ADVANCED ENERGY MATERIALS

Supporting Information

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Size-Controlled Synthesis of IrO_2 Nanoparticles at High Temperatures for the Oxygen Evolution Reaction

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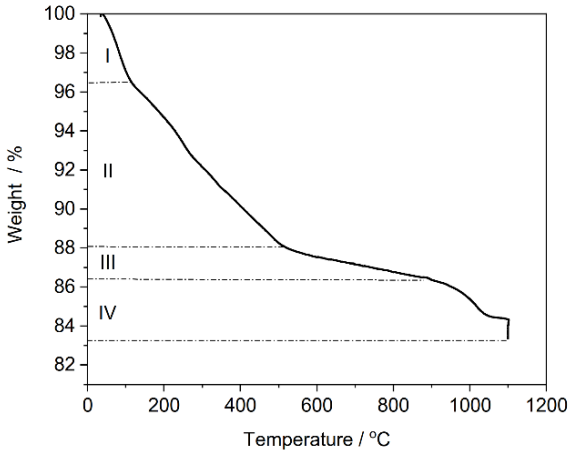

Figure S1. TGA analysis of as-synthesized IrO_x encapsulated in silica.

The TGA analysis was carried out under a synthetic air atmosphere with a 2 °C min^{-1} temperature ramp with 3h of annealing at 1,100 °C. The first weight loss in the region of 100 °C (zone I) is attributed to the release of adsorbed water. We hypothesize that weight loss in the temperature region 200-800 °C (zones II and III) is a merged effect of silanol condensation (dehydroxylation), decomposition of surfactant (Brij 30), and oxidation of the oxyhydroxide.[22] The weight loss at temperatures above 900 °C (zone IV) we hypothesize to be due to the partial decomposition of iridium oxide nanoparticles.[23, 24]

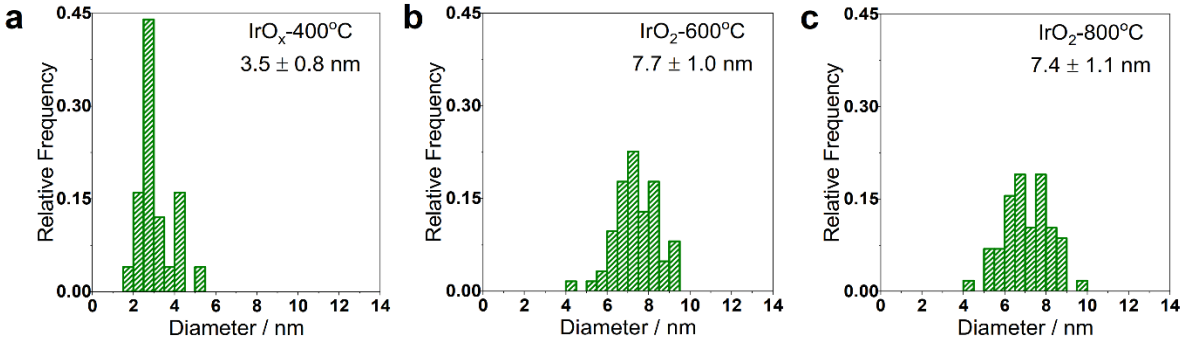

Figure S2. Particle size distribution histogram and mean Sauter diameter of (a) IrO_x-400°C, (b) IrO_2-600°C, and (c) IrO_2-800°C

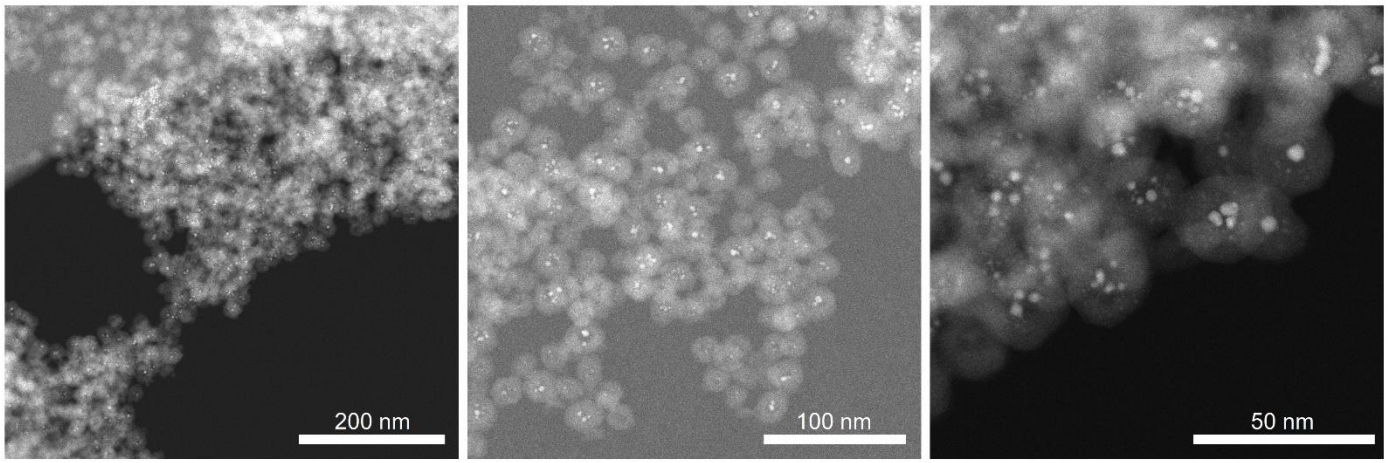

Figure S3. *Ex-situ* HAADF-STEM images of IrO_x-400°C.

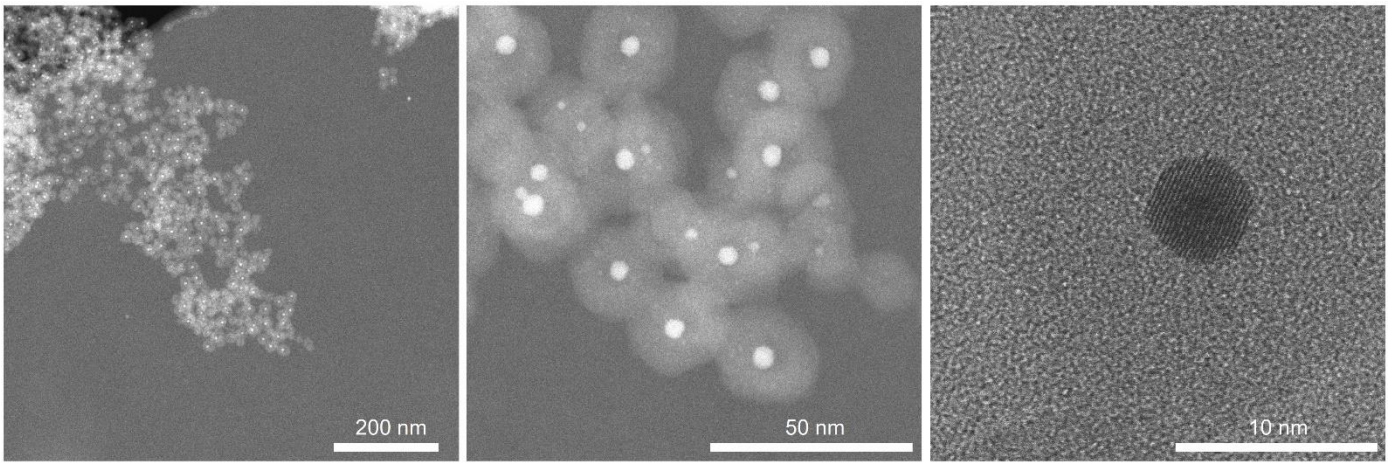

Figure S4. *Ex-situ* HAADF-STEM images of IrO_2-600°C.

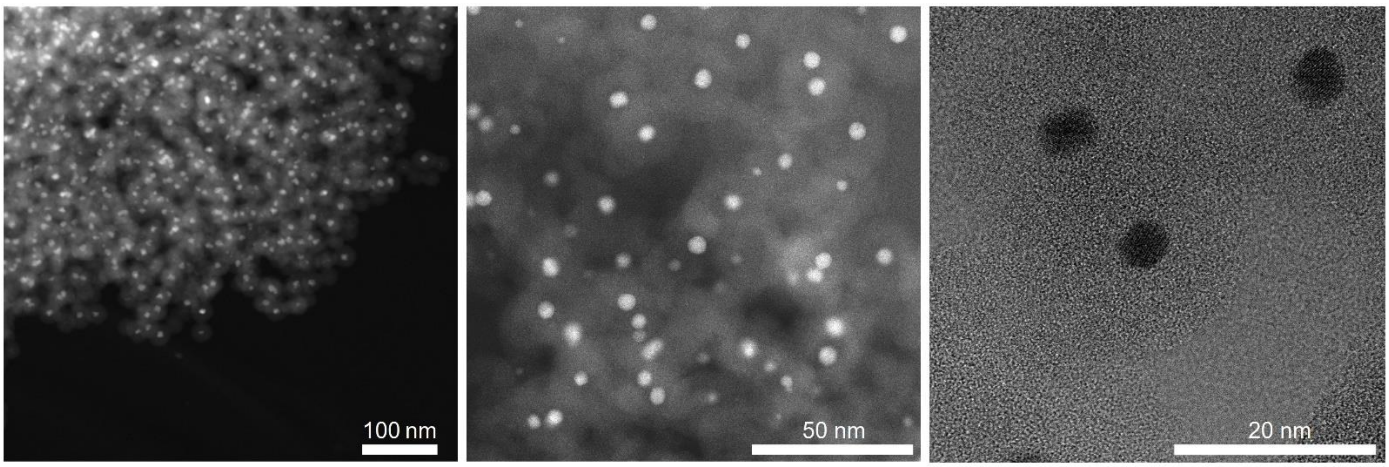

Figure S5. *Ex-situ* HAADF-STEM images of IrO_2-800°C.

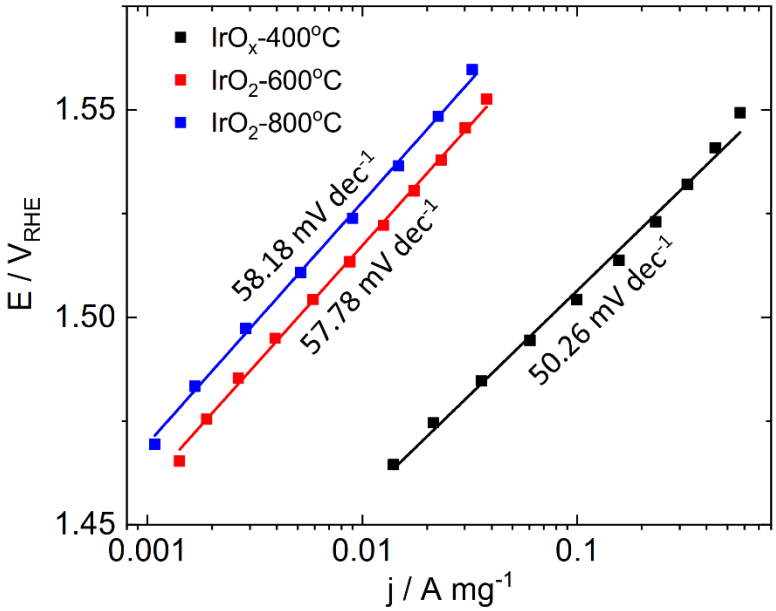

Figure S6: Tafel slope of synthesized samples annealed at the corresponding temperatures.

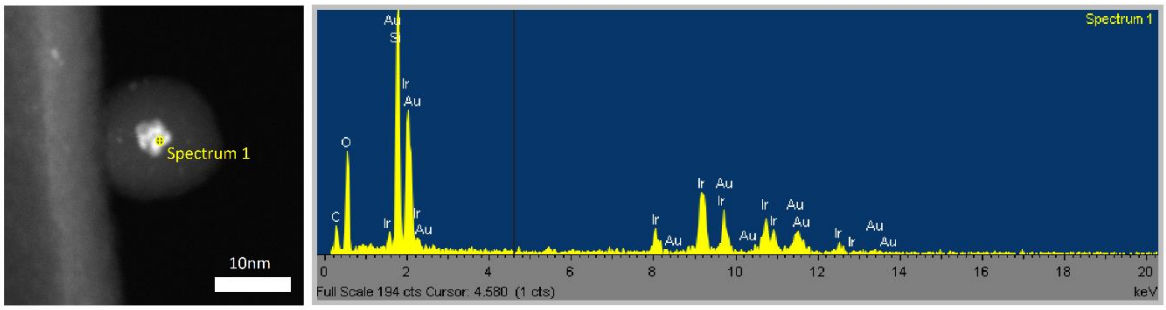

Figure S7. *Ex-situ* HAADF-STEM image of IrO_x-400°C with energy dispersive X-ray (EDX) analysis.

The EDX analysis of IrO_x-400°C reveals the predominate presence of iridium and oxygen. Gold and carbon signals stem from the TEM grid.

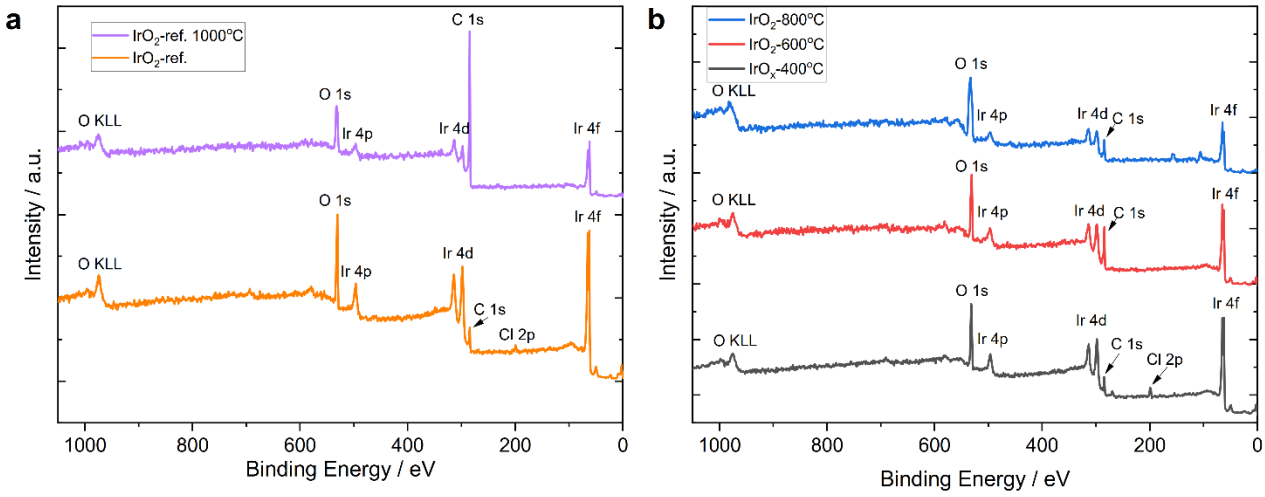

Figure S8. XPS surveys scanned with a pass energy of 20 eV with binding energy calibrated by C 1s assigned to 284.7 eV. (a) Iridium oxide pristine reference catalyst (IrO_2-ref.) and calcined at 1000 °C (IrO_2-ref.1000 °C). (b) Synthesized iridium oxide nanoparticles calcined at 400 °C, 600 °C, and 800 °C.

Table S1. The measurement protocol for OER activity determination with RDE setup.

Method	Potential range (V_{RHE})	Scan rate (mV s^{-1})	Number of cycles
Cyclic voltammetry 1	0.05-1.40	200	200
Cyclic voltammetry 2	0.05-1.40	50	3
Linear sweep voltammetry at 900 rpm	1.30-1.60	10	4
Linear sweep voltammetry at 1600 rpm	1.30-1.60	10	3

To obtain first insights into the activity, cyclic voltammetry measurements between 0.05 and 1.40 V_{RHE} in N_2-saturated 0.1 M $HClO_4$ at a scan rate of 200 mV s^{-1} were performed, followed by 3 cycles at 50 mVs^{-1}. The activity of the catalysts was determined from the first LSV at 900 rpm at 10 mV s^{-1}.

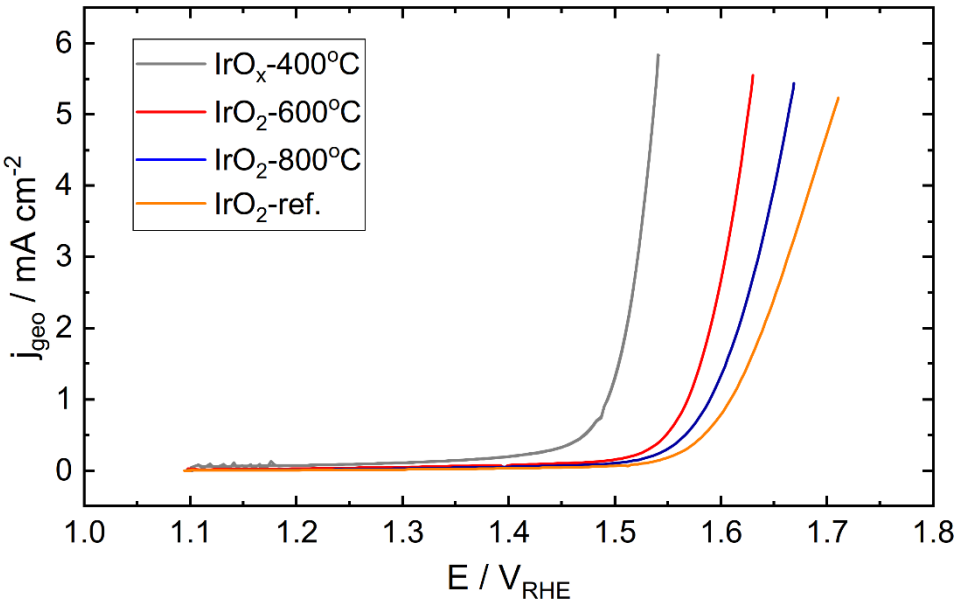

Figure S9. First linear sweep voltammetry (LSV 1) recorded in the scanning flow cell setup in 0.1 M $HClO_4$. The curves were iR-corrected.

By using a scanning flow cell, the flow profile was altered, and the activity was measured. Here, the same trend in OER activities (**Figure S9**) was confirmed when compared to RDE measurements (**Figure 4b**).

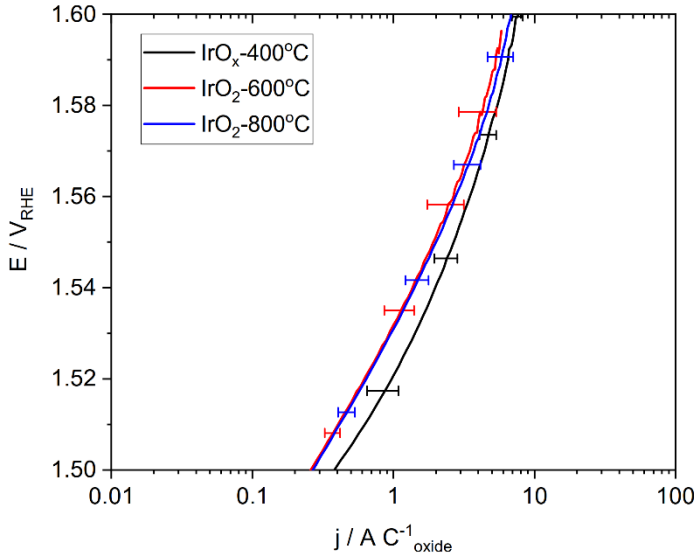

Figure S10. Charge normalized OER activities of synthesized catalysts thermally treated at 400 ºC, 600 ºC, and 800 ºC.

The charge was determined by integration of the highlighted pseudo-capacitive area (**Figure 4a**) in the potential window from 0.40 to 1.30 V_{RHE} within which iridium (III) oxidizes to iridium (IV). This method is suggested for the ECSA determination of IrO_2.[45] These values were used to normalize OER current to charge, thus expressing the specific activity of the synthesized catalysts.

Table S2. The measurement protocol for stability assessment of catalysts by SFC coupled to ICP-MS.

Method	V-range	Scan rate	Cycles
LSV 1	1.10 V_{RHE} – 5 mA cm^{-2}	10 mV s^{-1}	1
CV	0.05 – 1.40 V_{RHE}	50 mV s^{-1}	3
LSV 2	1.10 V_{RHE} – 5 mA cm^{-2}	10 mV s^{-1}	1
SQW	0.05 – 1.60 V_{RHE}	3 s / step	50
LSV 3	1.10 V_{RHE} – 5 mA cm^{-2}	10 mV s^{-1}	1

Table S3. Comparison of the average mass normalized OER activities at 1.53 V_{RHE} obtained by RDE and SFC.

Sample	Mass activity RDE	Mass activity SFC
IrO_x-400°C	241.37 mA mg^{-1}	220.18 mA mg^{-1}
IrO_2-600°C	15.26 mA mg^{-1}	15.11 mA mg^{-1}
IrO_2-800°C	12.33 mA mg^{-1}	12.19 mA mg^{-1}
IrO_2-ref.	5.54 mA mg^{-1}	4.17 mA mg^{-1}

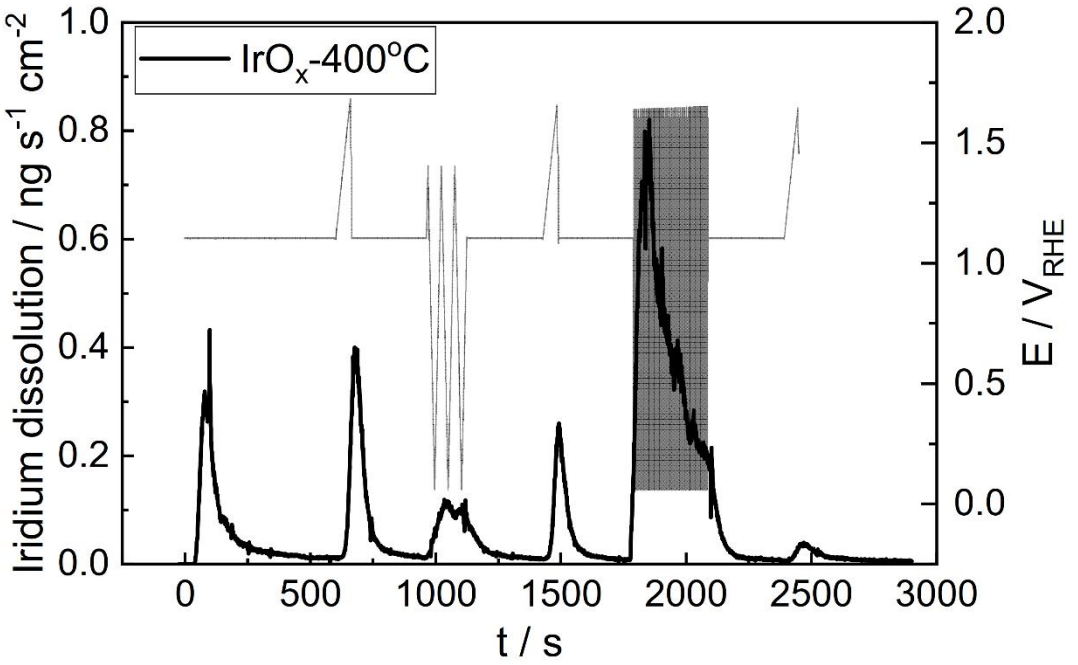

Figure S11. Dissolution of iridium in IrO_x-400°C during the stability assessment protocol.

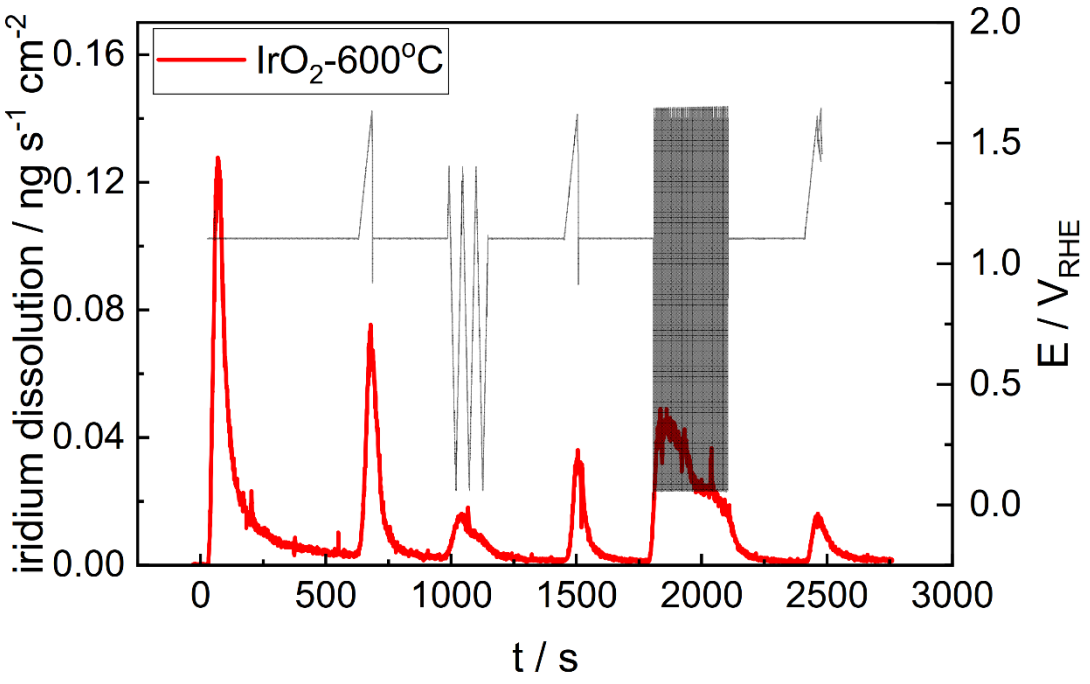

Figure S12. Dissolution of iridium in IrO_2-600°C during the stability assessment protocol.

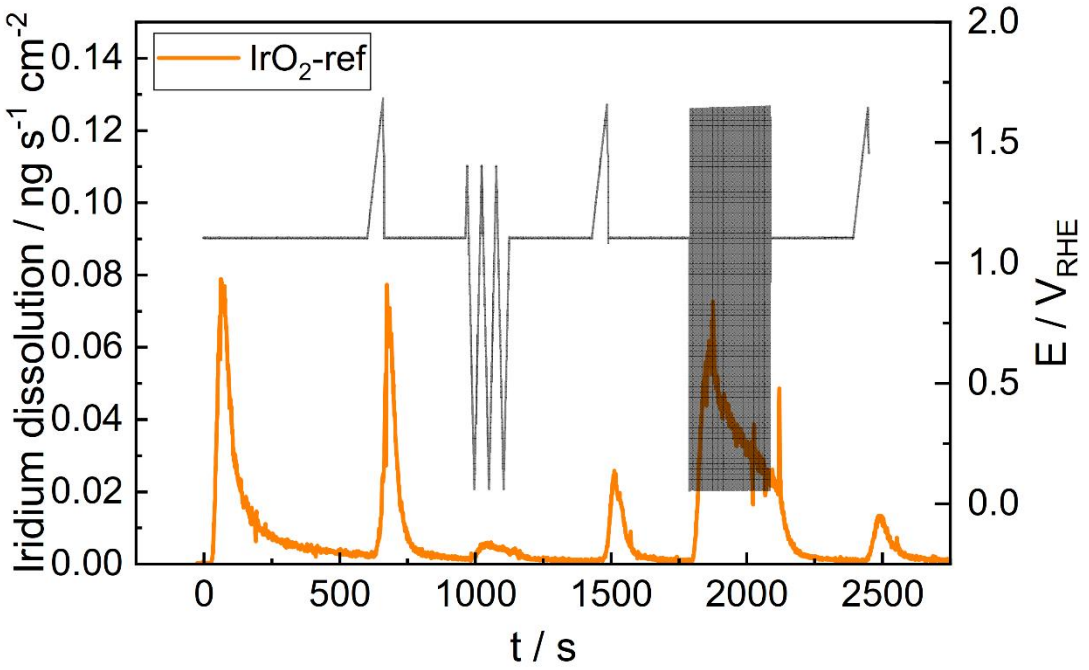

Figure S13. Dissolution of iridium in IrO_2-ref. during the stability assessment protocol.

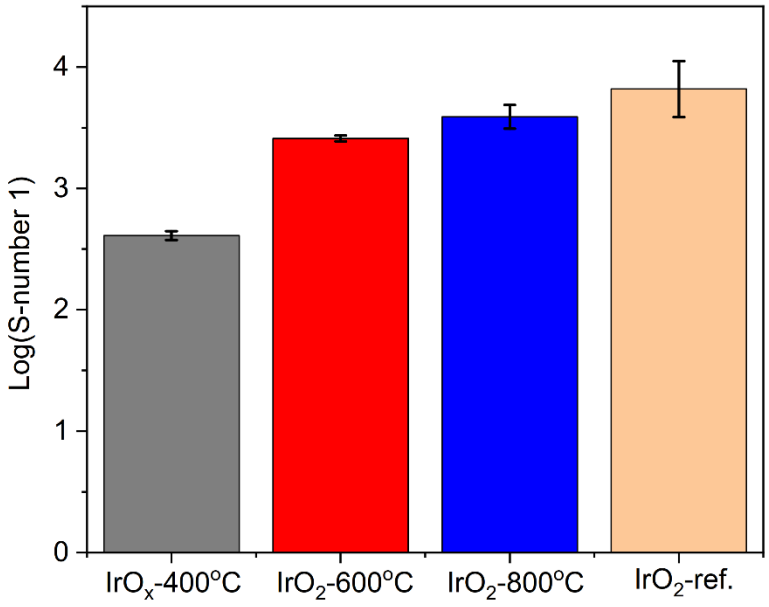

Figure S14. S-numbers of iridium oxide calcined at 400°C, 600°C, 800°C and the reference catalyst obtained during the first LSV in the measurement protocol (**Table S2**).

Movie S1. *In-situ* STEM movie montage of IrO_x nanoparticles encapsulated in silica at 200 °C during the heat treatment (link)

Movie S2. *In-situ* STEM movie montage of IrO_x nanoparticles encapsulated in silica during the heat treatment from 200 °C to 400 °C (link)

Movie S3. *In-situ* STEM movie montage of IrO_x nanoparticles encapsulated in silica at 600 °C during the heat treatment (link)

Movie S4. *In-situ* STEM movie montage of IrO_x nanoparticles encapsulated in silica at 800 °C during the heat treatment (link)