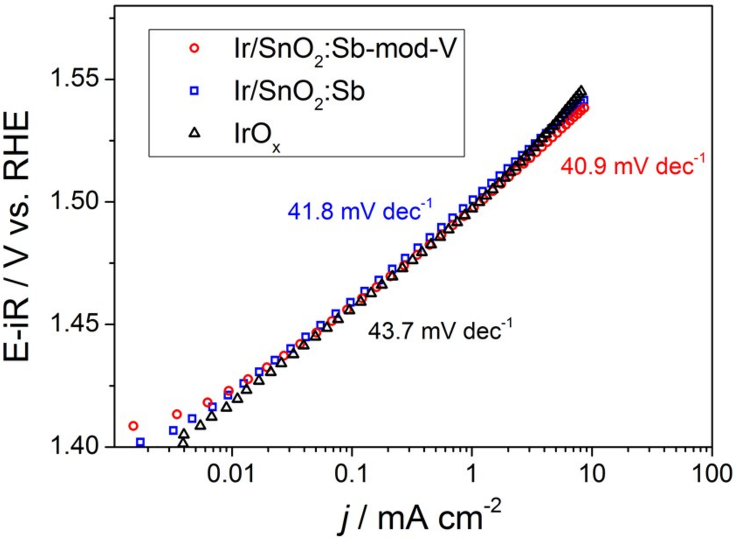

Fig. S9 Tafel slope determination of Ir/SnO_2:Sb-mod-V, Ir/SnO_2:Sb and IrO_x.

XPS analysis on V content of Ir/SnO_2:Sb-mod-V electrode before and after electrochemical oxidation:

To track V content changes after electrochemical oxidation, Ir/SnO_2:Sb-mod-V catalytic ink (containing Nafion ionomer) was deposited on an Au foil; then the electrochemical protocol (see Seq. 1 and Seq. 2 in Table S1) was applied. The elemental composition of the catalytic layer was analyzed by XPS before and after the electrochemical protocol. Detailed V2p spectra are shown in Fig. S10. Apparently, the V2p peaks showed a significant decrease after electrochemical operation, implying that vanadium was rapidly dissolving during the electrochemical operation. From the Ir:V peak area ratio, it was concluded that ca. 95 at.% of vanadium vanished after the electrochemical operation.

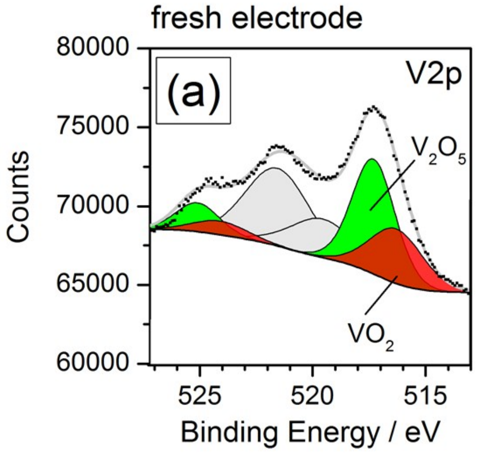

Fig. S10 XPS analysis: detailed V2p spectra of Ir/SnO$_2$:Sb-mod-V (a) before and (b) after electrochemical characterization. The deconvoluted peaks of O1s satellites (grey), VO$_2$ (red) and V$_2$O$_5$ (green) are shown.

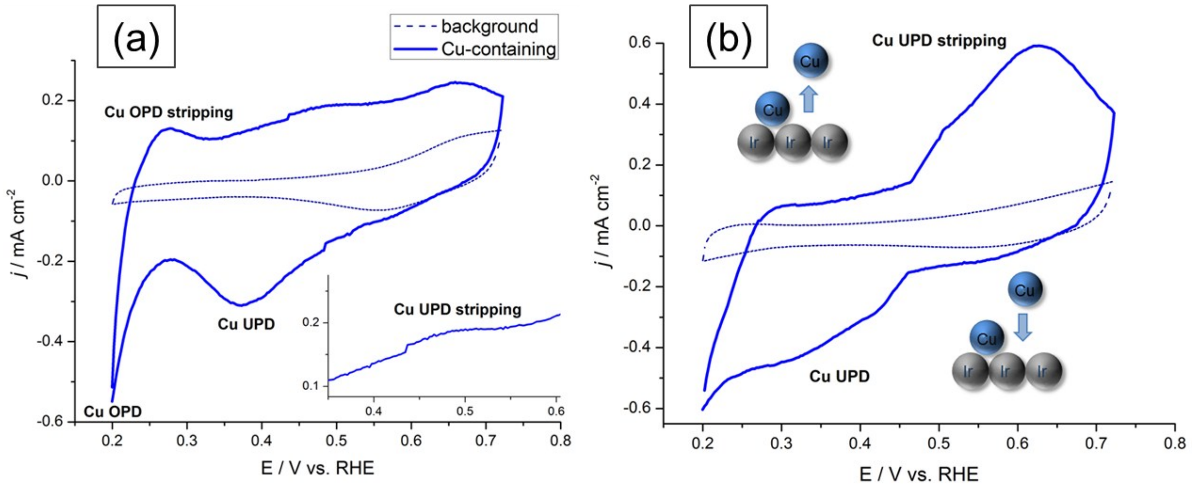

Fig. S11 Cu-UPD measurements of (a) Ir/SnO$_2$:Sb and (b) unsupported IrO$_x$.

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