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Ruiz Esquiús, Jonathan, Morgan, David J. , Spanos, Ioannis, Hewes, Daniel G., Freakley, Simon J. and Hutchings, Graham J. 2020. Effect of base on the facile hydrothermal preparation of highly active IrO<sub>x</sub> oxygen evolution catalysts. *ACS Applied Energy Materials* 3 (1) , pp. 800-809. 10.1021/acsaem.9b01642

Publishers page: <http://dx.doi.org/10.1021/acsaem.9b01642>

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## **The effect of Base on the Facile Hydrothermal Preparation of Highly Active IrO<sub>x</sub> Oxygen Evolution Catalysts**

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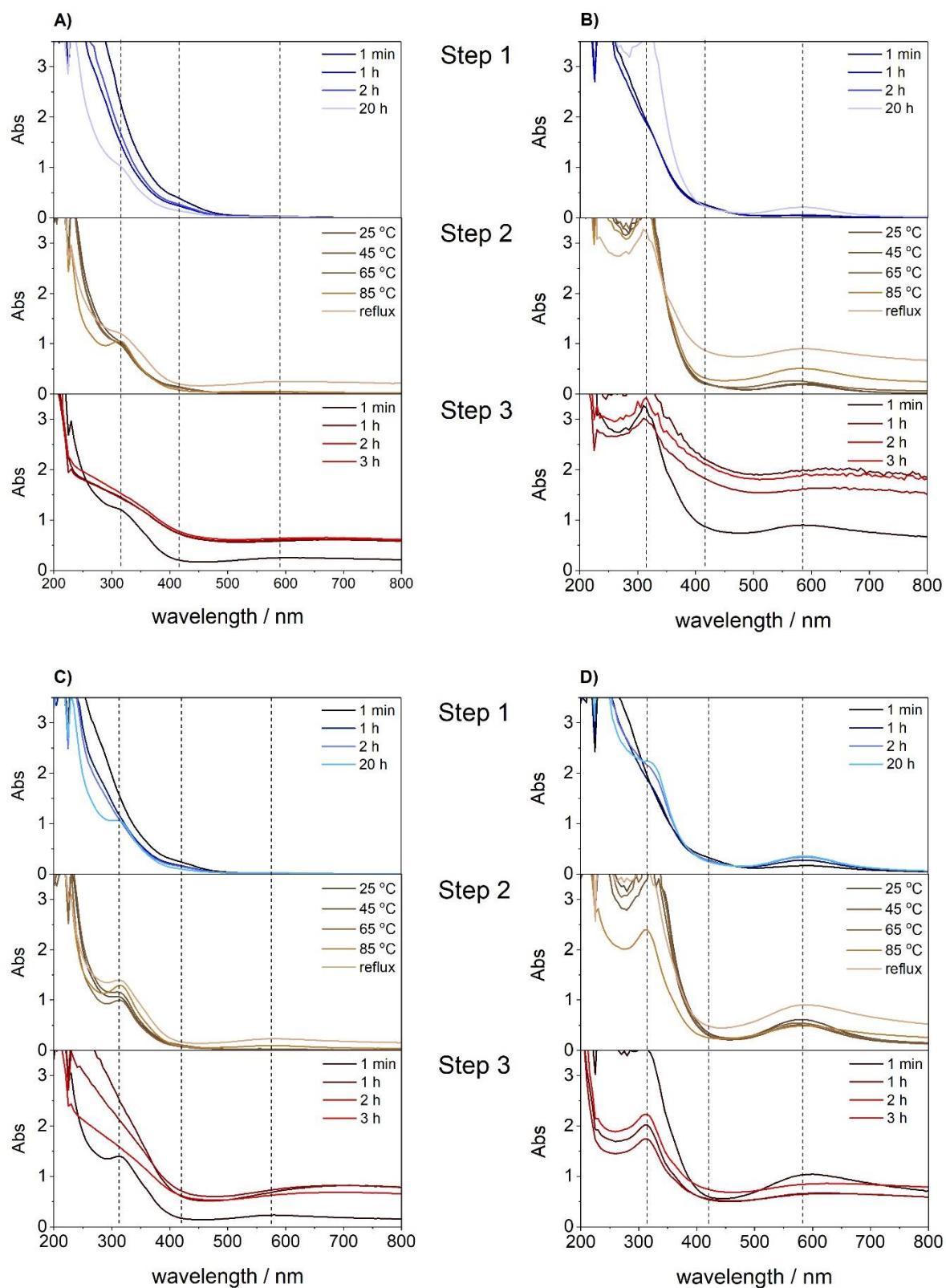
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## 1. Catalyst characterisation

### Ultraviolet – Visible Spectroscopy (UV-Vis)

UV-Vis was employed to monitor the conversion of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (Sigma Aldrich) to amorphous iridium oxo-hydroxides using different bases ( $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$  or  $\text{KOH}$ ) following a hydrothermal synthesis.  $\text{Ir}(\text{H}_2\text{O})_3\text{Cl}_3$ ,  $\text{Ir}(\text{OH})_6^{3-}$  and the formation of  $\text{Ir}_n\text{O}_m$  oligomers can be observed at 400 nm, 320 nm and 580 nm respectively.<sup>(1)</sup> The  $\text{IrO}_x$ -base synthesis were performed in a 100 ml three-neck bottom flask with a reflux condenser attached to the middle neck, and rubber septa sealed the other two flask necks. Temperature was controlled using an oil bath and the solution was continuously stirred with the aid of a magnetic bar. 1 mmol of  $\text{IrCl}_3$  and 8 mmol of base ( $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$  or  $\text{KOH}$ ) were dissolved in 40 ml of deionised water at 25 °C. Reaction aliquots were obtained by sampling 0.1 ml through the rubber septum using a syringe and diluting in a UV cuvette with 2 ml of deionised water. The synthetic protocol was divided in three distinct steps to facilitate data interpretation: Step 1 comprised stirring at 25 °C for 20 h, Step 2 consisted in heating the solution from 25 °C to reflux, Step 3 was the reflux of the reaction mixture for 3 h. In Step 2, the temperature was increased by 10 °C at a time, and the temperature was allowed to stabilise for 5 minutes before acquiring a UV-Vis spectra.

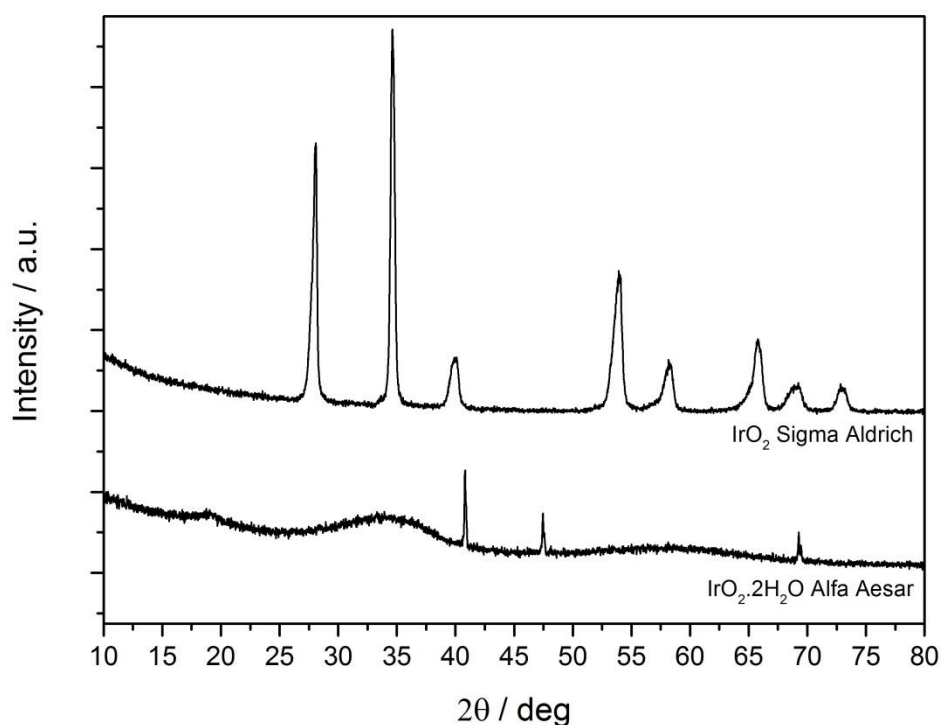
On one hand, for carbonate bases ( $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in Figure S1a and S1c respectively),  $\text{Ir}(\text{H}_2\text{O})_3\text{Cl}_3$  is hydrolysed to  $\text{Ir}(\text{OH})_6^{3-}$  at 25 °C (Step 1), in order to observe  $\text{Ir}_n\text{O}_m$  oligomer formation heating to 85 °C - reflux is necessary. On the other hand, for hydroxide bases ( $\text{NaOH}$  and  $\text{KOH}$  in Figure S1b and S1d respectively), the formation of oligomers is observed after stirring at 25 °C for 20 h. However, to obtain  $\text{IrO}_x$  precipitation heating to 85 °C - reflux is as well required.



**Figure S1.** UV-Vis monitoring of the hydrothermal conversion of  $\text{IrCl}_3$  to  $\text{IrO}_2$  during step 1 (stirring at 25 °C for 20 h), step 2 (heat from 25 °C to reflux) and step 3 (reflux for 3 h) of the hydrothermal conversion of  $\text{IrCl}_3$  to  $\text{IrO}_2$  using a)  $\text{Na}_2\text{CO}_3$  and b)  $\text{NaOH}$  c)  $\text{K}_2\text{CO}_3$  d)  $\text{KOH}$  as a base.

### X-ray powder diffraction (XRD)

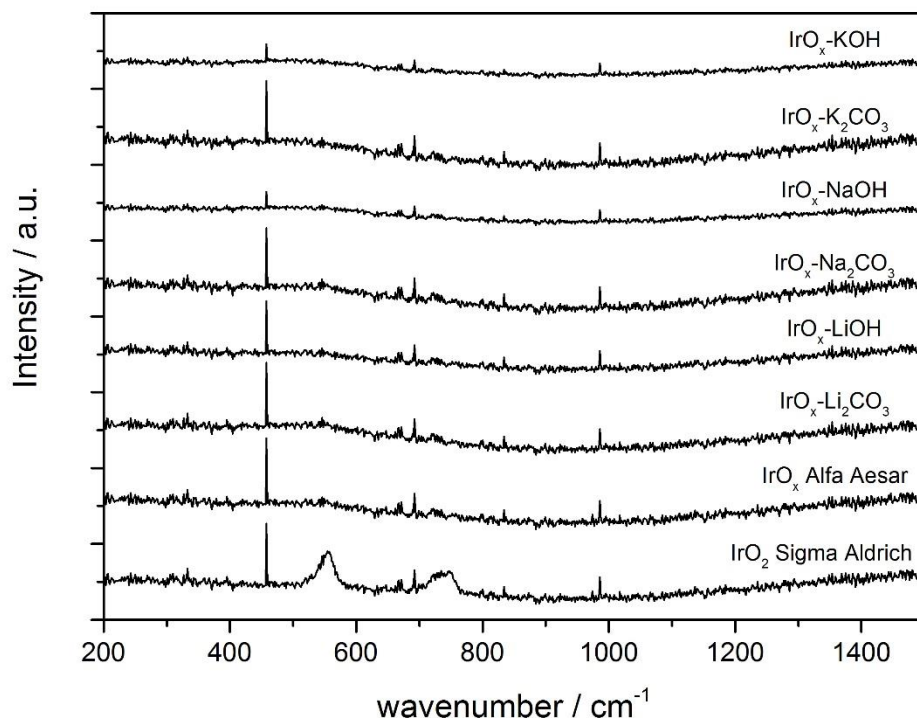
XRD was used to analyse the crystalline phases present in the commercially sourced rutile  $\text{IrO}_2$  (Sigma Aldrich,  $\text{IrO}_2$ -SA) and hydrate  $\text{IrO}_2$  (Alfa Aesar,  $\text{IrO}_x$ -AA) standards (Figure S2). In good agreement with published characterisation for these materials,<sup>(2)</sup> only rutile (JCPDS-015-0876) was observed for  $\text{IrO}_2$ -SA, whilst metallic iridium (JCPDS-006-0598) was detected for  $\text{IrO}_x$ -AA. According to Pfeifer *et al.*,<sup>(3)</sup> metallic iridium is present at the core of  $\text{IrO}_x$ -AA while  $\text{IrO}_x$  hydrated is localised at the outer layer.



**Figure S2.** XRD pattern for commercial crystalline and amorphous  $\text{IrO}_2$  samples from Sigma Aldrich and Alfa Aesar (Premion) respectively.

### Raman spectroscopy

Raman spectroscopy was employed to confirm XRD characterisation, which suggested that synthesised  $\text{IrO}_x$ -base materials had no large order crystallinity. data acquisition was performed at 5 % laser intensity, 500 accumulations and 5 s of exposure time. A1g and Eg modes at  $752\text{ cm}^{-1}$  and  $561\text{ cm}^{-1}$  characteristic of rutile  $\text{IrO}_2$ <sup>(4,5,6)</sup> were observed for  $\text{IrO}_2$ -SA. Whilst the absence of these adsorption bands for  $\text{IrO}_x$ -AA and synthesised  $\text{IrO}_x$ -base catalysts confirmed the absence of rutile crystalline phase (Figure S3). The sharp peak at  $459\text{ cm}^{-1}$ ,  $986\text{ cm}^{-1}$  and  $1368\text{ cm}^{-1}$  correspond to artefacts generated from the silicon wafer.



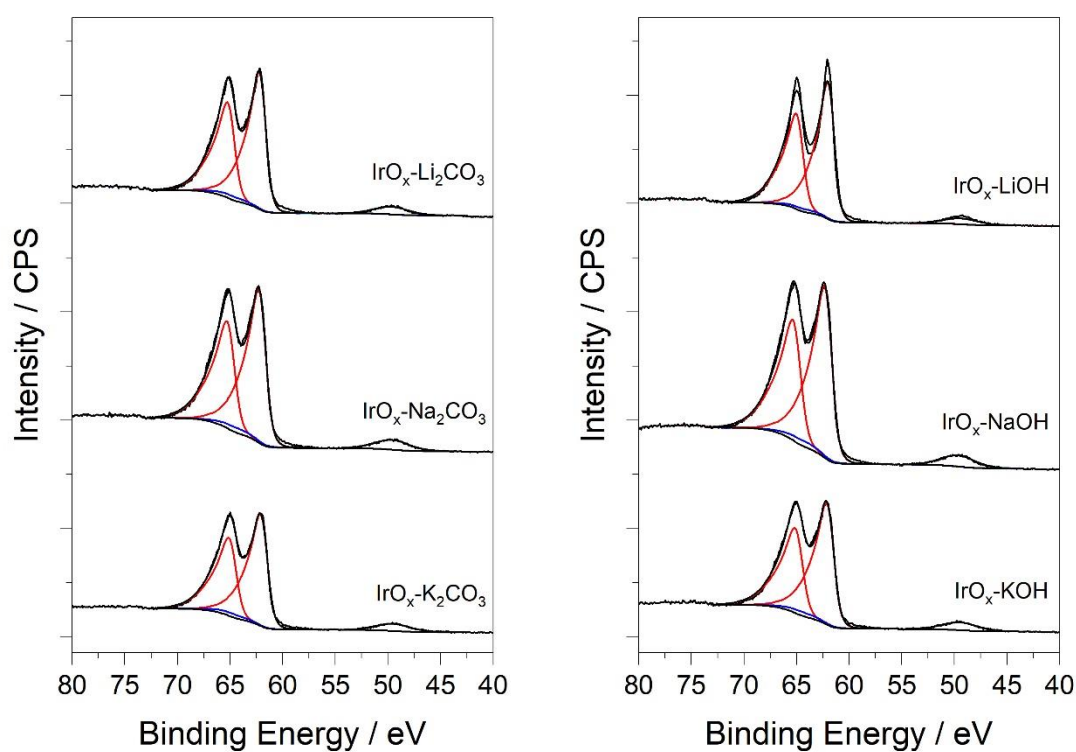
**Figure S3.** Raman spectroscopy for commercial standards and hydrothermally prepared  $\text{IrO}_x$  catalysts.

### X-ray photoemission spectroscopy (XPS)

The peak fitting model developed by Morgan *et al.*<sup>(7)</sup> was used on the Ir(4f) and O(1s) spectra acquired for  $\text{IrO}_x$ -base catalysts. In figure 4a, the Ir(4f) of rutile  $\text{IrO}_2$ -SA and hydrate  $\text{IrO}_x$ -AA were compared. Rutile  $\text{IrO}_2$  was centred at 61.9 eV, in accordance with being formed entirely of Ir(IV),<sup>(2,3)</sup> whilst  $\text{IrO}_x$ -AA was centred at 62.5 eV and showed a comparably broader peak envelope attributed to the presence of Ir(III) sites. Recorded Ir(4f) spectra for synthesised  $\text{IrO}_x$ -base catalysts (Figure S4) were shifted towards higher binding energy and broader than  $\text{IrO}_2$ -SA, comparable to commercial  $\text{IrO}_x$ -AA, indicating the presence of Ir(IV)/Ir(III) sites and in agreement with its amorphous structure.

The Ir/O ratio, obtained from the XPS quantification of Ir(4f) and O(1s), indicated an excess of oxygen compared to the stoichiometric oxide (Table S1). The excess of oxygen observed from the Ir/O ratio can be explained by the presence of surface hydroxide and water/carbonates at 531.1 eV and 532.4 eV respectively, apart from the oxide presence detected at 530.2 eV (Figure S5).



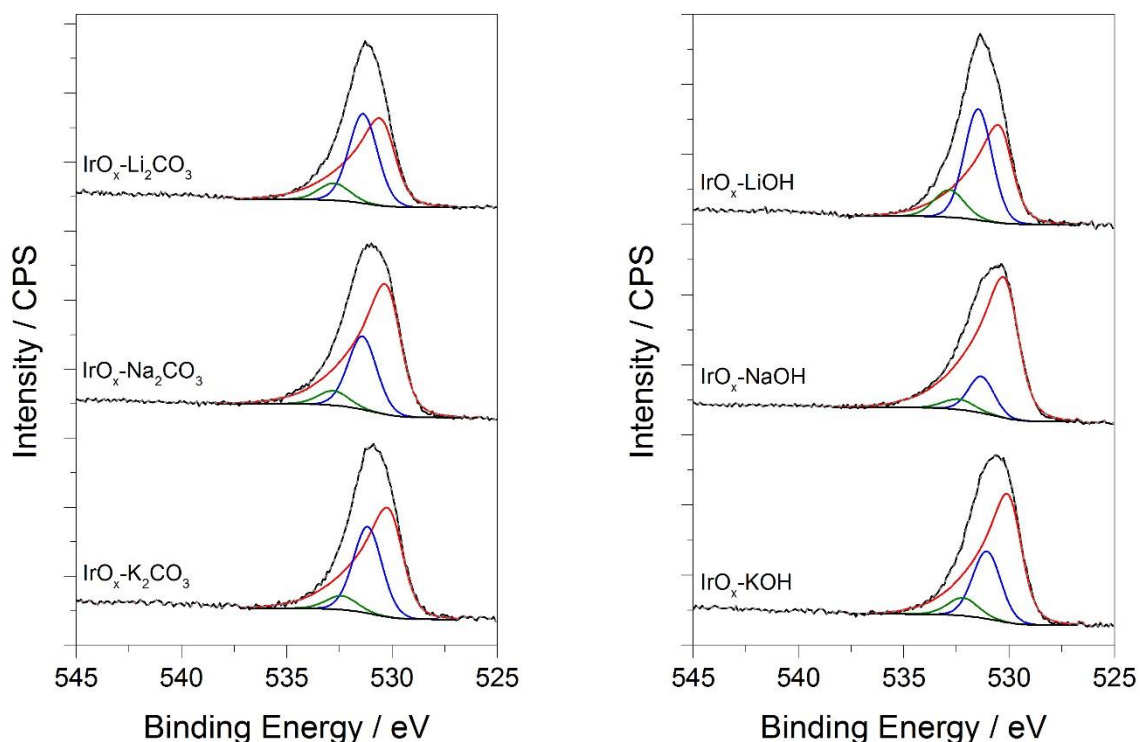


**Figure S4.** Ir(4f) XPS spectra for hydrothermally prepared synthesised IrO<sub>x</sub> catalysts. Red and blue fittings correspond to Ir(4f) and Ir(5p) respectively.

**Table S1.** Ir/O ratio obtained from the XPS quantification of the Ir(4d) and O(1s) peaks.

Catalyst	Ir/O ratio	Catalyst	Ir/O ratio
IrO <sub>2</sub> Sigma Aldrich	0.49	IrO <sub>2</sub> Alfa Aesar	0.31
IrO <sub>2</sub> -Li <sub>2</sub> CO <sub>3</sub>	0.32	IrO <sub>2</sub> -LiOH	0.32
IrO <sub>2</sub> -Na <sub>2</sub> CO <sub>3</sub>	0.29	IrO <sub>2</sub> -NaOH	0.33
IrO <sub>2</sub> -K <sub>2</sub> CO <sub>3</sub>	0.33	IrO <sub>2</sub> -KOH	0.33





**Figure S5.** O(1s) XPS spectra for hydrothermally prepared IrO<sub>x</sub> catalysts using different bases. Oxide, hydroxide and water components are represented with red, blue and green lines respectively.

## 2. Electrochemical measurements

### Electrochemically active surface area (ECSA) normalised activity

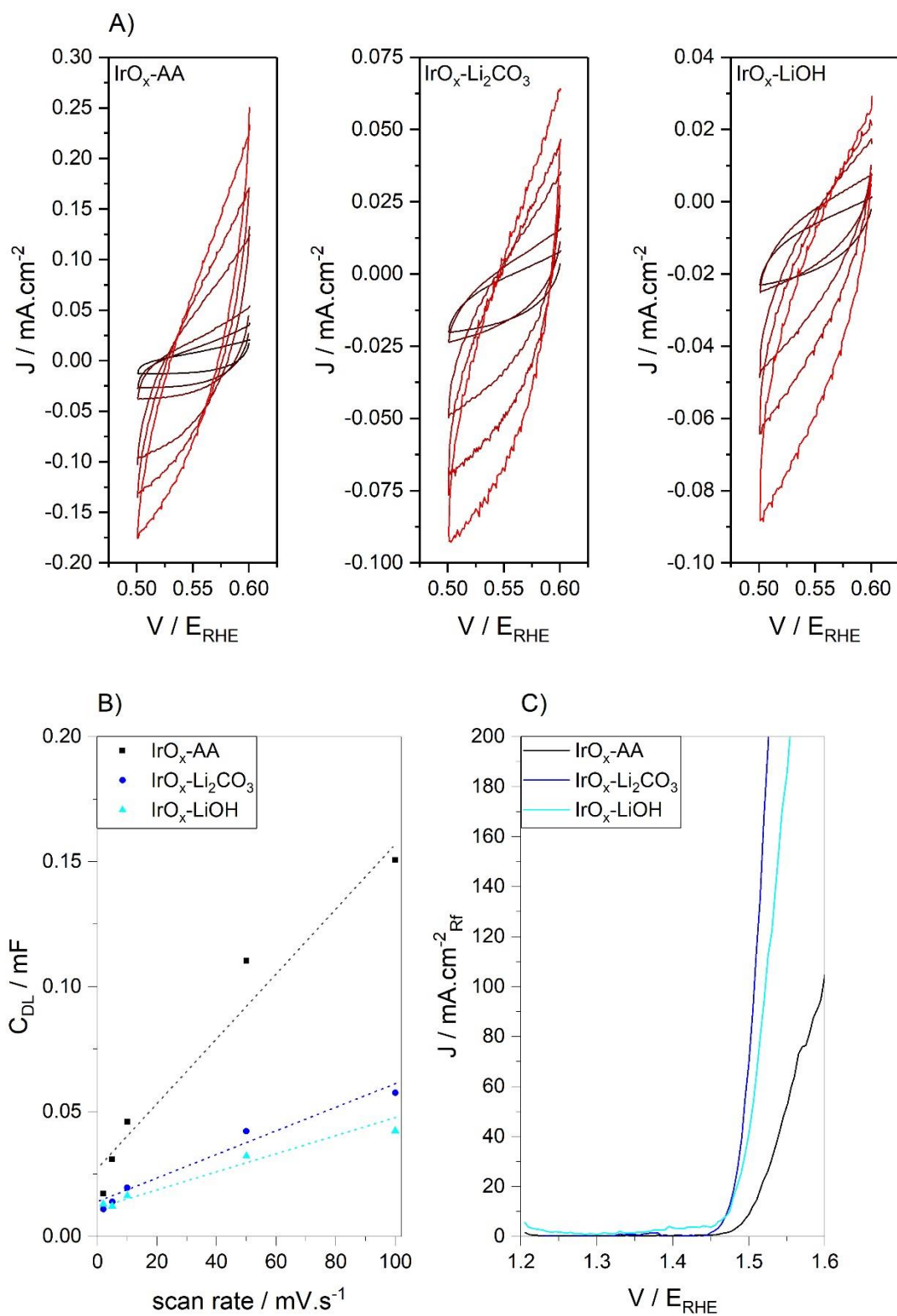
Intrinsic catalytic activity of hydrothermally prepared IrO<sub>x</sub> catalysts was obtained by LSV and normalised to the geometric surface area (figure 5 in main text). To confirm the higher activity of IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub> compared to IrO<sub>x</sub>-LiOH and IrO<sub>x</sub>-AA, intrinsic activities were normalised against the roughness factor, obtained from ECSA measurements,<sup>(8)</sup> and to the iridium mass.

ECSA measurements were performed on IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub>, IrO<sub>x</sub>-LiOH and IrO<sub>x</sub>-AA catalysts to evaluate the electrochemically available surface area during OER. To avoid the interference of Faradaic processes, cyclic voltammetry (CV) between 0.5 V<sub>RHE</sub> and 0.6 V<sub>RHE</sub> with scan rates at 2 mV·s<sup>-1</sup>, 5 mV·s<sup>-1</sup>, 10 mV·s<sup>-1</sup>, 50 mV·s<sup>-1</sup> and 100 mV·s<sup>-1</sup> were measured (Figure S6a). The slope obtained from plotting the average between the maximum anodic current density and the minimum cathodic current density,  $(J_{\text{max, an}} - J_{\text{min, cat}})/2$ , against the scan rate is the double layer capacitance (C<sub>DL</sub>) of the catalyst (Figure S6b).

The double layer capacitance can then be converted to the electrochemically active surface area by dividing it by the specific capacitance in acidic conditions ( $C_{s, ac.} = 0.035 \text{ mF} \cdot \text{cm}^{-2}$ ).

$$\text{ECSA} = C_{\text{DL}} / C_{s, ac}$$

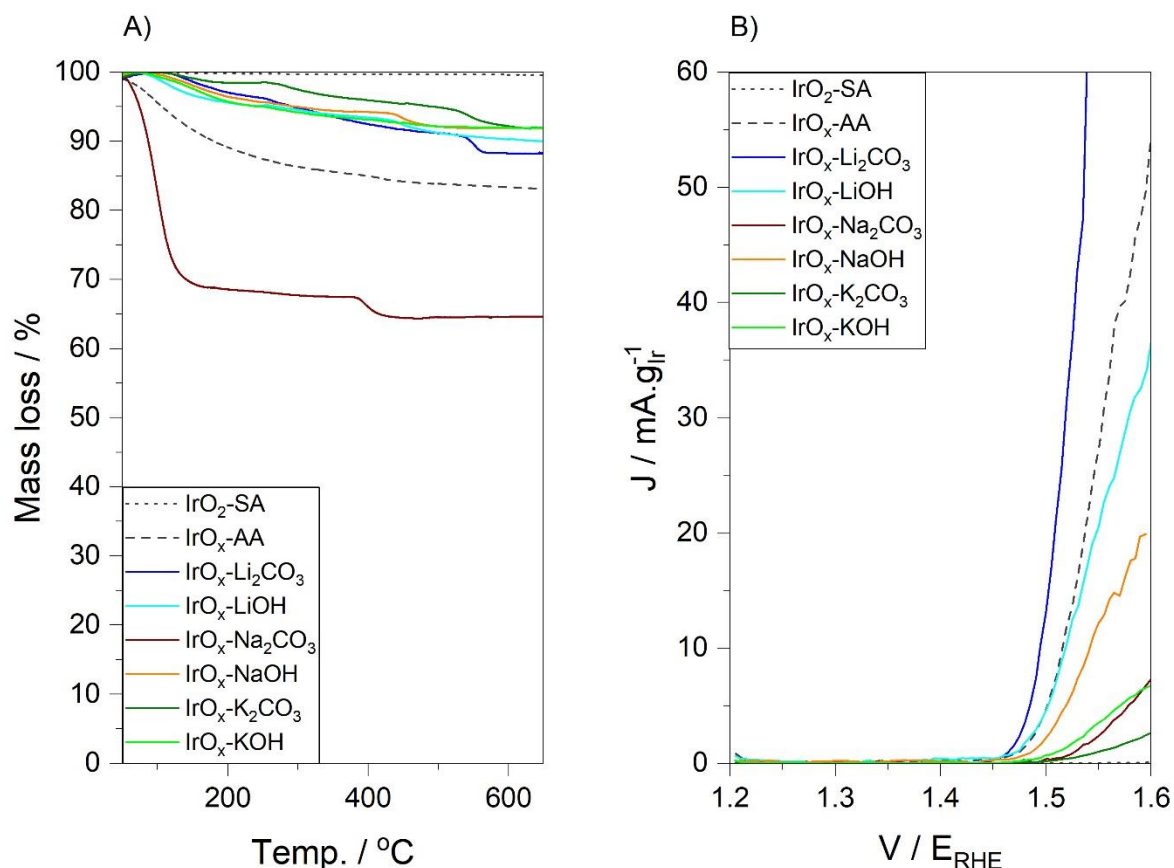
ECSA values of  $0.014 \text{ cm}^{-2}$ ,  $0.001 \text{ cm}^{-2}$  and  $0.037 \text{ cm}^{-2}$  were obtained for  $\text{IrO}_x\text{-Li}_2\text{CO}_3$ ,  $\text{IrO}_x\text{-LiOH}$  and  $\text{IrO}_x\text{-AA}$  respectively. The roughness factor ( $R_f$ ) of each catalyst can be obtained by dividing ECSA with the geometric surface area of the electrode (in this case  $0.196 \text{ cm}^2$ ). The measured  $R_f$  for  $\text{IrO}_x\text{-Li}_2\text{CO}_3$ ,  $\text{IrO}_x\text{-LiOH}$  and  $\text{IrO}_x\text{-AA}$  was 0.073, 0.044 and 0.190 respectively. Normalised activities with  $R_f$  confirmed the higher activity of  $\text{IrO}_x\text{-Li}_2\text{CO}_3$  compared to  $\text{IrO}_x\text{-LiOH}$  and  $\text{IrO}_x\text{-AA}$  (Figure S6c).



**Figure S6.** a) Double-layer capacitance measurements for the determination of ECSA, b)  $J_{\text{cat}} - J_{\text{an}}$  plotted against CV scan rate and c) roughness factor normalised activities for IrO<sub>x</sub>-AA, IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub> and IrO<sub>x</sub>-LiOH.

### **Iridium mass normalised activity towards OER**

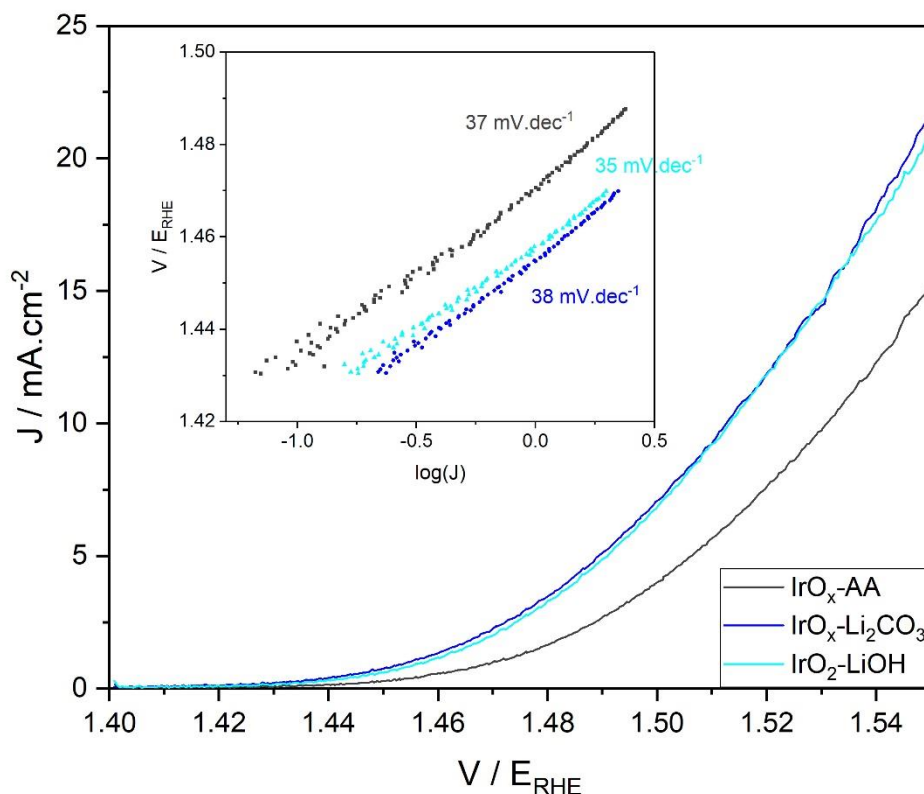
In this work, the catalyst concentration on the working electrode was kept constant at  $100 \mu\text{g}_{\text{cat}}\cdot\text{cm}^{-2}$ . Electrode surface area normalised activity for OER measured by LSV indicated the higher activity of  $\text{IrO}_x\text{-Li}_2\text{CO}_3$  compared to commercial  $\text{IrO}_x\text{-AA}$ , and the rest of prepared  $\text{IrO}_x$  catalysts. The main drawback against normalising OER catalyst activity to the electrode surface area is its dependence on the catalyst loading. Moreover, the determination of the ECSA, and the roughness of a catalyst, are subject to inaccuracies, which can vary on several orders of magnitude.<sup>(7)</sup> As discussed by Fabbri *et. al.*<sup>(9)</sup> it is best to normalise catalyst activity against the iridium mass loading. To determine the mass of iridium on the electrode thermogravimetric analysis (TGA) was performed on all catalysts (Figure S7a). TGA were recorded on a PerkinElmer TGA 4000 instrument under  $\text{N}_2$  (from  $30^\circ\text{C}$  to  $650^\circ\text{C}$  at  $5^\circ\text{C}\cdot\text{min}^{-1}$ ). The corresponding mass loss was assigned to surface hydroxide groups and to physisorbed water, which yielded rutile  $\text{IrO}_2$ . Through TGA results, the catalyst loading on the electrode ( $100 \mu\text{g}_{\text{cat}}\cdot\text{cm}^{-2}$ ) was converted to the iridium mass on the electrode and used to normalise the OER activity. Iridium mass normalised activities (Figure S7b) confirmed the higher activity of  $\text{IrO}_x\text{-Li}_2\text{CO}_3$  for OER compared to the other catalysts.



**Figure S7.** a) Mass loss obtained from TGA for synthesised IrO<sub>x</sub> and commercial IrO<sub>2</sub> standards; b) Iridium mass normalised activity for OER catalysts.

### Tafel slope

The slope obtained from plotting the ohmic drop corrected overpotential against the logarithm of the current density, described as Tafel slope, is an empirical parameter that contains information about the electrocatalytic activity and the reaction mechanism.<sup>(9,10)</sup> By comparing the experimental Tafel slope with theoretical calculations the rate determining step of the reaction can be elucidated. To correlate if differences in activity observed by LSV for IrO<sub>x</sub>-AA, IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub> and IrO<sub>x</sub>-LiOH catalysts can relate with different rate determining step during OER Tafel slopes were measured (Figure S8). Tafel slopes were derived from semi-steady-state conditions obtained from LSV measurements performed at a ramp rate of 0.5 mV·s<sup>-1</sup>. At low overpotential, measured Tafel slopes for IrO<sub>x</sub>-AA, IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub> and IrO<sub>x</sub>-LiOH were 37 mV·dec<sup>-1</sup>, 38 mV·dec<sup>-1</sup>, and 35 mV·dec<sup>-1</sup> respectively, in agreement with previously reported values (~40 mV·dec<sup>-1</sup>).<sup>(10,11,12,13)</sup> Indicating that different activity observed between catalysts are not attributed to differences in the OER rate determining step.



**Figure S8.** Semi-steady-state LSV polarization curves recorded between 1.4  $V_{\text{RHE}}$  and 1.55  $V_{\text{RHE}}$  at  $0.5\text{ mV}\cdot\text{s}^{-1}$  for  $\text{IrO}_x\text{-AA}$ ,  $\text{IrO}_x\text{-Li}_2\text{CO}_3$  and  $\text{IrO}_x\text{-LiOH}$  catalysts and obtained Tafel plots at low overpotential (1.43  $V_{\text{RHE}}$  - 1.47  $V_{\text{RHE}}$ ).

### **$\text{Li}^+$ , $\text{Na}^+$ and $\text{K}^+$ -doped Rutile $\text{IrO}_2$**

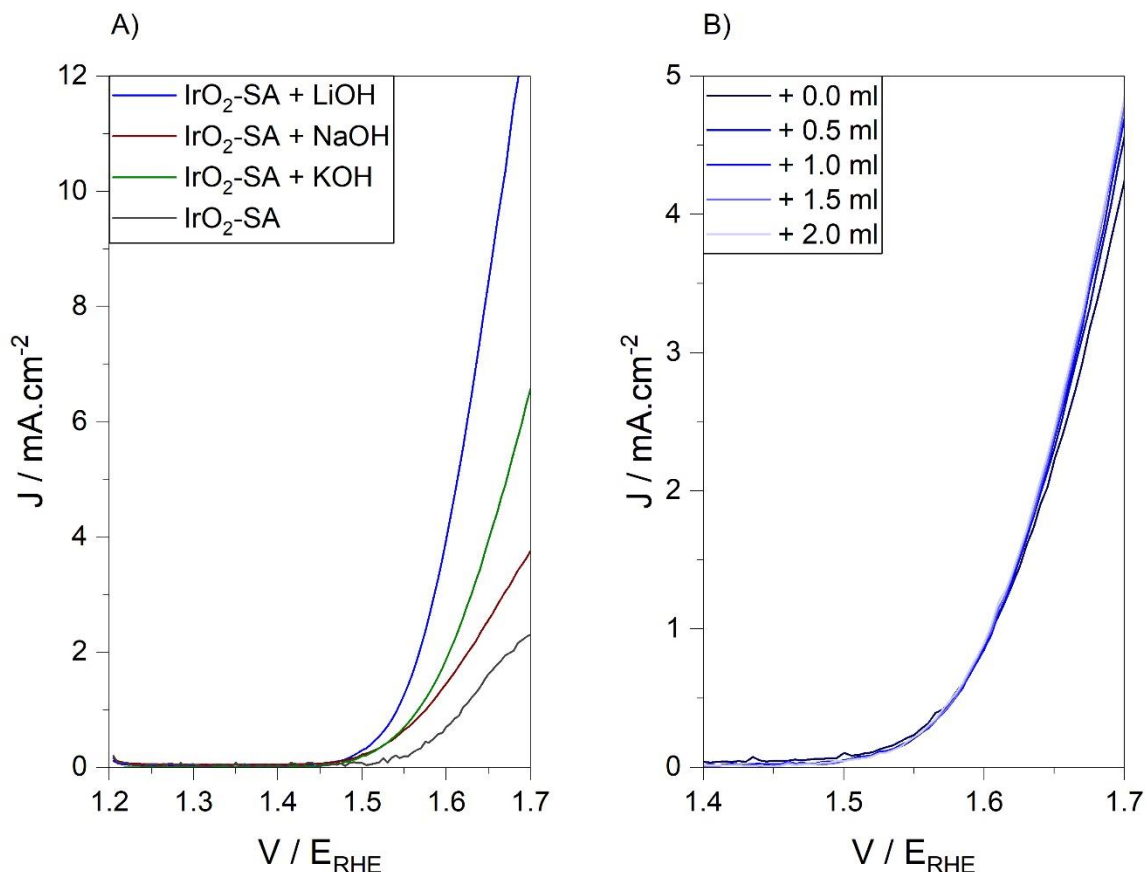
To confirm that lithium is acting as a promoter  $\text{IrO}_x$  catalyst for OER, rutile  $\text{IrO}_2$  from Sigma Aldrich was doped with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ . Gao *et.al.*<sup>(11)</sup> doped rutile  $\text{IrO}_2$  by its reaction with  $\text{LiOH}$ ,  $\text{NaOH}$  and  $\text{KOH}$  at  $300\text{ }^\circ\text{C}$ . After reaction the surface of  $\text{IrO}_2$  hydrolysed resulting in enhanced activity, nevertheless, the material doped with lithium showed higher activity compared to sodium and potassium towards OER, which was attributed to the higher promoting effect of lithium.

Since in the present work heat treatment was avoided, cation doping ( $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ ) was achieved during the catalyst ink preparation. For the catalyst ink preparation 5 mg of rutile  $\text{IrO}_2$  was re-dispersed in 1.23 ml of 0.1 M alkaline aqueous solution ( $\text{LiOH}$ ,  $\text{NaOH}$  or  $\text{KOH}$ ), 1.23 ml of ethanol and 40  $\mu\text{l}$  of nafion solution. The catalyst ink was sonicated for 30 min to ensure a homogenous dispersion, and then 10  $\mu\text{l}$  of the catalyst ink was drop-cast in the working electrode and dried under a  $\text{N}_2$  flow for 30 min. Doped-rutile  $\text{IrO}_2$  catalyst showed higher

catalytic activity than rutile IrO<sub>2</sub>-SA (Figure S9a), which can be attributed to the formation of surface hydroxide groups formed after alkaline treatment during the catalyst ink preparation. Nevertheless, higher activity was observed for Li<sup>+</sup>-doped rutile IrO<sub>2</sub> compared to Na<sup>+</sup> or K<sup>+</sup>-doped rutile IrO<sub>2</sub>, in line with the higher promoting effect of lithium.

To ensure that improved activity for OER, a part from the promoting effect of ink preparation in alkaline condition and concomitant IrO<sub>2</sub> surface hydroxylation, is related to the presence of Li<sup>+</sup>, a IrO<sub>2</sub>-SA electrode was prepared in standard conditions (1.23 ml H<sub>2</sub>O, 1.23 mL ethanol, 40 µl nafion solution) and measured in a standard 3-electrode cell (40 ml, 0.1 M HClO<sub>4</sub>) by LSV (1.2 V<sub>RHE</sub> - 1.7 V<sub>RHE</sub>, 5 mV·s<sup>-1</sup>). Catalytic activity for OER was measured after consecutive 0.5 ml addition of 0.1 M LiOH by LSV. As observed in Figure S9b, improved current density by LSV was measured after each consecutive addition. In acids conditions, the OER mechanism is not dependent on the reaction pH,<sup>(14)</sup> and hence, improved activity more likely relates with the presence of Li<sup>+</sup>. Nevertheless, further research is needed to understand whether lithium is acting as a promoter, changing the local structure of rutile IrO<sub>2</sub> forming active motifs or just increasing the population of active sites.





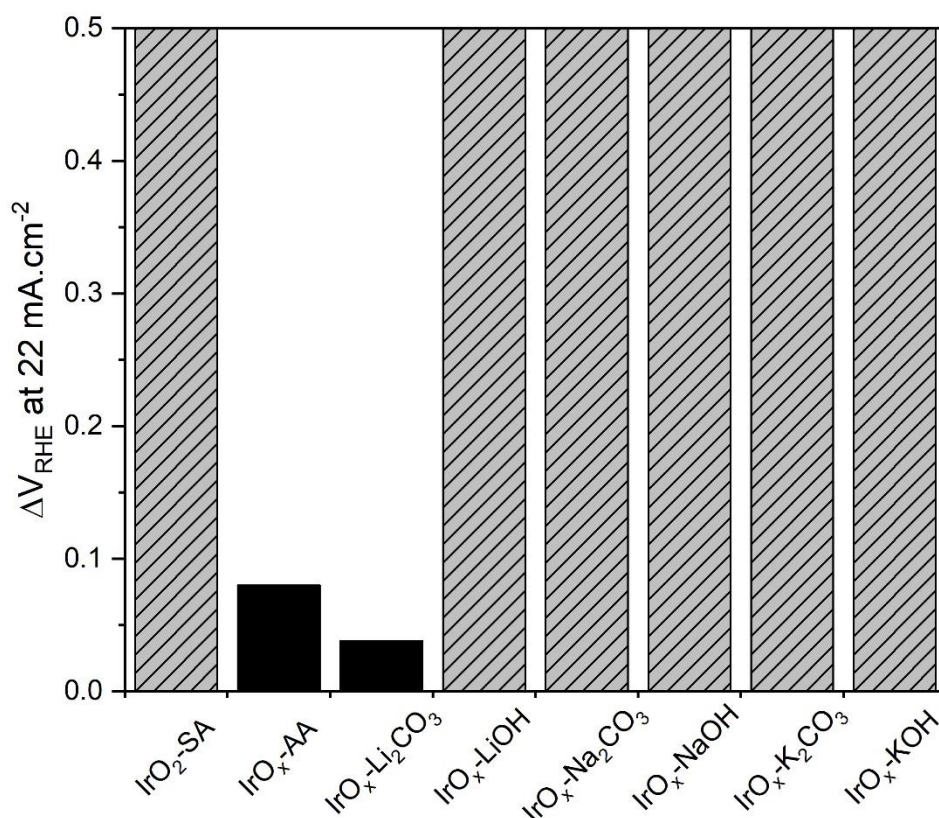
**Figure S9.** IrO<sub>2</sub>-SA catalytic activity towards OER determined by LSV (1.2  $V_{\text{RHE}}$  – 1.7  $V_{\text{RHE}}$ , 5  $\text{mV} \cdot \text{s}^{-1}$ ) for a) catalyst ink containing 0.1 M solution of LiOH, NaOH or KOH. b) addition of 0.1 M LiOH into the electrolyte.

### Catalyst deactivation towards OER

The electrochemical assessment of IrO<sub>x</sub> catalysts for OER in HClO<sub>4</sub> 0.1 M was performed in a 3-electrode flow cell described previously in literature.<sup>(8)</sup> Intrinsic catalytic activity was assessed by LSV (1.2  $V_{\text{RHE}}$  to 1.7  $V_{\text{RHE}}$  at 5  $\text{mV} \cdot \text{s}^{-1}$ ) at the beginning of the experiment. Rutile IrO<sub>2</sub> showed no significant current density in the potential range studied. It was observed that IrO<sub>x</sub>-NaOH, IrO<sub>x</sub>-Na<sub>2</sub>CO<sub>3</sub>, IrO<sub>x</sub>-KOH or IrO<sub>x</sub>-K<sub>2</sub>CO<sub>3</sub> performed poorly compared to commercial IrO<sub>x</sub>-AA. IrO<sub>x</sub>-LiOH showed comparable intrinsic activity to the commercial IrO<sub>x</sub>-AA (1.52  $V_{\text{RHE}}$  at 22  $\text{mA} \cdot \text{cm}^{-2}$ ), whilst IrO<sub>x</sub>-Li<sub>2</sub>CO<sub>3</sub> (1.50  $V_{\text{RHE}}$  at 22  $\text{mA} \cdot \text{cm}^{-2}$ ) outperformed the commercial IrO<sub>2</sub>-AA standard.

To determine the catalyst degradation occurred during CP (2 h, 10  $\text{mA} \cdot \text{cm}^{-2}$ ), the potential to reach a 22  $\text{mA} \cdot \text{cm}^{-2}$  current density by LSV before and after CP were compared (Figure S10). Catalysts in which glassy carbon corrosion was observed during CP, showed no activity in the consecutive LSV measurement. The catalytic activity of IrO<sub>2</sub>-LiOH was seriously compromised

after CP, and the current density measured by LSV did not reach  $22 \text{ mA}\cdot\text{cm}^{-2}$ .  $\text{IrO}_2\text{-Li}_2\text{CO}_3$  showed a potential increase of only 38 mV after CP compared to 80 mV for commercial  $\text{IrO}_2\text{-AA}$ .



**Figure S10.** Increase in the potential measured by LSV at a current density of  $22 \text{ mA}\cdot\text{cm}^{-2}$  before and after CP (2 h,  $10 \text{ mA}\cdot\text{cm}^{-2}$ ).

Iridium dissolution was measured with an ICP coupled to the electrochemical flow cell in the Max Planck Institute for Chemical Energy Conversion in Germany, as reported previously.<sup>(8)</sup> Hydrous  $\text{IrO}_x$  (Alfa Aesar) and  $\text{IrO}_x\text{-Li}_2\text{O}_3$  were drop coated in an Au ( $0.196 \text{ cm}^2$ ) electrode instead of a glassy carbon, used in previous measurements. The conversion of the recorded ICP signal to the iridium monolayers $\cdot\text{s}^{-1}$  was done as follows: The ICP sensitivity for Ir is 1 ppb, with a 2 h CP experiment at  $0.86 \text{ ml}\cdot\text{min}^{-1}$  the ICP sensitivity is  $0.014 \text{ ng}_{\text{Ir}}\cdot\text{s}^{-1}$  or  $2.2\times 10^{-5}$  monolayers $\cdot\text{s}^{-1}$ .

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