

Alkali Metal Iridates as Oxygen Evolution Catalysts Via Thermal Transformation of Amorphous Iridium (oxy)hydroxides.

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Efficient water-splitting is severely limited by the anodic oxygen evolution reaction (OER). Iridium oxides remain one of the only viable catalysts under acidic conditions due to their corrosion resistance. We have previously shown that heat-treating high-activity amorphous iridium oxyhydroxide in the presence of residual lithium carbonate leads to the formation of lithium-layered iridium oxide, suppressing the formation of low-activity crystalline rutile IrO₂. We now report the synthesis of Na-IrO_x and K-IrO_x featuring similarly layered crystalline structures.

Electrocatalytic tests confirm Li-IrO_x retains similar electrocatalytic activity to commercial amorphous IrO₂·2H₂O and with increasing size of the intercalated cation, the activity towards the OER decreases. However, the synthesised electrocatalysts that contain layers show greater stability than crystalline rutile IrO₂ and amorphous IrO₂·2H₂O, suggesting these compounds could be viable alternatives for industrial PEM electrolyzers where durability is a key performance measure.

Introduction

To transition to a hydrogen economy, efficient water electrolysis is crucial to storing renewable energy.^[1] The anodic oxygen evolution reaction (OER) under acidic conditions can often limit the overall performance of electrolyser devices due to high kinetic barriers requiring additional overpotential (η), leading to energy losses and inefficiency.^[2] A second challenge is to find catalysts that can operate under the required anodic potentials in an acidic environment without rapid deactivation through passivation or corrosion.^[3] To date, RuO₂ and IrO₂ are the most studied materials for OER under acidic conditions.^[4–6] The former displays high activity but shows low stability due to fast corrosion in acidic media. The relationship between stability and activity of various IrO₂ morphologies has been extensively studied in recent years.^[7] Colloidally prepared metallic Ir nanoparticles or deposited Ir metallic films have been shown to readily form amorphous iridium(oxy)hydroxide (Ir(O)_x(OH)_y) surfaces under OER conditions which is the active form of the catalyst.^[8,9] Ir(O)_x(OH)_y outperforms highly crystalline rutile IrO₂ (r-IrO₂) in terms of reduced overpotential (η) and amorphous Ir(O)_x(OH)_y materials have been shown to convert to rutile IrO₂

under thermal treatments >350 °C during preparation. Geiger *et al.* reported that annealing amorphous Ir(O)_x(OH)_y films results in rutile IrO₂ with reduced intrinsic activity, suggesting a fine balance between activity, stability, and structure of the catalyst.^[10] Using atom probe tomography to study the structural evolution of Ir oxides gives evidence for oxygen mobility/exchange with the electrolyte during the OER using isotopically labelled Ir¹⁸O₂.^[11] These results suggest that structural flexibility plays a key role in the activity of iridium oxides but may also trigger deactivation through corrosion.^[12] Crystalline IrO₂ has been generally shown to have lower activity but greater stability towards OER compared to the amorphous analogue.^[13]

The development of both active and stable IrO₂ catalysts remains a significant challenge and has been studied *via* a wide array of synthetic methods to control the morphological features of the material. Recently the role of alkali metals in both the OER electrolyte and the catalyst material has gained increasing attention.^[14] Koper *et al.* recently demonstrated that the addition of Li⁺ to a NaOH electrolyte increases the rate of OER over NiFe(OOH) catalysts by enhancing the mass transport of water through the structure.^[15] Furthermore, we recently demonstrated higher OER activity of iridium(oxy)hydroxides synthesised in the presence of alkali metal salts, such as Li₂CO₃ compared to commercial materials which had comparable geometric surface areas, surface atomic and electronic composition, and bulk structures.^[16] It was found that materials prepared with bases containing Li⁺ cations led to amorphous Ir(O)_x(OH)_y showing a significantly lower overpotential (η = 250 mV at 10 mA cm⁻²) and increased stability compared to commercial rutile IrO₂ or amorphous IrO₂·2H₂O. This higher activity, normalized to active electrochemical surface area (ECSA), suggested a possible promotional effect of residual alkali metal ions. Gao *et al.* synthesised a similar amorphous Li⁺-doped IrO_x catalyst with high activity (η = 270 mV at

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10 mA cm⁻²) suggesting that the presence of Li⁺ promotes flexible IrO₆ octahedra.^[17] Alkali-doped crystalline hollandite IrO₂ structures have also been reported by Sun *et al.* who synthesized K_{0.25}IrO₂ from IrCl₃/K₂CO₃ by annealing in air (600 °C, 6 h), and distorted IrO₆ octahedra were suggested to increase activity compared to rutile IrO₂.^[18]

Recently our group have shown that when amorphous Ir(O)_x(OH)_y contains residual Li⁺ from the hydrothermal precipitation the thermal conversion to low-activity rutile IrO₂ at 300–400 °C can be suppressed. Instead, on heat treatment a nanocrystalline Li-intercalated iridium oxide (Li-IrO_x) forms at relatively mild conditions (500 °C, 3 h).^[19] These Li-IrO_x electrocatalysts exhibit comparable activity and improved stability compared to the commercially available IrO₂·2H₂O, indicating this nanocrystalline iridate structure could be more practical for industrial applications where higher durability is necessary. In the present study, we show that starting from amorphous Ir(O)_x(OH)_y, it is possible to prepare alkali layered iridate materials containing Li⁺, Na⁺ and K⁺ by adopting the same synthetic approach by retaining residual alkali metal salts, *i.e.* Li₂CO₃, Na₂CO₃, K₂CO₃. We find the activity of the electrocatalysts is not improved when adding heavier alkali metals. However, these materials show higher stability than amorphous alkali metal-free iridium oxide and could be viable alternatives for more durable catalysts in industrial applications.

Experimental

Synthesis of Iridium Materials

Amorphous iridium oxyhydroxide, Ir(O)_x(OH)_y, was prepared following the method reported previously.^[16] 1 mmol IrCl₃ hydrate (Johnson Matthey) and 8 mmol of M₂CO₃ (M = Li⁺, Na⁺ and K⁺, 99.0+ % Sigma Aldrich, 99% Thermoscientific and 99.5% Thermoscientific, respectively) were dissolved in 10 mL of deionized water and stirred for 16 h at 25 °C. 10 mL of deionized water was added, followed by reflux for 3 h. The mixture was cooled to room temperature and the precipitate was recovered by centrifugation and dried at 60 °C for 16 h. Metal-doped iridium oxides, M-IrO_x (M = Li⁺, Na⁺ and K⁺) were obtained by heat treating the precursor Ir(O)_x(OH)_y containing the M₂CO₃ (M = Li⁺, Na⁺ and K⁺) in static air at temperatures between 510 and 525 °C for 3 h. Residual M₂CO₃ and Cl contamination were removed by washing with 1 L of hot and 1 L of cold deionised water *via* centrifugation. Finally, the solid obtained was dried overnight at 60 °C.

Catalyst Characterisation

Powder X-ray diffraction (XRD) patterns were obtained on a Stoe Stadi P powder diffractometer in transmission mode fitted with a Multi-MYTHEN detector and using a Cu K_α radiation source (λ = 1.5046 Å, 40 keV, 40 mA). The Harwell JEOL-ARM2000 Aberration-Corrected Transmission Electron Microscope was used to analyse the M-IrO_x electrocatalysts at 200 kV electron beam, with samples ground and dusted onto carbon-coated Cu TEM grids in bright field and high angular annular dark field (HAADF) STEM modes, as well as in TEM mode. Scanning electron microscopy (SEM) measurements were performed using a Hitachi SU3900 microscope. Powder samples were deposited on carbon tabs placed on aluminium sample holders, followed by gold coating. Images were acquired

using a 10 kV electron beam and employing both a backscattering electron (BSE) and a secondary electron (SE) detector. Ir 4f and O 1s X-ray photoelectron spectra (XPS) were obtained using a Thermo Fisher Scientific K-alpha⁺ spectrometer. Samples were analysed using a micro-focused monochromatic Al X-ray source (72 W) using an elliptical X-ray spot of ca. 400×600 microns. Data was recorded at pass energies of 150 eV for survey scans and 50 eV for high-resolution scans with 1 eV and 0.1 eV step sizes respectively. Charge neutralisation of the sample was achieved using low-energy electrons and argon ions. Fitting of the XPS data was carried out using the model summarised in Table S3, and following the Levenberg–Marquardt algorithm to minimize χ². Background correction was performed using a Shirley background. The O K-edge NEXAFS spectra were collected at the B07 beamline at the UK synchrotron facility Diamond Light Source (DLS) using a 400 l/mm Au grating of the monochromator.^[20] The exit slit was set to 0.5 μm x 0.04 μm and the fix focus constant (cff) to 2.0. Spectra were collected in total electron yield mode by detecting the drain current generated by the photoemitted electrons from the samples at a distance of approximately 200 μm. In Auger yield mode data were collected using the electron analyser of the VERSOX end station at DLS, setting the kinetic energy to 395 eV and pass energy 100 eV. Spectra were normalized to the maximum intensity at approximately 546 eV, after linear background subtraction. The relative energy calibration of the spectra was checked using features in the drain current of the beamline nozzle, fixing the μ_{3,0} resonance of r-IrO₂ to 530 eV.

XAS were recorded in transmission mode at the Ir L₃ edge, at the B18 beamline of the Diamond Light Source. Pellets were prepared by grinding powders with cellulose as a matrix for *ex situ* analysis. Working electrodes for *in situ* XAS measurements were prepared *via* drop-casting 47 μL of catalyst ink (5 mg catalyst in 2 mL of water, 0.5 mL of methanol) on a 12 mm TorayTM carbon paper TGP-60 to obtain catalyst loading of ~100 μg_{cat} cm⁻². 1 μL Nafion 5%wt was deposited on top of the catalyst ink once this was dry. Three scans per sample were recorded, and the averaged signal was used for data analysis. The measurements were performed using a QEXAFS setup with a fast-scanning Si (111) double crystal monochromator. For the *in situ* measurements, the time resolution of the data acquisition was ~200 s/spectrum. XANES and EXAFS data were interpreted using IFEFFIT within the Demeter software package (Athena and Artemis),^[21] using structural models available from ICDD as cited in the text. *In situ*, XAS measurements were carried out using a sealed cell filled with a 0.1 M HClO₄ and with catalyst inks deposited on carbon paper as working electrodes. A Pt wire and a Ag/AgCl electrode were used as counter and reference electrodes, respectively.

Catalyst Testing

Catalysts were tested on a three-electrode setup in a 0.1 M HClO₄ (Honeywell, 70%) electrolyte using a Biologic SP-300 potentiostat. A coiled Pt wire (127 μm diameter, 99.99%, Advent Research Materials) was used as the counter electrode, a rotating disk glassy carbon electrode (5.00 mm disk diameter, 0.196 cm² geometric surface area, model AFE5T050GC, Pine Research) was used as the working electrode, and a Ag/AgCl electrode (ALS Co. Ltd., model RE-1B, E⁰_{Ag|AgCl} = +0.195 V_{RHE}) was used as the reference electrode. To prepare the catalyst ink, 5 mg of catalyst, 2.0 mL of water, 0.5 mL of methanol was sonicated for 30 min. 20 μL of the catalyst ink was drop-cast onto the GC working electrode and dried under an IR lamp. The catalyst activity toward OER was measured by linear sweep voltammetry (LSV, 0.2 to 1.8 V_{RHE} at 5 mVs⁻¹), at room temperature. The current densities in the LSV plots were obtained by normalising the measured currents by the electrode geometric

surface area. Catalyst stability was assessed by chronopotentiometry (CP, 2 h and 25 h, at 10 mA cm⁻²). The double-layer capacitance (C_{DL}) was obtained from CVs in the 0.4–0.5 V_{RHE} region at different scan rates (2, 5, 10, 40, 80, and 100 mV s⁻¹). The ECSA was obtained by dividing the C_{DL} by the specific capacitance in acid media ($C_{s,ac}$ = 0.035 mF cm⁻²) and the roughness factor (Rf) was calculated by dividing this by the geometric surface area. Tafel slopes were derived from semi-steady-state conditions obtained from LSV measurements performed at low overpotential (1.43–1.56 V_{RHE}, 0.5 mV s⁻¹). Reported values are expressed against the reversible hydrogen electrode (RHE), with values obtained according to $E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^0 + (0.059 \text{ V} \times \text{pH})$, and with the pH of 0.1 M HClO₄ measured as ~1.

Results and Discussion

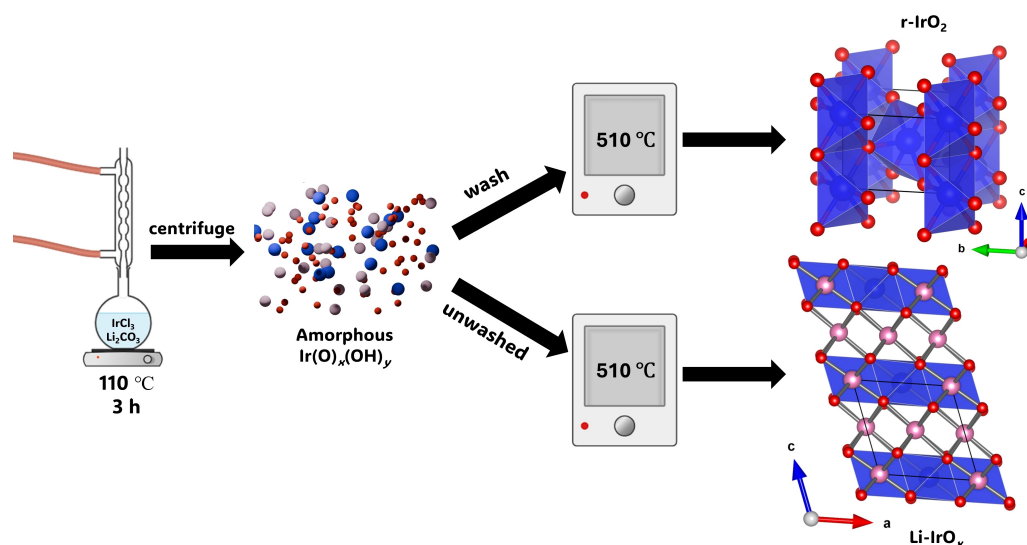
The facile synthesis of amorphous Ir(O)_x(OH)_y using Li₂CO₃ as a precipitating agent produced an active and relatively stable IrO_x material compared to commercial IrO₂·2H₂O when tested under our experimental conditions (see experimental section). We demonstrated that by retaining residual Li₂CO₃ in the parent material by omitting a washing step, the thermal transition to rutile IrO₂ (r-IrO₂) at ~400 °C under air is suppressed and instead, a nano-crystalline lithium iridate is formed (see Scheme 1).^[19]

Both β-Li_xIrO₃ and α-Li_xIrO₃ contain layered Ir-oxo sheets made predominantly from Ir-O₆ octahedra with both in-plane and interlayer Li⁺ with characteristic interlayer spacings of ~0.48 nm consistent with $x = 2$.^[22] Lithium iridate preparation methods typically involve the use of high-temperature solid-state or molten salt synthesis with prolonged reaction times, e.g. β-Li₂IrO₃ synthesis was reported previously by treating Ir/IrO₂ and Li₂CO₃ at 1080 °C for 30 h or heating IrCl₃ in molten LiOH at 700–900 °C.^[23–25] In this case, we propose starting from an amorphous Ir(O)_x(OH)_y, which has higher structural flexibility than crystalline Ir black or r-IrO₂, makes this solid state reaction/

transition more facile with the intimately mixed Ir(O)_x(OH)_y/Li₂CO₃ product of the precipitation.

Initially, we synthesised amorphous Ir(O)_x(OH)_y using Li₂CO₃, Na₂CO₃ and K₂CO₃ as precipitating agents using identical procedures. X-ray diffraction (see Figure 1a–c) shows that the as-synthesised materials remain amorphous with only broad diffraction features at ~35° before any thermal treatment. Additional contaminant diffraction features were consistent with the respective residual metal carbonates. The three Ir(O)_x(OH)_y samples containing residual Li⁺, Na⁺ and K⁺ were subsequently calcined under static air for 3 h at 510, 500 and 525 °C for Li-IrO_x, Na-IrO_x and K-IrO_x respectively. The heat treatment in the presence of residual alkali metal carbonates suppressed the formation of rutile IrO₂ in each case and led to the formation of layered iridium oxide structures. In particular, low angle reflections develop at 2θ angles, ~19°, ~17° and ~13° for $M = \text{Li}^+$, Na^+ and K^+ respectively. The interlayer d -spacing values corresponding to those reflections are 4.7, 5.0 and 6.9 Å for $M = \text{Li}^+$, Na^+ and K^+ correlating with the increasing size of the incorporated alkali metal cation. The interlayer distance found for Li-IrO_x is consistent with previous results and the β-Li₂IrO₃ phase reported by O'Malley *et al.* who prepared samples by heating Li₂CO₃ and Ir metal at 750 °C 12 h before increasing the temperature to 1050 °C [ICSD-246025].^[26] It should be noted that the synthesis of K-IrO_x was successful only when a large excess of K₂CO₃ (~10x) was ground with the synthesised Ir(O)_x(OH)_y before annealing. By contrast, the synthesis of Li-IrO_x and Na-IrO_x required no additional carbonates other than those used in the precipitation step before thermal treatment.

To confirm the presence of the layered phases, refinements of structural models were carried out using the Le Bail method.^[27] Structural models for previously reported lithium iridate (Li₂IrO₃) and sodium iridate (Na₂IrO₃), both featuring a monoclinic $C2/m$ structure,^[26,28] as well as for potassium iridate (K_{0.3}IrO₂·0.6H₂O), featuring a trigonal $R\bar{3}m$ structure,^[29] show good agreement with the data (see Figure 1d–f, Supplementary



Scheme 1. Synthesis of Ir(O)_x(OH)_y with Li₂CO₃ as a precipitating salt, followed by the divergent routes for the synthesis of r-IrO₂ or Li-IrO_x. Blue, red and pink atoms represent iridium, oxygen and lithium, respectively.

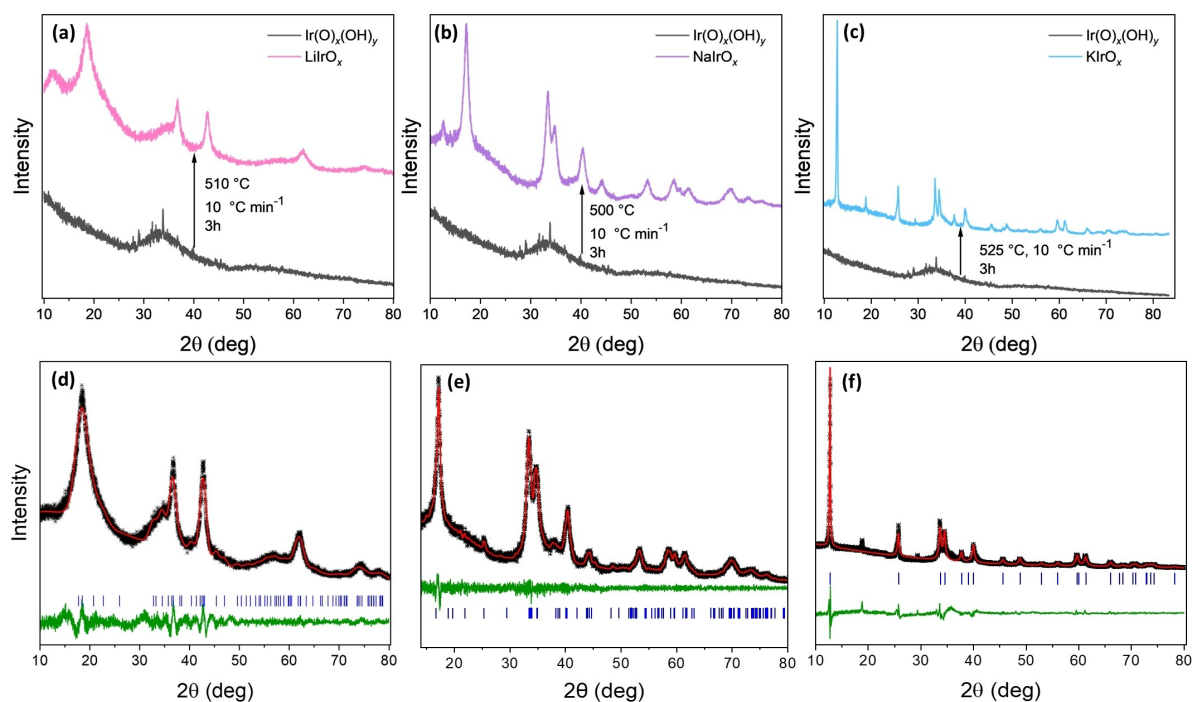


Figure 1. Powder X-ray diffraction patterns and corresponding Le Bail refinement of layered IrO_x structures (a-b) Li- IrO_x (c-d) Na- IrO_x (e-f) K- IrO_x . The black crosses, red and green lines in the refinements are experimental, calculated intensities and difference curves, respectively. Vertical markers indicate the position of the expected Bragg reflections.

Table 1). It should be noted that the diffraction patterns for Li- IrO_x and Na- IrO_x feature broad reflections, indicating these materials consist of nanocrystalline domains. In contrast, K- IrO_x features sharper reflections, indicating larger crystallites. Applying the Scherrer equation to the lowest angle reflections allows the determination of average crystallite dimensions, with their sizes having values of ~ 3 , ~ 7 and ~ 36 nm for Li- IrO_x , Na- IrO_x and K- IrO_x , respectively.^[30] Low magnification scanning electron microscopy (SEM) of $M\text{-IrO}_x$ ($M = \text{Li}^+$, Na^+ , K^+) (see Figure 2a–c) shows that the Li- and Na- IrO_x have no distinct morphological features whereas the K- IrO_x shows needle-shaped particle morphology (see Figure 2c). High-resolution aberration-corrected transmission electron microscopy (HR-TEM) suggests that Li- IrO_x is polycrystalline with nanocrystalline domains, consistent with previous findings and similar to the Na- IrO_x sample. By contrast, TEM images of the K- IrO_x suggest this material features significantly larger crystallite domains support-

ing our observations from the powder XRD patterns for each compound.

The bulk electronic structure of the series was studied by X-ray absorption spectroscopy at the Ir $L_{3/2}$ -edge. The near edge region of the absorption spectrum is characterised by a resonance corresponding to a $2p_{3/2} \rightarrow 5d$ electronic transition, generally referred to as the white line (WL), which is sensitive to absorber symmetry, ligand environment, and oxidation state (d-state occupancy). Figure 3a shows that r- IrO_2 , $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$, and the synthesised metal iridates have similar white line positions (11,218.6–11,219.3 eV) defined by the minimum in the second derivative. Comparison of Ir^0 ($5d^7$), IrCl_3 ($5d^6$), and IrO_2 ($5d^5$) (see Figure S1) suggests a mixed valance Ir(IV)/Ir(III) species with average formal oxidation states of $\sim \text{Ir}^{+3.7}$ for $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ and the synthesised metal iridates thought to be associated with some degree of hydration in the samples when considering commercial IrO_2 as a reference for $\text{Ir}^{+4.0}$. This higher bulk oxidation state

Table 1. EXAFS model fitting parameters for first shell Ir–O of catalysts measured at the Ir- L_3 -based on IrO_2 [ICSD 56009] and with floated CN and R. Fitted data range k 3–12 and R 1.5–2.5 Å.

Sample	Scattering Path	CN	R (Å)	$2\sigma^2$ (Å ²)	S_0^2	E_f (eV)	$R_{\text{factor}} + \text{reduced-}\chi^2$
r- IrO_2	Ir–O	5.8 ± 0.3	1.97 ± 0.01	0.002(4)	0.79 ^[a]	10.3 ± 0.6	0.030 (734)
$\text{IrO}_2 \cdot 2\text{H}_2\text{O}$	Ir–O	6.0 ± 0.6	2.00 ± 0.01	0.005(1)	0.79 ^[a]	10.0 ± 1.2	0.008 (6122)
Li- IrO_x	Ir–O	6.2 ± 0.6	1.99 ± 0.02	0.005(1)	0.79 ^[a]	9.9 ± 1.3	0.004 (8937)
Na- IrO_x	Ir–O	5.9 ± 0.3	1.99 ± 0.01	0.004(5)	0.79 ^[a]	9.7 ± 0.6	0.012(4204)
K- IrO_x	Ir–O	6.0 ± 0.4	1.99 ± 0.02	0.004(3)	0.79 ^[a]	9.8 ± 0.8	0.012 (5676)

^[a] S_0^2 fixed at a value of 0.79 determined by fitting Iridium chloride as a standard with a fixed CN = 6.

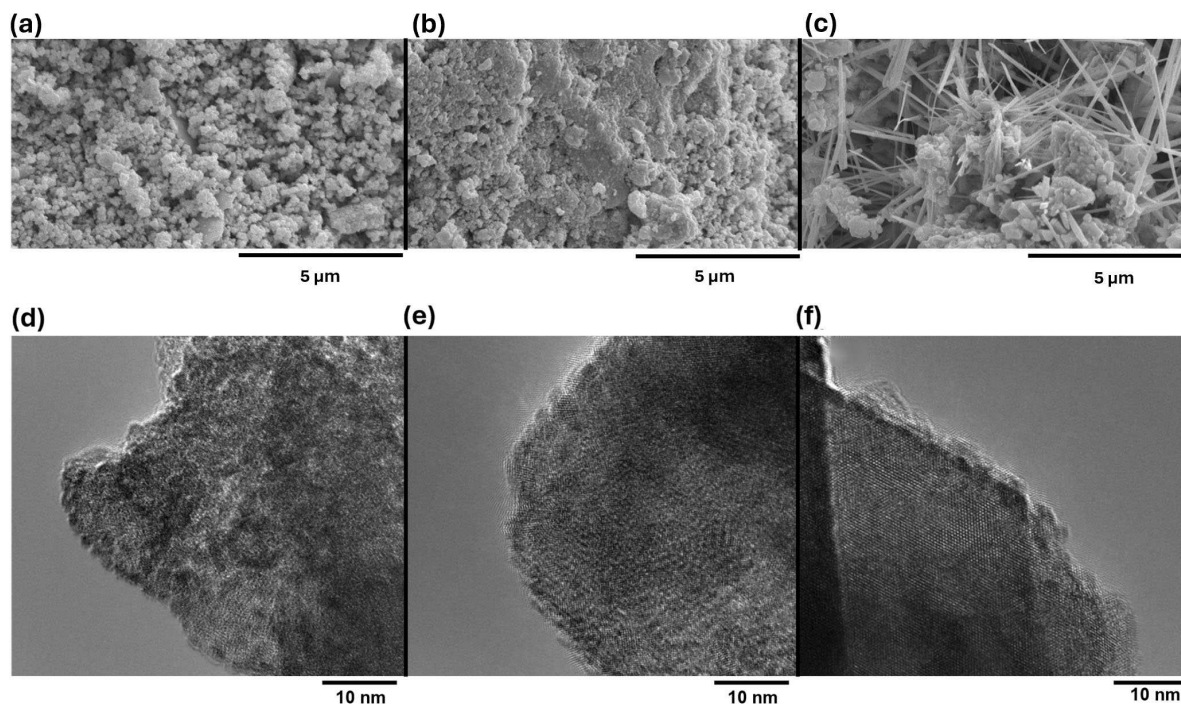


Figure 2. SEM and HR-TEM images, showing nanocrystalline domains, for (a,d) Li-IrO_x, (b,e) Na-IrO_x, in (c,f) K-IrO_x, suggesting higher crystallinity for the latter compound.

of commercial rutile IrO₂ is supported by a shift to higher energy of the absorption edge compared to the other materials studied (inset Figure 3a). Fourier-transformed EXAFS (non-phase corrected) are shown in Figure 3b. All samples show 1st shell scattering intensity consistent with Ir-O_x coordination in the 1st shell, fitting a single Ir-O scattering path (see Table 1) suggests that all samples could be considered to have an Ir-O₆ coordination with CN ~6.^[31] For the samples which show a formal oxidation state < Ir^{4.0} the Ir-O bond is ~2.01 Å compared to 1.98 Å for rutile IrO₂ consistent with a lower average oxidation state of the Ir centre. Considering the 2nd coordination shell which for rutile IrO₂ consists of two Ir-Ir and additional Ir-O scattering paths the synthesised iridates (which also include the possible effects of light scattering elements) show different long-range structures when considering the scattering intensity between 2.5–4 Å and the k-space phasing (Figure S2).^[32,33] This intensity suggests that rather than the regular edge and corner-sharing Ir-O₆ units in crystalline rutile materials, the layered iridates have shorter Ir-Ir₁ and Ir-Ir₂ coordination shells.

The OER activity of the commercial standards, r-IrO₂ and amorphous IrO₂·2H₂O, and the synthesised *M*-IrO_x samples (*M*=Li⁺, Na⁺ and K⁺) in 0.1 M HClO₄ was assessed by LSV (0.2–1.8 V_{RHE}, 5 mV s⁻¹) (see Figure 4a–d). Amorphous IrO₂·2H₂O exhibits the greatest activity towards OER, reaching a current density of ~67 mA cm⁻² at 1.8 V_{RHE}, followed by Li-IrO_x, which shows a current density of ~55 mA cm⁻² (see Figure 4a) at the same applied potential. In sharp contrast, r-IrO₂ shows the lowest activity amongst the electrocatalysts investigated, with a current density of 36 mA cm⁻² at 1.8 V_{RHE}, consistent with

previous findings.^[19] The activities of the Na-IrO_x and K-IrO_x catalysts are intermediate, with the former showing a current density of 45 mA cm⁻², while the latter 35 mA cm⁻² and therefore similar performance to r-IrO₂. LSV curves also showed a first redox event occurs at ~0.8 V_{RHE} for IrO₂·2H₂O and ~0.9 V_{RHE} for Li-IrO_x and a second redox event at ~1.2 V_{RHE} for both samples, indicating Ir³⁺/Ir⁴⁺ and Ir⁴⁺/Ir⁵⁺ transitions occur at the surface, consistent with previous observations for amorphous iridium oxide and Li-IrO_x (see Figure S3).^[19] Similar features are observed for Na-IrO_x and K-IrO_x, albeit much less pronounced than the higher activity electrocatalysts suggesting lower activity surfaces. Finally, r-IrO₂ does not show any indication of such transitions occurring at potentials below ~1.45 V_{RHE} – i.e. the onset region for OER. This further indicates that r-IrO₂ exhibits a significantly lower redox activity, consistent with its poor activity towards OER, as discussed in previous reports.^[19,34] To further assess the OER activity, the overpotentials at 10 mA cm⁻² (η¹⁰) have been determined. r-IrO₂, IrO₂·2H₂O and Li-IrO_x showed a η¹⁰ of 390 and 280 and 310 mV, respectively, whereas Na-IrO_x and K-IrO_x reached the benchmark current density at 350 and 360 mV, respectively. Iridium mass-normalised current densities confirm the same trends as the LSV curves (see Figure 4b).

OER activity was normalised against the roughness factor (*R_f*) obtained by electrochemically active surface area (ECSA) measurements (see Figure S4). ECSA values of 0.73, 0.16, 0.05, 0.15 and 0.41 cm² for r-IrO₂, IrO₂·2H₂O, Li-IrO_x, Na-IrO_x and K-IrO_x, respectively, were determined through double layer capacitance methods. The *R_f* for each catalyst can be determined by dividing the ECSA by the electrode geometric area.

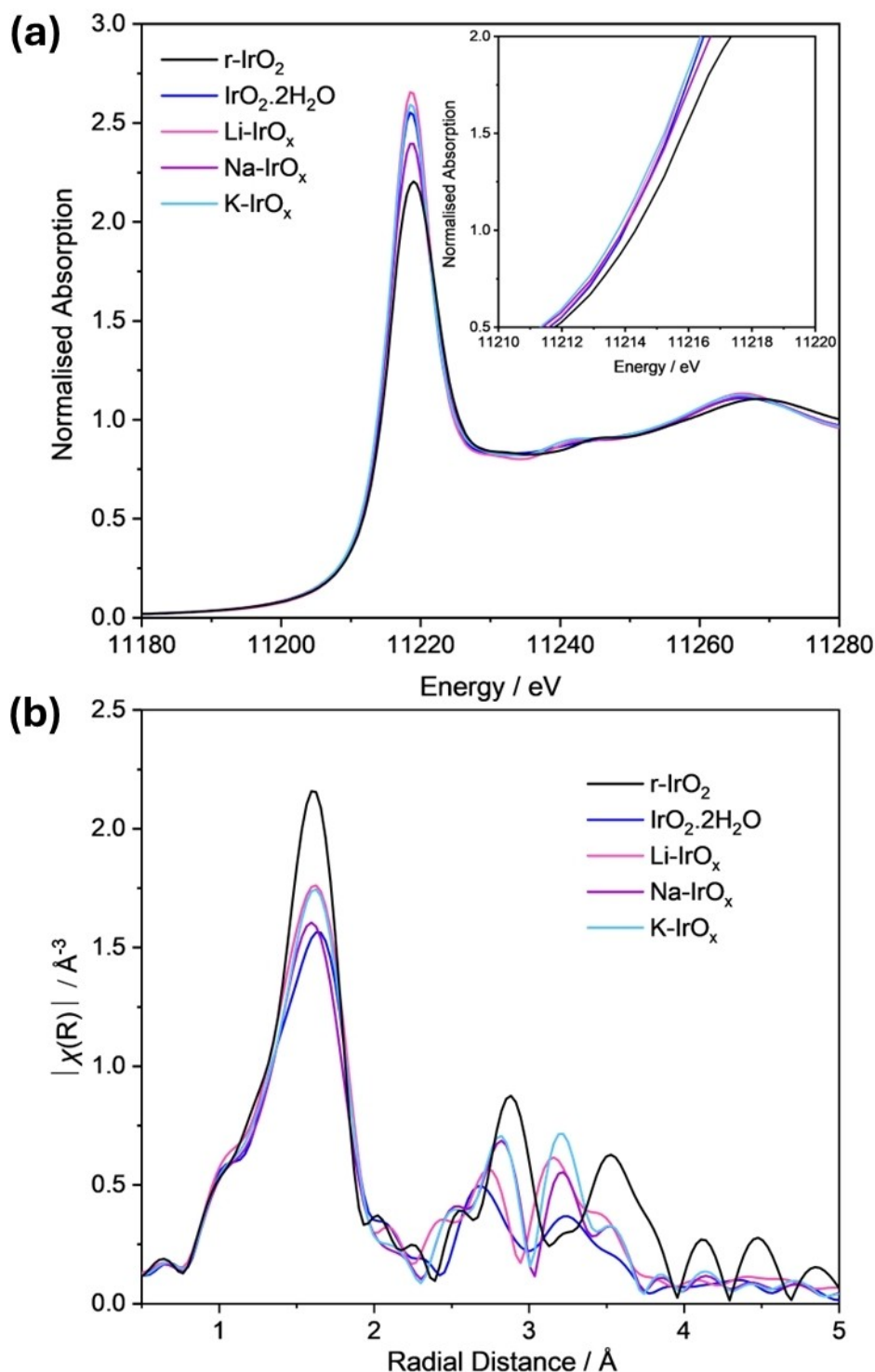


Figure 3. a) Transmission Ir-L₃-edge XANES and b) Fourier transformed EXAFS of commercial rutile IrO₂ and amorphous IrO₂·2H₂O and synthesised Li⁺, Na⁺ and K⁺ iridates.

The determined R_f values are 3.72, 0.83, 0.24, 0.77 and 2.08 for r-IrO₂, IrO₂·2H₂O, Li-IrO_x, Na-IrO_x and K-IrO_x respectively. The activities normalised by R_f reveal that Li-IrO_x shows much higher normalised activity compared to the other electrocatalysts (see Figure 4c) showing a possible promotional effect of Li⁺ in the OER catalysts compared to alkali metal-free systems. Tafel

slopes were derived from semi-steady-state conditions obtained from linear sweep voltammetry (LSV) measurements performed at a scan rate of 0.5 mV s⁻¹ (see Figure 4d). At low overpotentials, Tafel slopes were 38.8, 47.6, 54.7 and 59.2 mV dec⁻¹ for IrO₂·2H₂O, Li-IrO_x, Na-IrO_x and K-IrO_x respectively. These results are consistent with those observed from LSV curves,

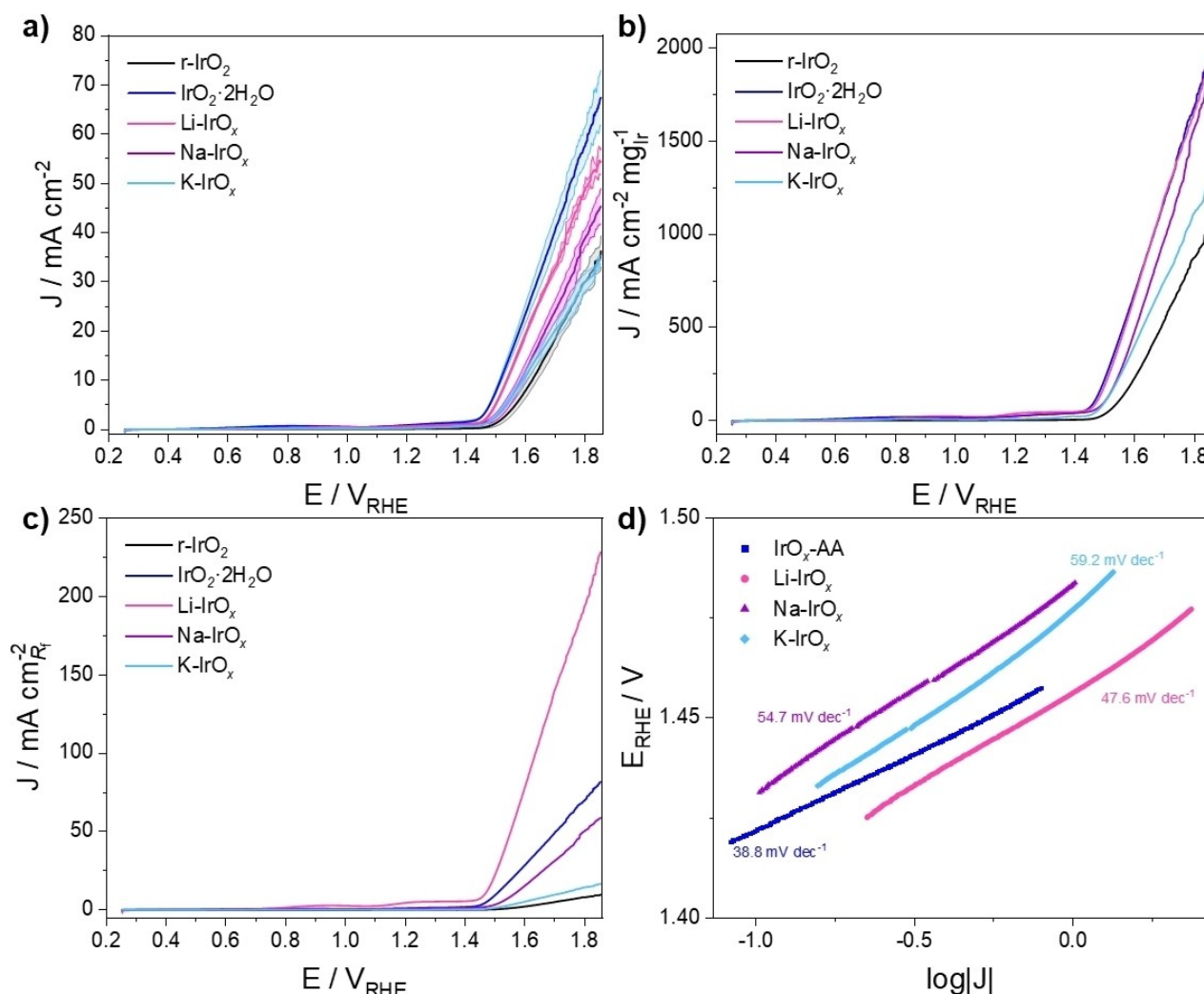


Figure 4. (a) As-measured, (b) mass-normalised and (c) roughness factor-normalised current densities of commercial IrO₂ standards and synthesised *M*-IrO_x catalysts (*M* = Li⁺, Na⁺, K⁺) measured by LSV (0.2–1.8 V_{RHE} at 5 mV s⁻¹, RDE at 2500 rpm). Shaded areas in Figure A represent standard deviations over multiple LSV measurements. (d) Tafel plots at low overpotential obtained from the linear region of LSV polarization curves at 0.5 mV s⁻¹

confirming the higher intrinsic activity of IrO₂·2H₂O and Li-IrO_x compared to the Na- and K-containing analogues.

In situ XAS during electrochemistry was conducted in 0.1 M HClO₄ at a potential above and below the OER onset for each sample. As XAS is a bulk technique the formal oxidation state changes represent only the average oxidation states of the materials and changes are likely to only come from redox active sites at the surface or near-surface while the bulk remains largely unchanged. The Ir-L₃ edge of the catalyst series was measured after immobilisation onto carbon paper and immersion in the electrolyte. Compared to the as prepared samples the immersed catalysts showed lower white line positions as determined by the minimum in the second derivative. This suggests that when compared to the samples that have been dried before spectral acquisition the amorphous and layered samples in electrolyte have a higher density of unoccupied states due to hydration/protonation. An exception is r-IrO₂ which maintains a formal oxidation state close to Ir⁴⁺ consistent with its highly ordered structure which is less amenable to

water penetration into the bulk or surface hydroxylation. Subsequently, the potential was increased to 1.4 V_{Ag/AgCl} in 100 mV steps from 0.9 V_{Ag/AgCl} to allow spectral acquisition at each potential. Figure S5 shows the XANES spectra acquired in electrolyte with no applied potential and at 1.0 and 1.4 V_{Ag/AgCl} to represent the state of the catalyst above and below the OER onset. On application of potential the white line position of rutile IrO₂ remains unchanged indicating no significant observable change in bulk oxidation state above the OER onset. FT-EXAFS (see Figure S5b) shows no significant changes in the scattering intensity consistent with 1st shell Ir-O₆ or the 2nd coordination shell Ir-Ir. A summary of the fitting of the first shell, Table 2, is consistent with an Ir-O_x coordination of 5.6 ± 0.6 when under OER conditions with an Ir-O bond length of 1.98 Å (full fitting parameters are reported in Table S2). In contrast, on application of potential, commercial IrO₂·2H₂O demonstrates a shift in the white line position to higher energy indicating oxidation beyond r-IrO₂ and a corresponding change in Ir-O bond length from 2.02 to 1.96 Å consistent with a higher

Table 2. Summary of EXAFS fitting for *in situ* experiment.

Sample	Conditions	Ir-O _x CN	R (Å)	White Line Position/eV	Average Oxidation State
r-IrO ₂	In electrolyte	5.8 ± 0.8	1.98 ± 0.01	11218.3	3.8
	1.4V _{Ag/AgCl}	5.6 ± 0.6	1.98 ± 0.01	11218.3	3.8
IrO ₂ ·2H ₂ O	In electrolyte	5.4 ± 0.5	2.02 ± 0.01	11217.9	3.5
	1.4V _{Ag/AgCl}	5.1 ± 0.5	1.96 ± 0.01	11219.0	4.5
Li-IrO _x	In electrolyte	6.1 ± 0.6	2.02 ± 0.01	11217.6	3.2
	1.4V _{Ag/AgCl}	5.8 ± 0.7	2.01 ± 0.01	11217.8	3.4
Na-IrO _x	In electrolyte	5.7 ± 1.2	2.03 ± 0.02	11217.4	3.0
	1.4V _{Ag/AgCl}	5.5 ± 0.4	2.02 ± 0.01	11218.4	3.9
K-IrO _x	In electrolyte	5.4 ± 1.4	2.01 ± 0.02	11217.8	3.4
	1.4V _{Ag/AgCl}	5.8 ± 0.6	1.97 ± 0.01	11218.5	4.0

^[a] S_o² fixed at a value of 0.79 determined by fitting Iridium chloride as a standard with a fixed CN = 6.

oxidation state Ir species and more facile redox processes observed in the LSV experiments. A reduction in Ir–O CN on polarisation suggests the formation of O-vacancies in the structure which have been reported to be both involved in the reaction mechanism and a trigger for dissolution and catalyst deactivation.^[12] In contrast, the Li-IrO_x shows much less pronounced changes in polarisation, which could partly be ascribed to the lower ECSA compared to IrO₂·2H₂O. On immersion in the electrolyte, only slight changes in CN and Ir–O bond length are observed despite the high activity of the sample, possibly suggesting that the activity in this sample is not strongly correlated to the formation of O-vacancies or that the structure has enhanced stability towards O-vacancy formation. The Na-IrO_x sample shows oxidation on the application of potential inferred from a shift in white line positions without significant changes in Ir–O CN or Ir–O bond length again suggesting OER activity without significant loss of Ir–O coordination.

The surface-sensitive spin-orbit split Ir 4f X-ray photoelectron spectra for the as-prepared samples in Figure 5a were fitted using the theory-based model developed by Pfeifer *et al.* and summarised in Table S3.^[35,36] A peak with a maximum at 61.7 eV and Doniach-Šunjić (DS) lineshape together with the associated shake-up satellites ~1.0 eV higher in binding energy (BE) is consistent with the Ir4f_{5/2} component of Ir^{IV} in rutile IrO₂. An additional DS component at 62.4 eV BE (~7 eV upshifted from Ir^{IV} in rutile IrO₂) was also observed and an associated satellite peak which cannot be unequivocally assigned based on existing literature. A peak at 5 eV higher BE than Ir^{IV} was earlier associated with bulk Ir^{III}.^[37] However, recently, Ir surface species with a formal oxidation state >5 bound to μ₁-O on (110) terraces or μ₁-OH on (111) terraces of IrO₂ surfaces were suggested to contribute to this feature.^[38] Consistently with L₃-edge XANES and XRD analysis, Ir 4f XPS shows that Li-IrO_x is the sample that least resembles the electronic surface structure of rutile-type IrO₂. In analogy to previous computed XPS, one could postulate that differences are related to a higher abundance of protonated oxygen-bearing Ir-octahedra species.

The O1s XPS spectra of the as-prepared samples are depicted in Figure 5b. The fitting includes 6 components as summarised in Supporting Table 3, between 529.1–533.6 eV. In terms of assignments, M–O species with O in a formal oxidation state –2 contribute to the spectra below 531 eV, whereas above this BE, hydroxylated and carbonated species are found.^[39] Thus, it can be concluded that the Li-IrO_x surface is dominated by surface hydroxylated species, whereas both Na- and K-containing samples present a majority of M–O species consistent with the larger crystallites found for these samples. The additional peak at 529.5 eV in Na- and Li- compared to K- indicates a coexistence of different metal-O bonds beside the rutile-type Ir–O₆ bonds. According to literature this component is inconsistent with any of the possible Li–O(H), Na–O(H) and K–O(H) bonds and therefore likely related to an Ir–O bond in a different environment than rutile-type Ir–O₆ bonds. The O K-edge NEXAFS is highly diagnostic to differentiate O species and identify features related to high OER activity.^[40,41] The O K-edge for the samples, Figure S6, shows the 528–534 eV region which represents the 1s → O2p hybridized with 5 d metal states which have t_{2g}–e_g symmetry. Both Auger electron yield (AEY) and total electron yield (TEY) spectra show that the pre-edge peaks differ significantly in relative intensity among the samples. Commercial rutile-type IrO₂ (r-IrO₂) is characterized by resonances at ~529 eV and ~530 eV, associated with bulk μ₂-O and μ₃-O, respectively. While the latter is typical in rutile IrO₂, the former is not typically found in highly crystalline rutile IrO₂. A μ₂-O ~529 eV is associated to Ir^{III} in the bulk and is shifted to higher energy when protonated. Consistent with earlier work, this resonance is predominant in the pre-edge region of the O K-edge of Li-IrO_x, and is convoluted with the μ₃-O resonance, which presents lower intensity compared to r-IrO₂. Na-IrO_x presents mainly the μ₂-O resonance, indicating that this is the predominant species in the layered oxide structures. A correlation can be drawn between the population of O species and the energy of the Ir L₃-edge (inset Figure 3a) as well as the Ir–O distance. For the commercial r-IrO₂ the white line shifts to higher energy compared to the other materials studied,

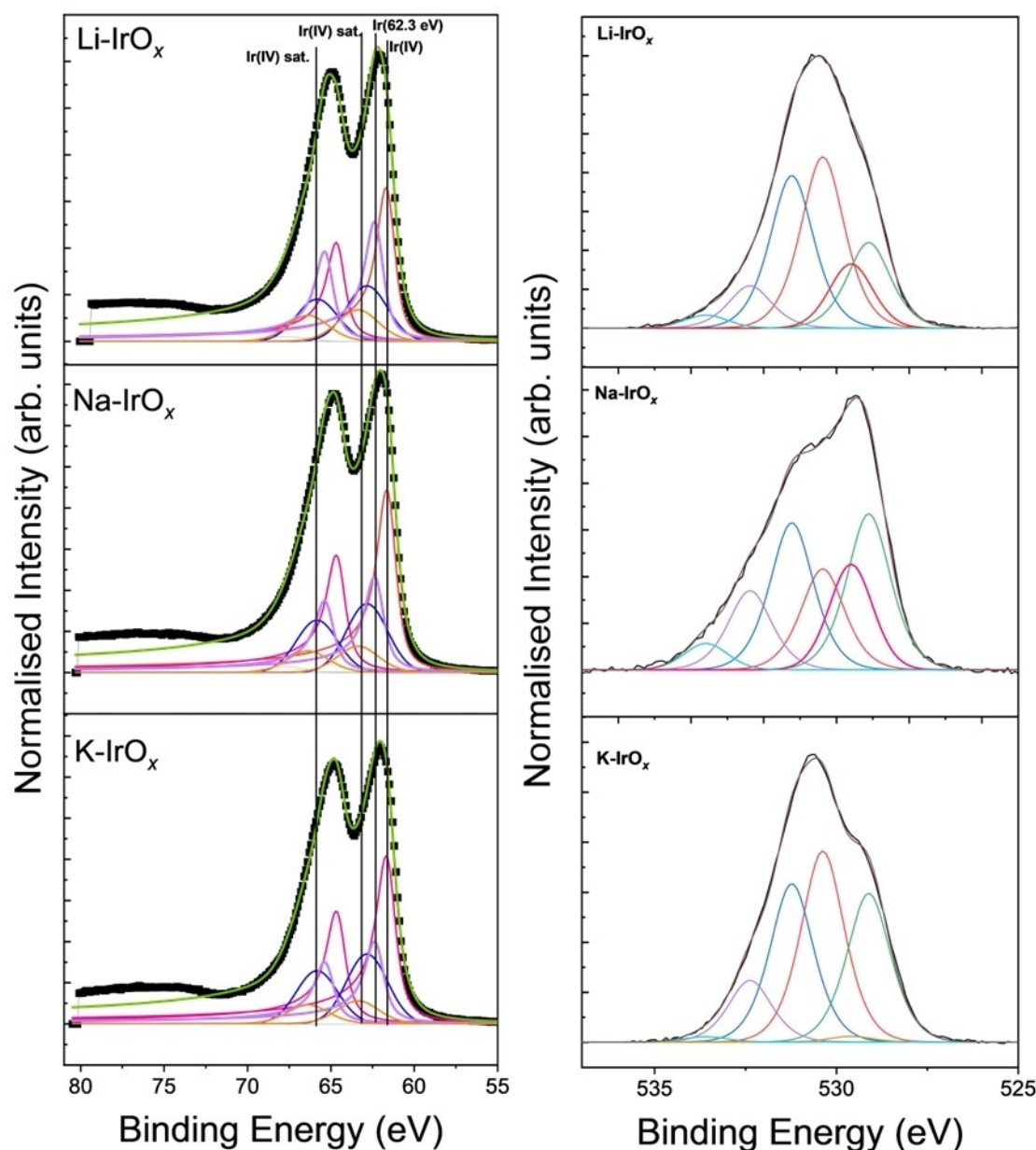


Figure 5. Fitted Ir 4f (left) and O1s (right) XPS spectra for Li-IrO_x, Na-IrO_x and K-IrO_x obtained in UHV.

consistent with a shorter Ir–O bond and a μ_3 -O resonance in the O K-edge spectrum. K-IrO_x is characterized by two well resolved pre-edge peaks, with a resonance consistent with μ_3 -O species, whereas a lower energy resonance is shifted to higher energy than μ_2 -O, possibly due to protonation (μ_2 -OH). The pre-edge is almost absent in IrO₂·2H₂O in AEY, while in TEY presents resonances at energies similar to K-IrO_x, although, the relative intensity of the two resonance is the opposite. A decrease of the intensity is in general observed when the bond covalency is low (O2p- t_{2g} hybridisation) and the ionic character is high. The broad resonance above 537 eV reflects the Ir–O bond distance distribution. Peak maxima at lower energy for Li-IrO_x and IrO₂·2H₂O and to a lesser extent for Na-IrO_x and K-IrO_x indicate longer Ir–O bonds than IrO₂, consistent with the L₃-edge

EXAFS data (Figure S3). It is possible to postulate that the intercalation of Li⁺, Na⁺ and K⁺ between the IrO₆-layers is reflected in the elongation of Ir–O bonds pointing towards the interlayer space as well as an increase of the ionic character of this bond.

The stability of the electrocatalysts was assessed *via* chronopotentiometry at a benchmark current density of 10 mA cm⁻². All the M-IrO_x samples (M=Li⁺, Na⁺ and K⁺) showed good stability over 2 h with no evidence of degradation, while the commercially available amorphous IrO₂·2H₂O showed deactivation within the first ~30 minutes of operation, with the results for IrO₂·2H₂O and Li-IrO_x consistent with previous findings,^[19] and showing that the layered catalysts indeed offer potentially more durable alternatives to amor-

phous iridium oxide (see Figure 6). Longer tests at the benchmark current, *i.e.* 10 mA cm^{-2} , have revealed that the $M\text{-IrO}_x$ electrocatalysts can sustain longer periods of operation and suggest that Li-, Na- and K-IrO_x can operate for up to ~22, ~15 and ~8 h, respectively, outperforming commercial r-IrO_2 and $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ inks prepared in the same way (see Figure 7).

Conclusions

It was previously shown that residual Li^+ suppresses the formation of crystalline rutile IrO_2 during mild heat treatment ($\sim 500^\circ\text{C}$) of amorphous iridium oxyhydroxides, leading to a nanocrystalline lithium iridate which is more active compared to rutile IrO_2 synthesised in the absence of Li^+ at similar temperatures. Such an iridate has shown comparable activity to amorphous iridium oxyhydroxides and improved durability. We focused on synthesising sodium and potassium-containing

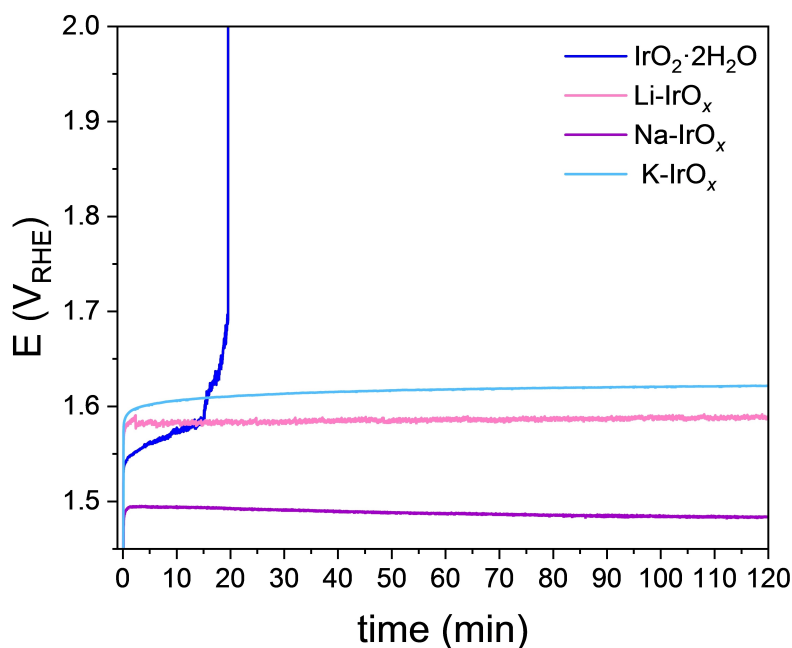


Figure 6. Stability of electrocatalysts assessed *via* chronopotentiometry (2 h at 10 mA cm^{-2}).

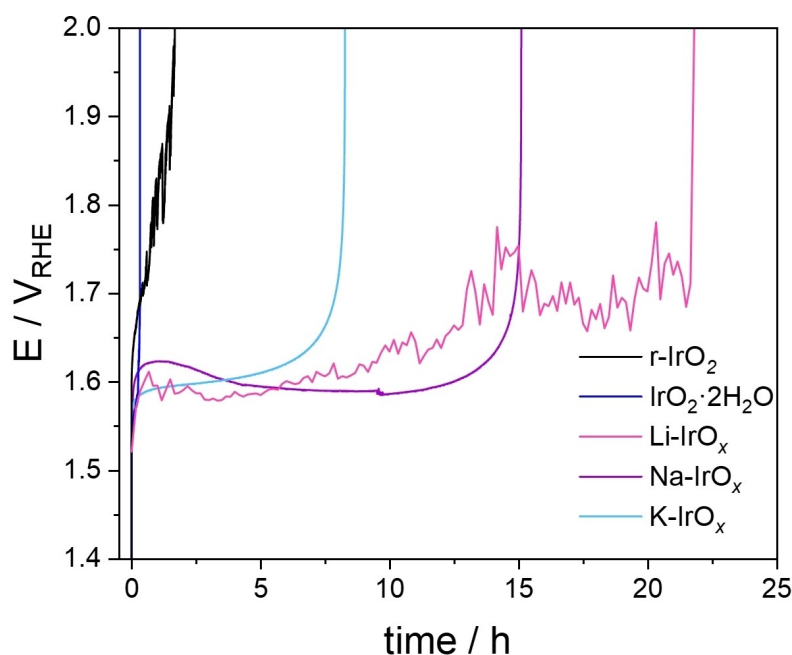


Figure 7. Stability of electrocatalysts assessed *via* chronopotentiometry for longer acquisition times (25 h at 10 mA cm^{-2}).

analogues, namely Na-IrO_x and K-IrO_x, using a similar mild heat treatment method. We demonstrate that incorporating interlayer alkali metal cations into layered iridium oxides provides a route to obtain materials with enhanced activity compared to rutile IrO₂ with higher stability. In particular, Li-IrO_x, Na-IrO_x and K-IrO_x outperform r-IrO₂ albeit the measured activity decreases with larger cations, *i.e.* Li⁺ > Na⁺ > K⁺. Despite this, they have been shown to withstand electrocatalytic conditions in acidic media for more than 15 h compared to commercial r-IrO₂ and IrO₂·2H₂O which are stable for <1 h under the same experimental conditions. These results have further confirmed that layered structures could allow for orthogonality between activity and stability, with stability being the most significant limitation for the fabrication of industrial PEM electrocatalysts.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

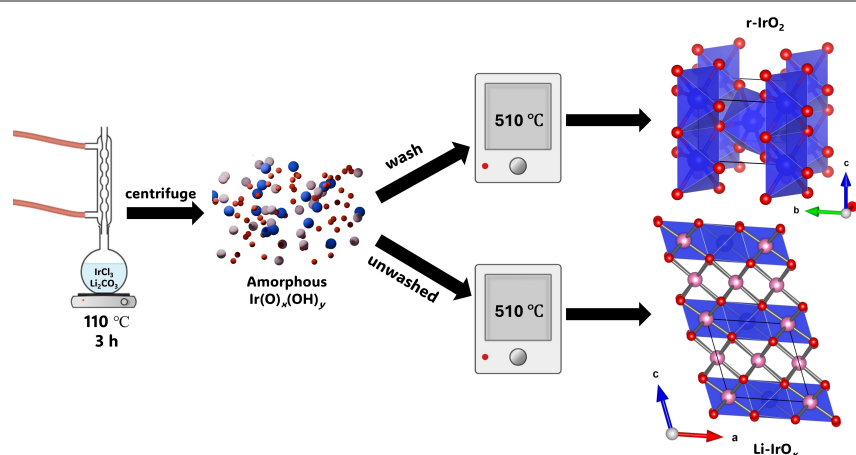
Keywords: electrocatalysis · oxygen evolution reaction · iridium oxide · amorphous iridium oxo-hydroxide · hydrothermal synthesis

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Amorphous iridium oxyhydroxides are converted to alkali metal intercalated layered oxides through simple thermal treatments with suppression

of rutile formation and show enhanced stability in the acidic oxygen evolution reaction.

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Alkali Metal Iridates as Oxygen Evolution Catalysts Via Thermal Transformation of Amorphous Iridium (oxy)hydroxides.

