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A dissolution/precipitation equilibrium on the surface of iridium-based perovskites controls their activity as oxygen evolution reaction catalysts in acidic media

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Abstract: Recently, Ir^(V)-based perovskite-like materials were proposed as oxygen evolution reaction (OER) catalysts in acidic media with promising performance. However, iridium dissolution and surface reconstruction were observed, questioning the real active sites on the surface of these catalysts. In this work, Sr₂MIr^(V)O₆ (M = Fe, Co) and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄ were explored as OER catalysts in acidic media. Their activities were observed to be roughly equal to that previously reported for La₂LiIrO₆ or Ba₂PrIrO₆. Coupling electrochemical measurements with iridium dissolution studies under chemical or electrochemical conditions, we show that the deposition of an IrO_x layer on the surface of these perovskites is responsible for their OER activity. Furthermore, we experimentally reconstruct the iridium Pourbaix diagram which will help guide future research in controlling the dissolution/precipitation equilibrium of iridium species for the design of better Ir-based OER catalysts.

The electrochemical production of hydrogen fuel via water splitting has long been explored as a potential way to store clean and renewable energy. The key challenge for water splitting lies in improving the efficiency of the kinetically-slow, rate-limiting oxygen evolution reaction (OER) ($2\text{H}_2\text{O} = 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$).^{[1][2]} While a large variety of transition metal oxides have been studied as promising OER catalysts in alkaline media,^{[3][4][5][6]} the design of active and stable catalysts in acidic media has proven challenging.^{[7][8][9][10][11]} The few materials established as suitable OER catalysts in acidic media are mostly Ir-based metal oxides, such as rutile IrO_2 ,^{[12][13]} electrodeposited IrO_x ,^[14] or more recently Ni-substituted IrO_x .^{[15][16][17]} Recently, Ir-based perovskites have been reported as promising candidates in acidic media.^{[18][19][20]} The high OER activity of these Ir-based perovskites was ascribed to the formation of electrophilic $\text{O}^{(l-)}$ surface species favoring the nucleophilic attack of water.^{[11][20][21]} However, dissolution of iridium, alkali and/or rare earth elements in acidic electrolytes has been observed after close examinations of some $\text{Ir}^{(V)}$ -based perovskites, such as $\text{La}_2\text{LiIr}^{(V)}\text{O}_6$ ^[20] and $\text{Ba}_2\text{PrIr}^{(V)}\text{O}_6$,^{[7][19]} indicating their drastic structural instabilities in harsh acidic conditions.^[12] Furthermore, the presence of IrO_2 nanoparticles was revealed on the surface of $\text{La}_2\text{LiIr}^{(V)}\text{O}_6$ after cycling.^[8] Given this array of observations, a legitimate question arises upon the origin of the OER activity on the surface of these perovskites. Therefore, it is important to understand the OER mechanism of these $\text{Ir}^{(V)}$ -based perovskites as well as the effect of iridium dissolution on their catalytic behaviors, in order to improve their performances and/or guide future research in designing new active and stable OER catalysts in acidic media.

We herein investigate the catalytic behaviors of three $\text{Ir}^{(V)}$ -based OER catalysts in acidic media, $\text{Sr}_2\text{Mlr}^{(V)}\text{O}_6$ ($\text{M} = \text{Fe}, \text{Co}$) with a double perovskite structure and $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ with a Ruddlesden-Popper (RP) structure. Their OER activities were compared with those measured for $\text{La}_2\text{LiIr}^{(V)}\text{O}_6$ and $\text{Ba}_2\text{PrIr}^{(V)}\text{O}_6$.^{[7][19]} Coupling electrochemical measurements with iridium dissolution studies, we propose a ubiquitous 'dissolution-electrodeposition/precipitation' mechanism for the origin of OER activities measured for these perovskites.

Structural and electronic properties of $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$, $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ and $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$ are shown in the supporting information (Figures S1-S4) and their catalytic behaviors in Figures 1a-1c. $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$ exhibits an enhanced OER activity compared to commercial micron-size IrO_2 (~ 3 fold) (Figure 1d) and a stable electrochemical performance with an overpotential of ~ 330 mV at 10 $\text{mA}/\text{cm}^2_{\text{oxide}}$ for 24 h (Table S2, Figure S10). Unlike $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$, the OER activity measured for $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$ was initially low (1th cycle), but gradually increased within 50 cycles to an activity comparable to that of $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$ (Figure 1b). The catalytic behavior of $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ with a RP structure is surprisingly similar to that of $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$ perovskite regardless of apparent differences of their crystal structures (inset of Figure 1). More interestingly, the OER activities recorded for $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$, $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ and $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$ after the activation step (50 cycles) are roughly equal to those of previously reported $\text{Ir}^{(V)}$ -based perovskites $\text{Ba}_2\text{LnIr}^{(V)}\text{O}_6$ and $\text{La}_2\text{LiIr}^{(V)}\text{O}_6$ when normalized by their BET surface areas (Figure 1d).^{[19][20]} These observations suggest that the final OER activity of $\text{Ir}^{(V)}$ -based perovskite-like catalysts is independent of the crystal structure as well as the composition of the catalyst. This odd phenomenon drove us to reconsider the nature of the catalytic active sites for these $\text{Ir}^{(V)}$ -based perovskites.

As mentioned earlier, dissolution of iridium has been previously observed for Ir-based perovskites in acidic media.^{[7][8][9]} As a key active element in all $\text{Ir}^{(V)}$ -based catalysts, the loss of iridium from the bulk as well as the presence of leached species in electrolytes should affect their catalytic behaviors. In order to better understand the impact of iridium dissolution, we considered an extreme case where samples of $\text{Ir}^{(V)}$ -based perovskites were deliberately soaked to dissolve in 0.1 M HClO_4 (SI. 4). The resulting solutions all exhibit a similar purple-pink color, corresponding to a soluble species with a common broad absorption peak at ~ 520 nm in their UV-Vis spectra (Figure 2a). Amorphous IrO_2 precipitants were observed when this purple-pink solution was heated up (Figure S5). This together with the UV-Vis further confirms that all of these $\text{Ir}^{(V)}$ -based perovskites partially dissolve in the acid to form a common purple-pink solution containing soluble iridium species.

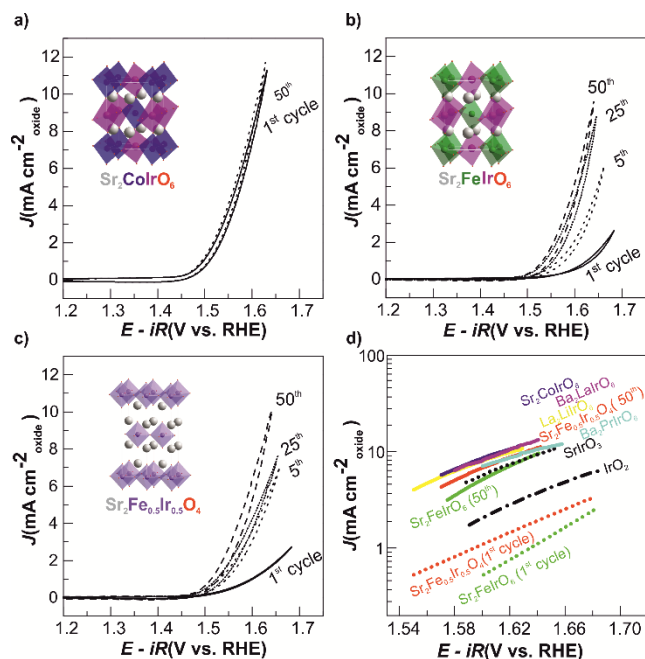


Figure 1. Structures (inset) of and CVs recorded for a) $\text{Sr}_2\text{CoIr}^{(V)}\text{O}_6$, b) $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$ and c) $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ in 0.1 M HClO_4 with a scan rate of 10 mV/s. d) Tafel plots for selected catalysts scaled with their BET surface areas (Table S2).

This purple-pink iridium solution was then used as 'Ir-containing electrolyte' to investigate its contribution in catalyzing the OER using a blank glassy carbon electrode (GCE) (Figure 2c). The results were compared with a control experiment conducted by cycling a blank GCE in fresh electrolyte. We observed that the GCE cycled in the 'Ir-containing electrolyte' gradually became OER active along cycling, while that cycled in fresh electrolyte exhibited negligible OER activity (Figure 2b). Moreover, the activation feature (1st to 50th cycle) observed with the GCE cycling in the 'Ir-containing electrolyte' is strikingly similar to that recorded for $\text{Sr}_2\text{FeIr}^{(V)}\text{O}_6$ and $\text{Sr}_2\text{Fe}_{0.5}\text{Ir}_{0.5}^{(V)}\text{O}_4$ (Figure 1), suggesting a similar catalytic mechanism. After electrochemical measurements in the 'Ir-containing electrolyte', some traces of blue-black particles were observed on the surface of the GCE. These particles were confirmed to contain iridium by energy-dispersive X-ray (EDX) analysis (Figure S6). Therefore, it's reasonable to conclude that the OER-active species are IrO_x (or hydrated $\text{IrO}_x \cdot m\text{H}_2\text{O}$) gradually electrodeposited during the cycling process onto the surface of the GCE from the purple-pink Ir-containing electrolyte. It's worth nothing that not all soluble iridium species (e.g. K_2IrCl_6) could deposit into IrO_x . This experiment demonstrates that the leached iridium species in the electrolyte can actually return to the surface of the catalyst and affect its OER activity. Careful examination of the pseudocapacitive region of the CV reveals a reversible feature at ~ 0.92 V vs. RHE (Figure 2b), agreeing with that observed during electrodeposition of hydrous iridium oxide film from soluble precursors^{[22][23][24][25]}. The small peak separation (~ 23 mV) suggests the formation of a non-diffusional, surface-bound species, which is consistent with the deposition/dissolution of $\text{IrO}_x \cdot m\text{H}_2\text{O}$ in our experiment. The growing intensity of this reversible feature as well as the expansion of the pseudocapacitive region along cycling (Figure 2b) suggests an increasing amount of active IrO_x deposited on the electrode, leading to the enhanced OER activity.

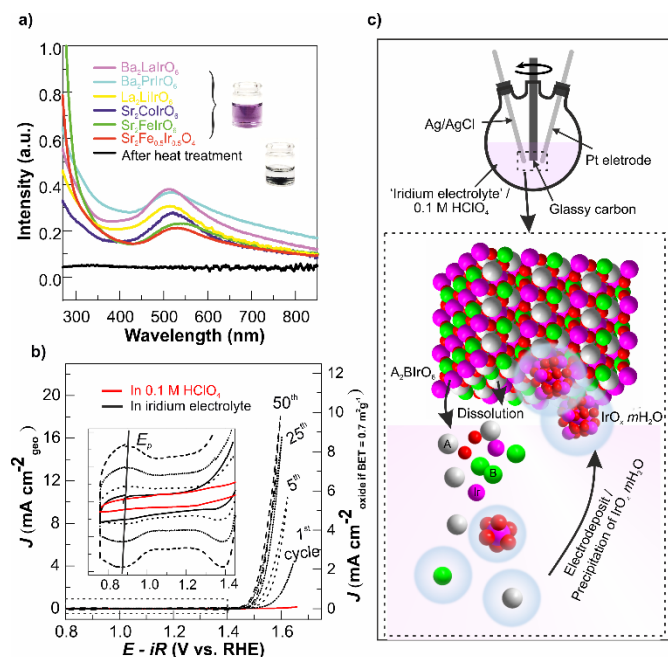


Figure 2. a) UV-Vis spectra recorded from purple-pink solutions prepared by dissolving Ir^(VI)-based perovskites (SI. 4), and the solution after heat treatment in a microwave. b) The CVs recorded for the blank GCE in 0.1 M HClO₄ or Ir-containing electrolyte (the right y-axis is scaled assuming a normal loading of 10 μ g catalysts with BET = 0.7 m²/g as that of Sr₂FeIrO₆); Inset is the zoomed-in pseudocapacitive region. c) Experimental set-ups and the proposed OER catalytic mechanism involving the ‘dissolution-electrodeposition’ of iridium species.

The similarities between the OER behaviors recorded for Sr₂FeIr^(VI)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(VI)O₄ and that recorded for a blank GCE in the ‘Ir-containing electrolyte’ suggests that their OER catalytic mechanism involves the ‘dissolution-electrodeposition’ of iridium species as depicted in Figure 2c. In this mechanism, the catalyst suffers leaching of iridium from its bulk structure when soaked in acidic electrolytes and subsequently the leached iridium species are electrochemically deposited as IrO_x·mH₂O onto the surface of the catalyst to give rise to the OER activity. The electrodeposition of IrO_x·mH₂O occurs when the applied external potential exceeds its ‘precipitation potential’ that we estimate from our CV results to be $E_{p-IrO_x} \approx 0.92$ V vs. RHE. Therefore, the OER activity of these perovskites is strongly correlated with the surface morphology and the amount of deposited IrO_x·mH₂O, but independent of the actual structure or composition of these perovskites. This conclusion is consistent with the ex-situ X-ray absorption measurements at Ir L₃-edge where a reduction of the Ir oxidation state (formation of Ir^(III/IV)O_x) was observed for both Sr₂FeIr^(VI)O₆ and Sr₂CoIr^(VI)O₆ after CV measurements (Figure S7).

To probe the ‘dissolution-electrodeposition’ of iridium species, an elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted to trace the dissolution of iridium upon time (Figure 3b, Figures S11 and S12). Two parallel experiments were carried out for each catalyst: one with the catalyst operated at 1 mA/cm²_{oxide} to investigate the iridium leaching under electrochemical OER conditions (Ec), and the other with the oxide solely soaked in the electrolyte without applied currents to investigate the leaching process under chemical conditions (C). For Sr₂FeIr^(VI)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(VI)O₄, an increasing amount of leached iridium was detected within a soaking time of 24 hours (C) (Figure 3b), in good agreement with the UV-Vis. Interestingly, the concentration of leached iridium in the electrolyte operated under electrochemical conditions (Ec) is considerably less than that under chemical conditions (C), suggesting an electrodeposition of iridium species from the electrolyte onto the surface of the electrode in the former case. This result is in stark contrast to that of Sr₂CoIr^(VI)O₆ where similar iridium dissolution behaviors were observed under electrochemical (Ec) and chemical (C) conditions.

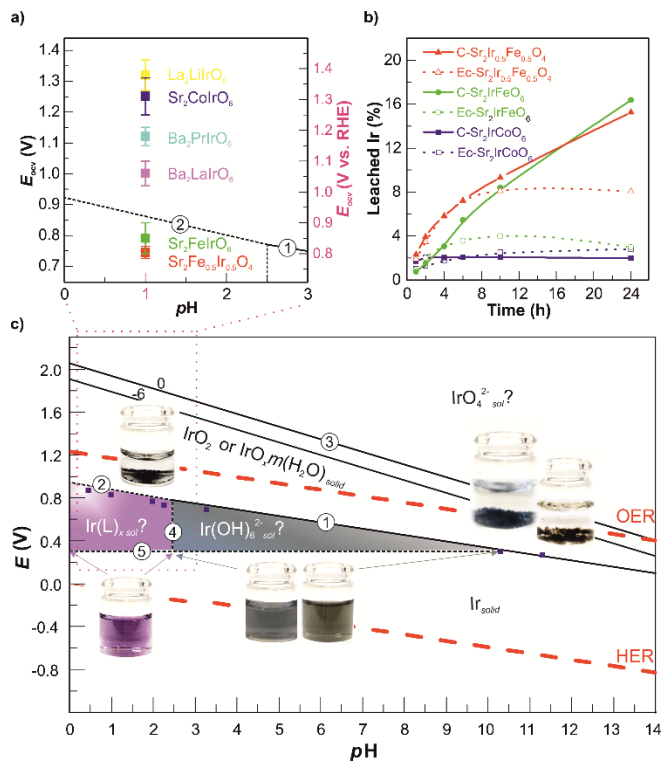


Figure 3. a) E_{OCV} measured for Ir^(V)-based perovskites. b) The percentage of leached iridium detected by ICP (error bar: 5 ~ 10%) under chemical (solely soaking) or electrochemical conditions (1 mA/cm²). Leached percentage = (leached mass of Ir) / (starting mass of Ir) * 100%. c) Iridium E_H -pH diagram.

When iridium dissolves off the structure of the perovskite, a solution containing soluble iridium species is formed. The precipitation of these soluble iridium species into the OER active IrO_xmH₂O particles on surface of the GCE should be potential dependent and follow the Pourbaix diagram of iridium. For Sr₂Felr^(V)O₆, and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄, their open circuit potentials (Figure 3a, $E_{OCV} \approx 0.85$ V and 0.80 V vs. RHE respectively) were measured to sit below the 'precipitation potential' ($E_{p-IrOx} \approx 0.92$ V vs. RHE) of IrO_xmH₂O. In contrast, the open circuit potential of Sr₂CoIr^(V)O₆ ($E_{OCV} \approx 1.31$ V vs. RHE) was measured to lie above E_{p-IrOx} . Therefore, the precipitation of IrO_xmH₂O occurs without any applied potentials when soaking Sr₂CoIr^(V)O₆ in the acidic electrolyte. This explains why the iridium concentration detected in the electrolyte under chemical conditions (C) was found similar to that under electrochemical conditions (Ec) for Sr₂CoIr^(V)O₆, while much greater for Sr₂Felr^(V)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄ (Figure 3b). The formation of Ir rich surface under Ec condition was also confirmed by the disappearance of Co on the surface by XAS (Figure S13). The precipitation of iridium species under both Ec and C conditions for Sr₂CoIr^(V)O₆ was further confirmed by EDX analysis where iridium rich particles were observed after treatment under both conditions (Figure S14).

All these observations suggest that the OER activity of Ir^(V)-based perovskites is eventually confined by the potential/pH (E_H -pH) domain where IrO_xmH₂O species are stable. Therefore, in order to predict the catalytic behavior of other Ir^(V)-based perovskite-like catalysts, we reconstructed the E_H -pH diagram of iridium (Figure 3c, and detailed in SI. 9) using our experimental results as well as the equations previously established by Pourbaix^[26]. The E_{p-IrOx} was used as the critical potential distinguishing soluble iridium species out of solid IrO_xmH₂O or IrO₂. Ir^(V)-based perovskites such as Sr₂CoIr^(V)O₆, La₂LiIr^(V)O₆, Ba₂PrIr^(V)O₆ and Ba₂LaIr^(V)O₆ were measured to possess an open circuit potential higher than E_{p-IrOx} (Figure 3a). At low pH, iridium species thus precipitate into OER-active IrO_xmH₂O at the open circuit potentials for these perovskites and their OER activities most likely originate from IrO_xmH₂O species precipitated at E_{OCV} . This assumption is further supported by the stable OER activities measured for these catalysts from the 1st to the 50th cycle. In contrast, for Sr₂Felr^(V)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄ with $E_{OCV} < E_{p-IrOx}$, the amount of precipitated OER-active IrO_xmH₂O is initially ≈ 0 and the initial OER activity (1st cycle) is thus low, revealing the intrinsic inactive feature of these Ir^(V)-based perovskites.^[20] Upon cycling, the OER-active IrO_xmH₂O is formed on the surface of Sr₂Felr^(V)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄ via an electrodeposition process triggered during CV measurements from 1.1 to 1.7 V vs RHE (potential > E_{p-IrOx}). Given that the amount of electrodeposited IrO_xmH₂O is correlated to the operation time at a potential above E_{p-IrOx} , the measured OER activity of Sr₂Felr^(V)O₆ and Sr₂Fe_{0.5}Ir_{0.5}^(V)O₄ is expected to increase gradually along cycling before being confined by the intrinsic activity of IrO_xmH₂O and the available oxide surfaces onto which it deposits (estimated to be the initial BET surface area of the perovskites). This is consistent with our experimental results that the OER activities after several cycles are similar (normalized by

BET) for every Ir^(V)-based perovskite regardless of their crystal structures or chemical compositions (Figure 1d). One could argue that a slower electrochemical leaching rate of Fe compared to Co (while Ir corrodes slow) could also explain different activation behaviors as observed for Ir-Fe and Ir-Co catalysts. However, Fe corrodes not slower than Co, but even faster in Sr₂Fe_{0.5}Ir_{0.5}O₄ (Figure S15). In addition, to further examine the dissolution-deposition mechanism, a potential of 1.30 V vs. RHE (corresponding to the E_{ocv} of Sr₂IrCoO₆) was applied on Sr₂IrFeO₆, resulting in an enhanced OER activity (1st cycle) in the following CVs due to increased deposition of IrO_x at a potential > E_{p-IrO_x} (Figure S16). These results further support the dissolution-deposit mechanism of Ir species.

We then investigated the evolution of the purple-pink Ir-containing solution as a function of pH by slowly adding in 1 M NaOH solution, and experimentally reconstruct an iridium E_H-pH diagram (Figure 3c, Figure S17). Line ① and ③ are plotted according to the equilibrium of Ir/IrO₂ (Ir + 2H₂O = IrO₂ + 4H⁺ + 4e⁻) and IrO₂/IrO₄²⁻ (IrO₂ + 2H₂O = IrO₄²⁻ + 4H⁺ + 2e⁻), respectively. Dashed line ② is plotted as the equilibrium between soluble iridium species Ir(L)_x and IrO₂ using E_{p-IrO_x} estimated earlier. When increasing the pH above ~ 2.5, a color change from pink to olive-green or blue was observed (dashed line ④). This color change matches with the shifting of the UV-Vis absorption peak to ~ 580 nm (Figure S18), which is a characteristic absorption for Ir^(IV) species.^{[17][27]} This change in color and in UV-Vis spectrum is possibly resulting from the replacement with H₂O or OH⁻ around iridium to form Ir(OH)₆²⁻ or Ir(OH)₂(ClO₄)₄²⁻.^{[27][28]} Study of the precise nature of these iridium species is challenging.^[28] Fractions of —Ir—O— or —Ir—OH— might be maintained during dissolution of Ir^(V)-perovskites, which facilitates the precipitation of OER-active IrO_x at potential above E_{p-IrO_x} (Figure 2c). Finally, adding more NaOH, the pH quickly increased and blue or olive-brown precipitates started to form. Filtering out the precipitates resulted in a colorless solution and disappearance of the UV-Vis absorption at ~ 580 nm, suggesting the precipitation of iridium species.

Our study highlights that the stability of Ir^(V)-based perovskite-like catalysts is limited in acidic media by the potential-dependent dissolution/precipitation equilibrium of iridium species. Though kinetics for iridium dissolution might be structure-dependent, this dissolution for perovskites is still extremely difficult to avoid owing to the heavy leaching of A-site alkali and/or rare earth elements in acidic electrolytes. Overall, even though the initial OER activity can reflect the intrinsic properties of Ir^(V)-based perovskites, the activity is eventually dominated by IrO_x·mH₂O which is the thermodynamically stable phase formed on their surface. Finally, our study reveals that the precipitation of IrO_x·mH₂O is dependent on the electronic structure of the catalyst since it is controlled by its open circuit potential. This finding offers a new avenue to design highly active OER surfaces in acidic media, complementing previous works where the dissolution/precipitation rates were controlled by change of the morphology (change in local concentration).^[29]

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Keywords: perovskite • oxygen evolution reaction • iridium dissolution • Pourbaix diagram

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