Cation insertion to break the activity/stability relationship for highly active oxygen evolution reaction catalyst

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The production of hydrogen at a large scale by the environmentally-friendly electrolysis process is currently hampered by the slow kinetics of the oxygen evolution reaction (OER). We report a solid electrocatalyst $\alpha$-Li$_2$IrO$_3$ which upon oxidation/delithiation chemically reacts with water to form a hydrated birnessite phase, the OER activity of which is five times greater than its non-reacted counterpart. This reaction enlists a bulk redox process during which hydrated potassium ions from the alkaline electrolyte are inserted into the structure while water is oxidized and oxygen evolved. This singular charge balance process for which the electrocatalyst is solid but the reaction is homogeneous in nature allows stabilizing the surface of the catalyst while ensuring stable OER performances, thus breaking the activity/stability tradeoff normally encountered for OER catalysts.
The spread of renewable energies has led to an ever-growing need to develop better electrochemical storage devices, such as electrolyzers\cite{1-3}. This calls for key research advances to enhance the cost/performance ratio of electrolyzers, a cornerstone of which is improving the electrochemical reactions at the electrodes by the development of new catalysts. Nevertheless, several reports point toward the complexity of these reactions that involve the transfer of ions and electrons at the solid/liquid interface\cite{4,5}. Considerable progress has thus been made toward designing efficient and noble metal-free hydrogen evolution reaction catalysts, but the other half reaction, namely the oxygen evolution reaction (OER), has proven to be more difficult\cite{6-8}. Indeed, the OER is associated with large kinetics losses, where overpotentials >300 mV are typically obtained at a current density of 10 mA cm$^{-2}$\cite{19}. Further, this phenomenon is related to the relative position of the Fermi level when compared to the reversible potential for water oxidation, as well as to the charge-transfer energy\cite{19-22}. In short, lowering the charge-transfer energy triggers the redox activity of oxygen ligand, leading to the involvement of lattice oxygen into the OER following the so-called lattice oxygen evolution mechanism. This involvement lowers the transition metal oxides coordination and thus destabilizes the surface of the catalyst, as now concluded by numerous research groups\cite{23-27,22}. Furthermore, when the conduction band or the Fermi level of the transition metal oxides falls below the redox level of O$_2$/H$_2$O at the operating pH, a driving force is created for the catalyst to oxidize water\cite{19,24}. Nevertheless, owing to the lack of charge balance mechanism, this reactivity is often counterbalanced by a dynamic cation dissolution/redeposition process and surface instabilities\cite{5,28-30,22}. Hence, a tradeoff is observed where lowering the Fermi level of the catalyst below the reversible potential for water oxidation increases the catalytic reactivity with water at the expense of its long-term stability\cite{13,26,31,22}. Eventually, a self-assembled surface composed of transition metal oxy(hydroxide) clusters is formed for these catalysts, as revealed by X-ray absorption spectroscopies (XASs)\cite{26,30} and high-resolution transmission electron microscopy (HRTEM)\cite{32}, which evolves in a dynamic fashion upon OER conditions alike electrodeposited amorphous films\cite{33,34,37,38,39}.

Strategies were thus recently developed in order to overcome this practical limitation associated with the activity/stability tradeoff for OER catalysts\cite{38,39}. Among them, the design of nanostructured or supported catalysts appears promising to reduce the rate of dissolution\cite{40-44}, with nevertheless the main limitation that the driving force for the transition metal oxide to be unstable is not suppressed.

In this work, we explore a chemical strategy that would enable breaking such activity/stability correlation. Herein, we develop an OER catalyst that Fermi level can be electrochemically lowered below the reversible water oxidation potential. Doing so, the catalyst chemically reacts with water at OER potentials, this reaction being counterbalanced by bulk cation exchange, thus preventing the structure decomposition/amorphization and ensuring a high stability while increasing the activity of the catalyst, when compared to the unreacted phase.

### Results

**Intercalation-stabilized catalysts for water oxidation.** This new catalyst for which the bulk participates to the stabilization of the catalyst can be viewed at the frontier between heterogeneous and homogeneous catalysts\cite{10,41,45}, hence we define them as intercalation-stabilized chemical catalysts (Fig. 1). Toward achieving the goal of breaking the activity/stability tradeoff for OER catalysts, we selected a transition metal layered oxide having an open two-dimensional crystal structure, α-Li$_2$IrO$_3$, and first studied its electrochemical behavior. The layered α-Li$_2$IrO$_3$ compound shows, when cycled in organic solvent, two successive oxidation events into α-Li$_2$IrO$_3$ and α-Li$_2$IrO$_3$ at ~3.5 V and 4.1 V vs. Li$^+$/Li, respectively (Fig. 2a). The redox potential for the formation of α-Li$_2$IrO$_3$ corresponds to the thermodynamic potential for water oxidation at pH ≥ 13 (Fig. 2b, c)\cite{46}, making it unstable toward water above this pH value. When using α-Li$_2$IrO$_3$ as OER catalyst in alkaline solution at pH 13, an irreversible oxidation peak is observed during the first cycle at ~1.23 V vs. RHE, corresponding to the formation of α-Li$_2$IrO$_3$ (Supplementary Figs. 1–3). Following this initial oxidation, a large OER activity with an overpotential as low as 290 mV at 10 mA cm$^{-2}$ is recorded in 0.1 M KOH (Fig. 2b, c). These numbers make α-Li$_2$IrO$_3$ one of the most active crystalline OER catalysts so far reported in alkaline conditions (Supplementary Fig. 4), validating a posteriori the choice of α-Li$_2$IrO$_3$.

![Fig. 1 Charge compensated chemical oxidation of water. Schematic illustration of a heterogeneous OER process on the surface of solid catalysts, b the OER proceeding on the surface of a solid catalysts with the bulk of the catalyst being redox-active accepting cations from the electrolyte upon OER, and c homogeneous catalysis with soluble molecular catalyst.](image-url)
Structural and chemical analysis. Strikingly, the OER overpotential at 10 mA cm$^{-2}$oxde was found 50 mV higher as KOH is replaced by NaOH or LiOH (Fig. 2b, c, Supplementary Figs. 5 and 6). No such cation dependence is observed when changing the crystallographic structure of α-Li$_2$IrO$_3$ and using its 3D β-Li$_2$IrO$_3$ (ref. 47) polymorph (Fig. 2b, c, Supplementary Figs. 5 and 6) or for IrO$_2$ (Supplementary Figs. 5 and 6). Accordingly, the Tafel slope was found lower for α-Li$_2$IrO$_3$ (=50 mV/decade) in KOH than in NaOH, as well as lower than the ones measured for β-Li$_2$IrO$_3$ in both KOH and NaOH (all being ~70 mV decade$^{-1}$; Fig. 2c). This structural dependence for the observed cation dependence rules out an effect related to a shift of adsorption energies of OER intermediates, as previously reported 48–51. Furthermore, no significant increase of the electrochemical active surface area or particle size is observed between NaOH and KOH (Supplementary Figs. 7 and 8), which excludes the effect of an increase of active sites to explain the enhanced OER performances, which rather originates from the in situ formation a new active phase at the OER potential, as discussed below.

Hence, to shed some light on both the effect of cation and the crystal structure, ex situ and in situ X-ray diffraction (XRD) studies were performed (Fig. 3a, Supplementary Fig. 9). In situ XRD first confirms the initial delithiation/oxidation and the formation of α-Li$_2$IrO$_3$ at ~1.23 V vs RHE, followed by a shift of the first main 003 diffraction peak for α-Li$_2$IrO$_3$ at 2θ = 18.7° to a lower angle of 2θ = 12.6° concomitant with the OER (Fig. 3a). Rietveld analysis on ex situ XRD indicates the formation of a phase resembling a hydrated birnessite, such as the previously described K$_2$MnO$_2$·nH$_2$O (ref. 52), with lattice parameters a = 3.03750(9) Å and c = 20.8279(14) Å (Fig. 3b). Within this model, disordered LiIr$_2$ layers are stacked along the [001] direction and separated by 6.9 Å (Fig. 3c). Potassium atoms, water molecules and the possibly remaining Li are sandwiched and statistically distributed between the LiIr$_2$ layers 53.

Intrigued by this structural transformation, we then electrochemically prepared α-Li$_2$IrO$_3$ in water-free organic electrolyte before to react it with KOH. Doing so, the formation of the new phase with an O3-type layered structure (space group R-3m) was observed once again (Supplementary Fig. 10), indicating a chemical reaction of α-Li$_2$IrO$_3$ with the alkaline solution. However, no such transformation was measured when cycling α-Li$_2$IrO$_3$ or soaking the electrochemically prepared α-Li$_2$IrO$_3$ in LiOH or NaOH solutions (Fig. 3d, Supplementary Figs. 11 and 12), despite the smaller ionic radius of Li$^+$ and Na$^+$ compared to K$^+$ (0.76 Å, 1.02 Å, and 1.38 Å, respectively). Similarly, no structural modification was recorded when soaking the oxidized 3D β-Li$_2$IrO$_3$ polymorph into KOH solution (Supplementary Fig. 12). Overall, these observations confirm the importance of the interplay between the crystallographic structure (α-Li$_2$IrO$_3$) and the alkaline cation (K$^+$) for triggering the phase transformation and to enhance the OER activity of the catalyst (Fig. 2e).

To access the chemical composition of the newly obtained phase, energy-dispersive X-ray spectroscopy (EDX), high-temperature XRD, thermogravimetric analysis (TGA), and solid-state nuclear magnetic resonance (ssNMR) measurements were carried out. Sample prepared in 1 M KOH was analyzed by
EDX and nearly 0.3 potassium per iridium atom was found (Supplementary Fig. 13), in agreement with the Rietveld refinement of the synchrotron XRD (Supplementary Table 2). High-temperature XRD indicates that the potassium-containing phase gradually evolves from 60 °C to 120 °C, leading to an intermediate phase with an interlayer distance of 6.2 Å (Supplementary Fig. 14). Complementary TGA analysis indicates that this phase change is associated with the loss of ~0.7 molecules of water per formula unit (Supplementary Fig. 15), giving an overall chemical formula close to Li$_{x}$K$_{0.3}$IrO$_{3}$.0.7H$_{2}$O (with $x \approx 1$). From the relatively low temperature at which water starts to be released (60 °C), we can assume the presence of water loosely bound to the lattice as further con

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delithiation step, as previously observed. Upon exposure of $\alpha$-Li$_1$IrO$_3$ to 1 M KOH, the insertion of potassium into the iridium oxide by the reduction of Ir back to an oxidation state comprised between 5 + ($\alpha$-Li$_1$IrO$_3$) and 4 + ($\alpha$-Li$_2$IrO$_3$). Hence, upon reaction with water, the catalyst is reduced, this process being selective to the cation since no reduction of Ir (i.e., no shift of the white line) was detected by XAS after soaking $\alpha$-Li$_1$IrO$_3$ in NaOH (Fig. 4a).

Using mass spectrometry (MS), we unravel the chemical origin of such phenomenon. When in contact with KOH solution, gaseous oxygen is spontaneously generated from the chemical reaction of $\alpha$-Li$_1$IrO$_3$, i.e., the oxidizing agent, with OH$^-$ that acts as a reductant (Fig. 4b, Supplementary Fig. 21). We further observe that increasing the concentration of KOH has two effects. First, it increases the kinetics for oxygen release as seen by the increase of the initial slope for the oxygen evolution as measured by MS. Secondly, and more importantly, the quantity of gaseous oxygen generated by this chemical reaction is directly correlated to the KOH concentration. We also observe that the chemical reaction is stoichiometric, where the amount of oxygen detected by MS linearly correlates with the amount of K$^+$ inserted into $\alpha$-Li$_1$IrO$_3$ during its reduction at different concentration of KOH, with a ratio of approximatively 1:4, as expected for the four electron OER process (Fig. 4c). Furthermore, a large concentration of OH$^-$ alone is not sufficient to chemically evolve gaseous oxygen, which also requires the use of adapted alkaline cations with small hydrodynamic radius and solvation energy (Fig. 2e), as well as open crystallographic structure, the combination of which being necessary to intercalate potassium and reduce $\alpha$-Li$_1$IrO$_3$ (refs. 38–39). Hence, when using NaOH or the 3D $\beta$-Li$_1$IrO$_3$ polymorph, no oxygen is chemically generated from the reaction with water in alkaline conditions and no cation intercalation proceeds.

Finally, worth noticing that full conversion into the birnessite structure as well as chemical evolution of oxygen take time, as observed by in situ XRD and MS measurements (Figs. 3a and 4b, respectively). Looking into greater details by HRTEM at the K$^+$ distribution on the surface of $\alpha$-Li$_1$IrO$_3$, inhomogeneities are observed depending on the surface orientation and the availability of the diffusion channels (Supplementary Fig. 22), suggesting anisotropic diffusion properties of hydrated K$^+$ cations inside the bulk structure.

While we demonstrated that the chemical reactivity of $\alpha$-Li$_1$IrO$_3$ with KOH triggers the intercalation of hydrated K$^+$, the question then arises regarding the reversibility of such process and if hydrated K$^+$ is electrochemically deintercalated from the birnessite phase at the OER potential. For that, after an initial activation in KOH, OER measurements were carried out in K$_2$HPO$_4$ buffered solution at pH 9 (Fig. 4d). Doing so, an oxidation event can be observed at a potential corresponding to the OER onset potential in more strongly alkaline conditions. This observation is further confirmed by in situ XRD measure that reveals the disappearance of the birnessite phase starting at ~0.6 V vs. NHE in K$_2$HPO$_4$ (Supplementary Fig. 23), while no such electrochemical oxidation was observed in Na$^+$-containing electrolytes (Supplementary Fig. 24). Comparing the initial oxidation event measured in KOH and corresponding to the formation of $\alpha$-Li$_1$IrO$_3$, the oxidation peak measured in K$_2$HPO$_4$ is limited, indicating that K$^+$ is presumably only partially deintercalated and that the main active phase remains the birnessite one. Nevertheless, the oxidized $\alpha$-Li$_1$IrO$_3$ form is partially regenerated during the OER. This regeneration will therefore trigger again the reactivity of the catalyst surface with water to generate gaseous oxygen and form again the birnessite phase. This observation indicates that, in addition to the classical electrochemical oxidation of water, this charge balance mechanism simultaneously occurs on the surface.

**Fig. 4 Chemical oxidation of water during birnessite formation.** a Ir $L_3$-edge XAS spectra probing the reduction of Ir after chemical reaction with KOH. b $O_2$ gas evolution as detected by online mass spectrometry when soaking $\alpha$-Li$_1$IrO$_3$ in KOH and NaOH solutions with increasing concentrations. c Linear relationship between the amount of intercalated K$^+$ ions in the birnessite phase (as deduced by EDX) and the $O_2$ gas evolution (as deduced from MS). d OER measurements in KOH at pH 14 compared to K$_2$HPO$_4$ at pH 9 demonstrating the K$^+$ deintercalation from the birnessite phase at the OER potential. e Proposed EC mechanism for $\alpha$-Li$_1$IrO$_3$ involving the electrochemical formation of a high valence $\alpha$-Li$_1$IrO$_3$ oxide (E step), followed by the chemically oxidation of water to generate $O_2(\alpha)$ assisted by K$^+$ intercalation into the birnessite structure (C step).
of the newly formed birnessite. However, this mechanism being associated with the transfer of 4 $K^+$ and 4 $e^-$ per mole of $O_2(g)$ evolved, as we previously uncovered (Fig. 4c), the collection efficiency for oxygen evolution as measured by rotating ring disk electrode (RRDE) does not decrease when comparing measurements performed in NaOH and KOH (Supplementary Figs. 25 and 26), suggesting a stable catalytic process associated with oxygen evolution. This behavior is unlike the one previously observed for some other crystalline catalysts, such as perovskites and for which the collection efficiency was found to be degraded during surface reactivity.

This charge balance mechanism can thus be schematically described as an electrochemical–chemical (EC) mechanism (Fig. 4e). During this EC mechanism, a high valence $\alpha$-Li$_i$IrO$_3$ oxide is first electrochemically formed (E step) before to chemically reacts with water to generate $O_2(g)$ (C step). It is worth stressing out that while the chemical oxidation of water on the surface of a high valence transition metal oxide is a thermodynamical event—the driving force for this reaction is given by difference between the redox potential for $K^+$ insertion/deinsertion into the catalyst and the reversible potential for water oxidation—it is only made possible by counterbalancing the charge with the insertion of cations into $\alpha$-Li$_i$IrO$_3$. To further understand the involvement of $K^+$ into the electrochemical process, the effect of both $K^+$ and $OH^-$ concentrations on the overall OER kinetics was assessed independently. By keeping the pH equal to 13 and adding potassium salt to the solution, an increase of the OER activity is observed (Supplementary Fig. 27). Unlike for $K^+$, when doing similar measurements with Na$^+$ no enhancement of the OER activity was measured. From these measurements, we can conclude that the kinetics of the OER is dependent on the concentration of $K^+$, which is needed to trigger the reformation of the birnessite phase that shows greater activity than the layered phase. Similarly, by mixing NaOH into 0.1 M KOH, hence keeping the concentration of $K^+$ constant while increasing the concentration of OH$^-$, the OER activity was found to increase (Supplementary Fig. 28). Looking into details at the Tafel plots for both sets of experiments, it can be seen that increasing the concentration of OH$^-$ mostly affects the kinetics in the potential region limited by mass transport, while increasing the concentration of $K^+$ affects both the mass transport limited region and the Tafel region. Nevertheless, the fact that the catalyst structure can reversibly switch from the layered to the birnessite structure, depending on the conditions renders the precise evaluation of the reaction orders for both $K^+$ and $OH^-$ uncertain.

**Computation study of OER intermediates.** Density functional theory (DFT) calculations were performed in order to assess the effect of this structural modification on the adsorption energies for the different OER intermediates $*OH$, $*O$, and $*OOH$ on the surface of the iridate catalyst (see Supplementary Figs. 29–33 and Supplementary Tables 3–7 for further details). Since different surface terminations were observed experimentally by HRTEM, the adsorption energies as well as the OER overpotential ($\eta$) were calculated on the [001] surface of $\alpha$-Li$_i$IrO$_3$, as well as on two different kinds of steps with armchair and zigzag-type termination of the IrO$_3$ layers (A-steps and Z-steps, respectively). The possibility of K, O, or Li vacancies was considered for all three surfaces, and the results for some plausible surface structures are plotted as purple markers in the volcano plot of Fig. 5 (see ESI for all the results). Points on the left leg of the volcano are limited by the formation of $*OOH$ from $*O$, while points on the right leg are limited by the oxidation of $*OH$ to $*O$. All sites on the [001] surface are found on the left leg of the volcano with rather large overpotentials, indicating that this surface is the less active for the OER. Instead, most of the step sites are found on the right leg or close to the top of the volcano. Corresponding models for the surfaces of the intercalated structure with stoichiometry Li$_i$$_{0.75}$$K_{0.25}$(H$_2$O)$_{0.50}$IrO$_3$ were then made (see inset in Fig. 5) and the calculated overpotentials for these sites, plotted as red markers in Fig. 5, were found to be greatly modified by the intercalation of hydrated $K^+$ into $\alpha$-Li$_i$IrO$_3$. This finding indicates that the charge balance mechanism and the formation of the birnessite phase induces a change in the energies of the OER intermediates, and potentially in the OER kinetics with the calculated overpotentials being found on top of the volcano. However, comparing these calculated overpotentials with the ones computed for $\alpha$-LiIrO$_3$ on the same active sites, it remains complex to assign the enhanced OER activity to one specific active site.

**Electrochemical and structural stability.** Finally, we could conclude that, in addition to triggering the formation of the birnessite phase that shows greater OER performances, the charge balance process is essential for stabilizing this iridium-based catalyst and therefore break the activity/stability relationship. For that, HRTEM analysis was performed after 300 cycles in KOH and show that the surface of the catalyst remains perfectly crystalline with no formation of amorphous surface (Fig. 6a), unlike previous observations made for other highly active catalysts, such as $Ba_{0.5}Sr_{0.5}CoO$_3$Fe$_2$O$_{5-δ}$(refs. 17,26,30,61). Furthermore, negligible amount of iridium was found leached during the OER for $\alpha$-LiIrO$_3$ (Supplementary Fig. 34). Therefore, the charge balance process allows for maintaining the structural integrity of the birnessite phase, which thus does not appear to show the obvious formation of self-assembled amorphous clusters on the surface of the catalyst. Hence, this stabilization process largely differs from the one previously observed for other transition metal oxides.

Furthermore, not only the catalyst’s surface is observed to be relatively stable, but the OER performances were found to be...
Fig. 6 Stable surface and OER performances allowed by the potassium intercalation process. a Postmortem HRTEM images for α-Li1IrO3 continuously cycled 300 times in 0.1 M KOH at a scan rate of 10 mV s⁻¹ within a potential range of 1.1–1.7 V vs. RHE. The scale bar is 1 nm. b OER performances with time for α-Li1IrO3 measured in 0.1 M KOH and compared with similar measurements performed in 0.1 NaOH. c and d show the CV curves of α-Li1IrO3 after certain times of OER performance in 0.1 M KOH and NaOH, respectively. e Corresponding Tafel curves.

retained at a current density of 10 mA cm⁻² oxide for over 40 h in 0.1 M KOH (Fig. 6b), unlike for NaOH for that it increases by 22% to 440 mV under similar conditions (Fig. 6b). This observation is reinforced by the analysis of cyclic voltammetry (CV) scans recorded every 4 h and that show no increase of the overpotential in KOH (Fig. 6c, e), unlike for NaOH for which the Tafel slopes show significant degradation of the OER performances for the layered phase (Fig. 6d, e, Supplementary Fig. 35). Hence, in addition to preserving the crystalline surface of the catalyst, the charge balance mechanism leads to sustained OER performances. In light of these results, mastering this charge balance phenomenon therefore provides a unique avenue for the future development of stable and active OER catalysts, which will call for a detailed investigation by integrating such catalyst in a practical AEMWE electrolyzer.

In summary, by a wise choice of open crystallographic structure combined with the use of alkaline cations with small hydrodynamic radius, we enable the electrolyte to be intercalated into the crystallographic structure of the layered iridium oxide during the chemical reactivity of the catalyst with water and therefore to participate to the overall charge balance phenomenon. Indeed, the use of in situ structural characterizations combined with gas analysis provide the demonstration that the chemical oxidation of water via the reactivity of the high valence oxide can be made reversible by the bulk insertion of hydrated K⁺ inside the α-Li1IrO3 structure, hence leading to the formation of a birnessite phase that possesses enhanced OER performances, while retaining perfectly stable structure and performances upon prolonged cycling. More importantly, similar bulk intercalation process governing the OER activity could be seen for another layered compound LiCoO2 (Supplementary Figs. 35–37), possibly making it a universal strategy to break the activity/stability relationship for OER catalysts. Hence, this work provides the fundamental understanding for experimental observations previously made for other layered compounds 62-65 and helps to rationalize previous observations made about the effect of alkaline ions on the OER kinetics 48,49. Finally, as usual with new findings, it asks for more theoretical development in order to fully uncover the potentiality of such mechanism in terms of performances, which will necessitate to include explicit solvent molecules as well as applied potential in order to fully capture this dynamic process.

Methods
Sample preparation. α-Li1IrO3 was synthesized by grinding IrO2 and Li2CO3 (in excess of 5%) according to literature 66. To obtain α-Li1IrO3, α-Li2IrO3 is first charged to 4.0 V vs. Li/ Li⁺ at a constant current of 1/20 C in a Swagelok-type cell against metallic Li anode, using a glass fiber separator and LP100 electrolyte (1.0 M LiPF6 in ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC) in a 1:1:3 weight ratio). The α-Li1IrO3 powder is then washed with DMF and dried at 25 °C. The synthesis of α-Li1IrO3 follows the same procedure, with the electrode (α-Li1IrO3) being charged to 4.6 V vs. Li/ Li⁺.

The α-Li1K0.3IrO3·0.7H2O phase was synthesized by a chemical strategy. The above synthesized α-Li1IrO3 powder is soaked in a 1.0 M KOH solution for >12 h. The resulting powder is collected by centrifugation and first washed with ultrapure water and then with a water/acetone mixture (1:1 v/v ratio) before being dried at 55 °C overnight.

The birnessite α-Li1K0.3IrO3·0.7H2O sample was prepared by an in situ electrochemical method by cycling α-Li2IrO3 in KOH solution. Ir-For that, catalyst thin film with a mass ratio of 8:1:1 of α-Li2IrO3 powder to acetylene black carbon to Nafion(r) was drop-casted on a glassy carbon electrode (2 × 2 cm²). The electrode is cycled in 1.0 M KOH solution within a potential range of 1.1–1.7 V vs. RHE for OER at a scan rate of 10 mV s⁻¹ for 50 cycles. After rinsing by excess amount of ultrapure water, the electrode is dried at room temperature. Powder is then collected from the glassy carbon electrode for further characterizations.

Electrochemistry measurements. Electrodes were prepared by drop-casting an ink containing oxide catalyst powder on a glassy carbon electrode (5 mm diameter) or a large glassy carbon plate (2 × 2 cm²). The glassy carbon electrode was loaded with 0.5 mg catalyst cm⁻² disk and a mass ratio of 8:1:1 of Ir-oxide catalyst to acetylene black carbon to Nafion®. In general, 10 mg of Ir-catalyst powder was mixed with 1.2 mg of acetylene black carbon and ~60 μL of Nafion solution (5 wt. %) in 2 ml of tetrahydrofuran solution. Homogeneous catalyst ink was prepared by ultrasonification for 10–20 min. A total of 10 μL of the as-prepared catalyst ink was then drop-casted on to a polished mirror-like glassy carbon electrode (5 mm in diameter), and dried in air at room temperature (25 °C).

OER measurements were carried out using a biologic MGP-30 potentiostat with rotating disk electrode (RDE, Pine Inc, US). The glassy carbon electrode loaded with catalyst is used as working electrode, and a KCl-saturated Ag/AgCl reference electrode (RE) and a Pt wire were employed as RE and counter electrode (CE), respectively. The Ag/AgCl RE is calibrated by using a reversible hydrogen RE (HydroFlex®, from Gaskatel, Germany) before and after each experiment. Potentials were then converted to the RHE scale. A scan rate of 10 mV s⁻¹ was used for all CV and rotation was set to 1600 rpm. Oxygen was bubbled into the electrolyte before the CV and potentiostatic measurements. KOH solutions with different concentrations were prepared by Milli-Q ultrapure water.
Electrochemical measurements were conducted at room temperature (25°C) otherwise mentioned. CV was also conducted at low temperature (4°C) using a low-temperature thermostatic bath (Shanghai Silon Scientific Instrument Inc.) Tafel curves were plotted from OER kinetic currents, which were obtained from taking the average between forward and backward scans to remove the capacitive current contribution, and then corrected with ohmic losses. Ohmic drops were corrected by subtracting the ohmic voltage drop from the measured potential, using the electrolyte resistance determined by high-frequency AC impedance, where iR-corrected potentials are denoted as E-iR (E as the current and R as the electrolyte resistance). Error bars represent standard deviation from at least three independent measurements. Currents were normalized by the Brunauer, Emmett, and Teller (BET) surface area.

RRDE (PINE Inc., US) was employed to evaluate the efficiency of the OER. The applied potential on the Pt ring electrode is set to 0.4 V vs. RHE for detecting O2 generated at the disk electrode. Rotation was set at 1600 rpm. Solutions were saturated with argon before measurement. The collection efficiency is calculated as \( \eta = \frac{q_{\text{theo}}}{q_{\text{meas}}} \) at a fixed potential (E = 1.58 V vs. RHE) where the oxygen evolution occurs. Electrochemical stability of Ir-based catalysts was evaluated by both long-term CV cycles and chronopotentiometry. Chronopotentiometry was conducted at a current density of 10 mA cm\(^{-2}\) in O2-saturated alkaline solutions for 40 h with CV being performed at different intervals.

chronoamperometry step, 1 ml of the electrolyte was taken out for the ICP measurement.

Density functional theory calculations. Spin-polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP), projector augmented-wave pseudopotentials and an energy cutoff of 585 eV. The atomic simulation environment was used to set up and analyze the structures. The exchange-correlation energy was described using the PBE functional, which was found to reproduce the lattice constants of bulk α-Li2IrO3 well (c.f. Supplementary Table 3 in ESL). We furthermore find that the functional is able to reproduce the experimental layer separation of 6.9 Å in the disordered phase (Li\(_x\)K\(_6\)(H\(_2\)O\(_{16}\))\(_{2}\)IrO\(_3\) (α-Li2IrO3)) experimentally, calculated to be 6.91 Å. The brillouin zone of bulk α-Li2IrO3 is sampled using a 4 x 3 x 4 Monkhorst-Pack k-point grid while the k-point mesh for the surface models are chosen such that the products |a| \( k_a \) and |b| \( k_b \) are both >25 Å and a single k-point is used in the c-direction perpendicular to the surface. The unit cell dimension along the c-direction is chosen such that a minimum of 12 Å separates the adsorbates from the periodic image of the slab, and a dipole correction is used to decouple the electrostatic potentials across the periodic boundaries. All structures are relaxed until the forces on all atoms are below 0.02 eV Å\(^{-1}\).

Three different models of the surfaces are considered (c.f. Supplementary Figures S1 and S3). The sample used in the construction of the ESL uses the surface shown in Figure S1. The XRD data indicated that the functional is able to reproduce the [001] surface that corresponds to a termination that follows the layers, a [102] termination that results in an armchair-type edge of the hexagonal IrO\(_2\) layer (A-step), and a [111] termination that results in a zigzag-type edge of the IrO\(_2\) layer (Z-step). All surfaces are modeled by three layer slabs of the bulk structure, with the bottom layer fixed in the bulk position during optimization. Given the harsh oxidizing conditions, all Li is assumed to be stripped from the surface, and the slab is thus terminated by an IrO\(_2\) layer at the top.

The OER is assumed to follow the pathway: (1) \( \text{H}_2\text{O}^\ast + \text{Ir} \rightarrow \text{OH}^\ast + \text{IrO}^\ast + \text{H}^+ + e^- \) \( \Delta G_1 \), (2) \( \text{OH}^\ast + \text{O}^\ast \rightarrow \text{OOH}^\ast + \text{Ir} \) \( \Delta G_2 \), (3) \( \text{OOH}^\ast + \text{Ir} \rightarrow \text{O}_2 \text{Ir} \) \( \Delta G_3 \), where \( \Delta G_1 \) represents a surface active site, where the intermediate is bound to one or more Ir atoms. Since our starting point is the O-rich surface, at least one oxygen atom must be removed to form a reactive site (c.f. ESL for further details). \( \Delta G_2 \) is the change in zero point energy, \( \Delta G_1 \) is the energy contribution arising from the change in entropy, \( \Delta G_1 \) is the change in solvation energy, and the last term is the CHE, with \( \Delta G_2 \) being the number of electrons in the reaction and \( \Delta G_1 \) being the numerical change of an electron. From the adsorption energies, the limiting potential for OER can be calculated as:

\[ \eta_{\text{lim}} = \max\left(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right) / e \]

The ZPE and entropy terms, and the solvation energies have not been calculated explicitly, but an estimate has been included in the results presented in Fig. 5. The estimation for the ZPE and entropy terms calculated in ref. \(^{71}\) (≤0.05, +0.05, and +0.40 eV for the \*OH, \*O, and \*OOH intermediates) and the solvation energies calculated for IrO\(_2\) in ref. \(^{72}\) (ca. –0.10, 0.0, and –0.30 eV for \*OH, \*O, and \*OOH) resulting in overall corrections of +0.25 eV, +0.05 eV, and +0.10 eV for \*OH, \*O, and \*OOH, respectively. A comparison of the results with and without these corrections is given in the ESL. The energy of \( \text{OH}_2 \) in the first phase is poorly described by GGA-type functionals, and is therefore corrected such that the free energy of formation of \( \text{H}_2\text{O} \) is reproduced. Some of this error may also be present in the O-O bond of the \*OOH intermediate, potentially giving rise to a small underestimation of the adsorption energy for this intermediate\(^{25}\).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. DFT optimized structures can be obtained from https://doi.org/10.5281/zenodo.3632908.
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Competing interests

The authors declare no competing interests.

Additional information

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