The importance of water structure and catalyst-electrolyte interface on the design of water splitting catalysts

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ABSTRACT: Hydrogen production technologies have attracted intensive attention for their potential to cope with future challenges related to renewable energy storage and conversion. However, the significant kinetic barriers associated with the oxygen evolution reaction (OER), one of the two half reactions at the heart of water electrolysis, greatly hinder the sustainable production of hydrogen at a large scale. A wide variety of materials have thus been designed and explored as OER catalysts. In this perspective, we briefly review the development of Ir-based OER catalysts in acidic conditions and discuss the limitations of a design strategy solely based on the physical and electronic properties of OER catalysts, highlighting the importance of understanding the catalyst-electrolyte interface which affects the stability and activity of the catalyst. We then share our perspective on a group of crystalline, bulk protonated iridates obtained via cation exchange in acidic solutions to be used as promising stable and active OER catalysts. Finally, we discuss the advances recently made in understanding the impact of the active sites environment on the OER kinetics, emphasizing the influence of the water structure and/or solvation properties of ions in the electrolyte. We highlight the importance of developing a better understanding of these influencing factors and incorporate them into our design of OER catalysts with enhanced properties.

Introduction

Driven by the growing demand for storing and converting renewable energies in the form of electricity, recent years have seen a boom in the design of materials with enhanced electrochemical properties. This is especially true for both half reactions at the heart of water splitting, namely the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Hence, a wide variety of materials have been recently developed and their electrocatalytic performances toward OER and HER investigated in order to achieve hydrogen production at large scale.¹ Nevertheless, while the development of materials for other electrochemical energy storage and conversion devices such as Li-ion batteries has long thrived thanks to the early understanding of the bulk properties required for the development of better electrodes^{2–6}, predicting surface properties to guide the design of novel materials for water electrolysis has always been a challenge.^{7–12}

Attempts to rationalize the performances of water splitting catalysts were historically rooted in the correlation existing between surface physical properties of solids and the energetics of the intermediate species, such as *O, *OH and *OOH intermediates that govern the OER kinetics, for instance.^{13,14} Pioneering works were first devoted to the study of the elec-

tronic properties of the so-called dimensionally stable anodes (DSA) for the OER.¹⁵ While initially ill-understood, the field rapidly expanded and the first physical descriptors controlling the OER kinetics on the surface of transition metal oxides were proposed by Trasatti.¹⁶ Significant efforts have since then been devoted to refine these descriptors and it is now commonly accepted that by increasing the electronegativity of the transition metal^{17–19} which lowers the Fermi level and reduces the charge transfer energy²⁰, an enhancement of the OER performances of transition metal oxides is observed. Similarly, the design of HER catalysts has also greatly benefited from the development of descriptors such as the hydrogen binding energy,^{10–12} helping uncovering a wide variety of early transition metal sulfides, phosphides or carbides as efficient and cost-effective HER catalysts to replace the state-of-the-art catalysts, e.g. platinum.²¹

In the last decade, we have thus seen the partitioning of research efforts in the field of electrocatalysis between materials-oriented studies encompassing the development of new water splitting catalysts guided by the use of physical descriptors, and more fundamental studies focusing on the interplay between the double layer structure and the catalytic properties of well-defined surfaces such as Pt or IrO₂.^{22,23} Never-

theless, the recent realization that boosting the performances of OER catalysts is accompanied by drastic surface instabilities highlights the limited accuracy of these descriptors in their powers to capture the electrocatalytic stability of the best OER catalysts.^{17,18,24,25} The discovery of electrocatalysts that exhibit not only active but also stable catalytic performances thus currently suffers from our general lack of understanding on how surfaces interact with their environment, more precisely, on how solvent-adsorbate or other weak interactions in the interfacial water structure affect the activity and stability of electrocatalysts²⁶ (Figure 1). One can therefore anticipate the growing need to integrate relevant concepts including dissolution/precipitation equilibrium, hydrogen bonding network and the structure of the double layer on the surface of transition metal oxides into the design of new active and stable OER catalysts.

Figure 1. Electrochemical interfaces and potential research focuses for water splitting electrocatalysts.

In this perspective, we thus aim at providing a framework of different research aspects inherent to the design of OER catalysts. We will first give a brief overview on the recent development of complex iridium-based oxides as OER catalysts under acidic conditions. Through that example, we will then discuss limitations inherent to a strategy solely based on the design of materials *in vacuo* and highlight the complex equilibrium governing the electrocatalytic activity as well as the stability of these iridium-based catalysts under the harsh acidic conditions. This will lead us to discuss the complexity of the interactions taking place on the surface of the catalyst as well as the importance of “spectator” ions in the OER kinetics, before to focus on the physical origin for the ions dependence of the OER activity of solid catalysts recently observed for a large variety of materials.

Development of complex iridium oxides as OER catalysts in acidic media

One of the greatest challenges in the exploration of state-of-art OER catalysts lies in the unfortunate correlation existing between the enhanced OER activity and the limited stability of the catalysts. Recognizing that limitation, research efforts have recently intensified to develop strategies to circumvent this issue. Among them, promising attempts were made to limit the dissolution of transition metal cations by using nanoporous catalysts,²⁷ by engineering the substrates/catalyst interactions to enhance the catalyst’s stability,^{28,29} by tuning the composition of buffer-containing electrolytes to ensure the re-

deposition of transition metal cations following a so-called self-healing process^{30,31} or by stabilizing MnO_2 .^{32,33} These approaches bring in phenomena occurring at the electrochemical interfaces into the design of effective OER catalysts, pointing out the need to understand and control the solid-solution equilibrium at the electric double layer in order to develop better performing catalysts. One example that highlights such a realization is the development of iridium-based oxides as OER catalysts in acidic conditions.

While most transition metal complex oxides are relatively insoluble in alkaline conditions and readily precipitates as hydroxides,^{34–40} only iridium and ruthenium oxides are sufficiently stable in acidic conditions, with ruthenium-based oxides being more active but less stable than their iridium counterparts.⁴¹ Therefore, numerous studies were devoted to the development of iridium-oxides as OER catalysts in acidic environment. Thermally prepared stoichiometric IrO_2 is found to be stable over time with a low dissolution rate of iridium but unfortunately exhibits limited OER activity, while electrochemically prepared hydrous iridium oxides, often referred to as IrO_x owing to our lack of understanding of their exact chemical composition, show much improved OER activities.⁴² To explain such difference, recent studies suggested that partial deprotonation of hydrous IrO_x catalysts leads to the decrease of the chemical potential of iridium (i.e. increased oxidation state) and the formation of so-called electrophilic ‘ O^{n-} ’ species in which electron holes are localized in O 2p states.^{43–46} These species are prone to react with water which serves as nucleophile following an acid-base reaction, thus reducing the barrier for O-O bond formation and giving rise to the enhanced OER activity of hydrous IrO_x . However, this improved activity is at the expense of its stability since triggering the reactivity of ‘ O^{n-} ’ species with water lowers the coordination of iridium which then becomes prone to dissolution. Therefore, hydrated IrO_x catalysts are found relatively unstable leading to a constant reconstruction of their surface under the OER conditions.

Encouraged by the fast development of complex transition metal oxides from the perovskite family as OER catalysts under alkaline conditions,^{9,47–50} complex iridium-based perovskites or pyrochlore catalysts have thus been recently studied as promising OER catalysts in acidic conditions, as summarized in Figure 2.^{51,52} We should first recall that proper normalization of the electrocatalytic performances of OER catalysts has been a longstanding issue, as recently discussed in several review articles.^{53,54} This is particularly true for amorphous catalysts whose surface is poorly defined and the concentration of active sites hard to estimate. Up to date, popular methodologies to normalize the OER activity use either the specific surface area as obtained by gas adsorption following the Brunauer-Emmett-Teller (BET) theory or the electrochemically active surface area (ECSA). The most common method to study crystalline catalysts remains the BET surface area, nevertheless this normalization method possesses limitations and can hardly be transposed to accurately estimate the concentration of active sites for amorphous surfaces.⁵⁴ In this paper, the OER activity of catalysts is normalized by their BET specific surface. One can observe in Figure 2a that the OER activities for Ir^{IV} -based perovskites and pyrochlores (e.g. SrIrO_3 , $\text{Y}_2\text{Ir}_2\text{O}_7$) differ only marginally from that of Ir-M mixed oxides (e.g. Li-IrO_x amorphous oxides, Ir-Ni oxides), despite the obvious differences in their crystallographic structures and chemical compositions (Figure 2c). This is in stark

contrast with observations previously made for OER catalysts in alkaline media for which modifying the crystal field and the nature of the neighboring atoms could change the metal-oxygen bond strength and thus affect the OER activity of transition metal oxides^{7,47,50,55}. Furthermore, not only do the OER activities of Ir^{IV}-based oxides appear rather insensitive to the chemical composition but the activities measured for Ir^V-based double perovskites are also found nearly invariant with respect to structure and chemical composition (Figure 2b). More strikingly, the OER activities measured for Ir^{IV}- and Ir^V-based catalysts in acidic conditions are very similar, with an overpotential of about $0.30 \text{ V} \pm 0.03$ at $1 \text{ mA/cm}_{\text{oxide}}^2$ for both series. This result is in contradiction with our understanding of the OER activity for transition metal oxides, which should be greatly dependent on the ionic-covalent character of the metal-oxygen bond that increases with the transition metal oxidation state. Moreover, Ir^V-based catalysts such as $\text{La}_2\text{LiIrO}_6$ which seems to show promising OER activity in acidic conditions has been reported inactive in alkaline media⁴⁴ while Ir^{IV}-based perovskites such as SrIrO_3 have been found very active.⁵¹

Figure 2. Tafel plots for **a)** Ir^{IV}-based and **b)** Ir^V-based oxides (data for IrO_2 ,⁵⁶ $\text{Bi}_2\text{Ir}_2\text{O}_7$,⁵² $\text{Y}_2\text{Ir}_2\text{O}_7$,⁵⁷ Li-IrO_x ,⁵¹ SrIrO_3 ⁵¹ and $\text{IrNi}_{0.9}\text{O}_x$ were extracted from references, the OER activity for other oxides was measured following the procedure described in the Supplementary Materials). BET surface areas used to plot the data are given in Table S1 of the Supplementary Materials. **c)** Crystallographic structures for rutile IrO_2 , hexagonal 6H-SrIrO_3 , pyrochlore $\text{A}_2\text{Ir}_2\text{O}_7$ and double perovskites A_2BiIrO_6 .

In addition to similarities in terms of OER activity, recent transmission electron microscopy (TEM) investigations revealed the formation of an amorphous IrO_x -type surface for numerous iridium-based OER catalysts after cycling in acidic conditions. Indeed, amorphous films were observed on the surface of IrNi-O^{58} and 6H-SrIrO_3 ⁵¹ catalysts after cycling (Figure 3, Figure S1 in the Supplementary Materials) while crystalline IrO_2 nanoparticles were observed for $\text{La}_2\text{LiIrO}_6$ apart from an amorphous layer on its surface⁴⁴ (Figure 3, Figure S1). As recently shown for pristine SrIrO_3 ,⁵¹ crystallization of IrO_2 nanoparticles could arise from exposure of the surface to the electron beam, while the rate of precipitation of iridium on the surface of these catalysts might impact the crystalliza-

tion process as well. Either way, the surface of these complex iridium oxides is found modified after cycling, and all these observations raised legitimate questions regarding the origin for the OER activity on the surface of Ir-based catalysts in acidic conditions.

Figure 3. High resolution TEM images showing the formation of amorphous IrO_x layer on the surface of Ir-Ni mixed oxide⁵⁸ (left, reprinted from ref 58 with permission) and 6-H-SrIrO_3 ⁵¹ (middle, reprinted in part from ref 51 under the terms of the Creative Commons CC BY license: <https://creativecommons.org/licenses/by/4.0/>) while crystalline IrO_2 were found on the surface of $\text{La}_2\text{LiIrO}_6$ after cycling⁴⁴ (right, reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Nature Energy, Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction, A. Grimaud et al., 2016).

Iridium dissolution/precipitation equilibrium on the surface of OER catalysts

The surface degradation for Ir-based catalysts is triggered by the leaching of thermodynamically unstable non-noble metals as well as by the dissolution of iridium. The latter is most severe in some Ir^V-based double perovskites. Indeed, as shown in Figure 2c, in order to stabilize Ir^V-based in double perovskites, 3D structures consisting of apex-linked octahedra with alternating IrO_6 and e.g. BO_6 are created in A_2BiIrO_6 . Dissolution of these non-noble elements subsequently leads to a collective deconstruction of the apex-linked network, resulting in disconnected IrO_6 fractions that are prone to dissolution in the electrolyte. Therefore, concomitant heavy dissolution of non-noble elements and iridium was observed for Ir^V-based double perovskites, which significantly jeopardize the catalytic stability of these Ir^V-based catalysts.

In order to evaluate the stability of different Ir-based catalysts, the concept of ‘stability factor’ (S-factor) given by the ratio of gaseous oxygen generated and the amount of dissolved iridium was recently introduced.⁴² In a classical corrosion scheme, the dissolution rate is assumed to follow the anodic current, which should lead to a similar S-factor for every oxide catalyst. However, the aforementioned experimental observations suggest a dissolution rate for Ir^V-based catalysts governed not only by the anodic current as generally assumed, but also greatly affected by factors such as associated chemical leaching of non-noble metals constituting the catalyst. The estimated stability factor for different catalysts might therefore vary and one can find a general trend with thermally prepared $\text{IrO}_2 > \text{hydrated IrO}_x \approx \text{Ir}^{\text{IV}}\text{-based oxides} > \text{Ir}^{\text{V}}\text{-based oxides}$ such as $\text{Ba}_2\text{PrIrO}_6$, $\text{La}_2\text{LiIrO}_6$ or $\text{Sr}_2\text{FeIrO}_6$ which are found the least stable.

Observing that iridium is rapidly leached out of perovskite-based catalysts even at the open-circuit voltage when no anodic current is applied, we recently demonstrated that the OER activity for these iridium oxides is in fact controlled by the re-deposition of amorphous IrO_x from dissolved iridium species onto the surface of the catalysts.⁵⁹ Realizing this, efforts must

be aimed at understanding this dissolution/precipitation which is evidently function of the nature of the dissolved iridium species. However, while the Pourbaix diagrams for most transition metals are well-established, the one for iridium still holds some uncertainties, especially at low pH. In order to highlight this gap in our understanding of the nature of the iridium dissolved species, we intentionally leached out a series of double perovskites in different concentrated electrolytes (HClO_4 , H_2SO_4 , or HCl) and measured their UV-Vis spectra in order to determine the strength of interaction between the dissolved Ir and the conjugated base (methods in the Supplementary Information). As shown in Figure 4 a), different soluble species are observed with the maximum absorbance shifting towards greater wavelengths following $\text{HClO}_4 < \text{H}_2\text{SO}_4 < \text{HCl}$. This shift indicates that while ClO_4^- anions might be considered as non-interacting with the dissolved iridium species, ligand exchange may occur between the iridium oxo species formed during the dissolution of the perovskite and SO_4^{2-} or Cl^- anions, with the exchange being stronger for Cl^- anions. Interestingly, we can qualitatively observe that $\text{Sr}_2\text{IrCoO}_6$ dissolves almost readily for both H_2SO_4 and HCl solutions but not for HClO_4 (Figure 4b), pointing towards the ligand induced displacement of the dissolution equilibrium. Furthermore, precipitation of SrSO_4 or other insoluble salts may affect this equilibrium as well. Consequently, $\text{Sr}_2\text{IrCoO}_6$ was found to exhibit stable performances in HClO_4 acidic solutions (within 20 cycles) while it suffers significant degradation along cycling in H_2SO_4 (Figure 5a). One must therefore be cautious when designing new OER catalysts for acidic conditions, as well as when comparing the stability metrics for these complex OER catalysts.

Figure 4. a) UV-Vis spectra measured for different acids in contact with Ir^{V} -based perovskite catalysts, as well as Ir^{IV} -based catalysts. b) UV-Vis spectra recorded over time for $\text{Sr}_2\text{IrCoO}_6$ in 1M H_2SO_4 or HClO_4 solutions showing the different dissolution rates in both acids.

Furthermore, the nature of anions in acidic electrolytes not only modifies the stability of the solid catalyst, but also affects the subsequent electro-deposition of IrO_x on the surface of the catalyst. To study this effect, blank glassy carbon electrodes were cycled in different acidic solutions (H_2SO_4 or HClO_4) containing soluble iridium species (Figure 5b and Supplementary Materials). As shown in Figure 5c and 5d, the pseudocapacitive current is found to quickly increase from the 1st to the 50th cycle, with the appearance of both redox peaks and a capacitive envelope suggesting the deposition of IrO_x from the soluble iridium precursors in both H_2SO_4 and HClO_4 . However, the redox features are found different for IrO_x electrodeposited in H_2SO_4 and in HClO_4 (Figure 5d). Specifically, the redox potential for IrO_x electrodeposited in HClO_4 (0.89 V vs. RHE) are shifted to lower potential, indicating that hydrated IrO_x is easier to oxidize than when electrodeposited in H_2SO_4 (0.96 V vs. RHE). This observation is in agreement with the previous work by Blakemore et al. reporting different redox behaviors and morphologies for IrO_x films deposited from different organic precursors.⁶⁰ Furthermore, a constant cathodic current is monitored in H_2SO_4 , presumably arising from the constant cathodic electrodeposition of IrO_x species that are more soluble in H_2SO_4 than in HClO_4 , as qualitatively discussed in Figure 4b. Nevertheless, as seen in Figure 5c, the final OER activity for the electrodeposited IrO_x when scaled by the geometric surface area of the electrode is not impacted by the nature of the acidic electrolyte, despite the different redox features observed in their pseudocapacitive regions. Thus, while IrO_x electro-deposited in these different conditions might have different morphologies, its impact on the intrinsic OER activities remain unclear. In our quest for designing better OER catalysts utilizing the full catalytic potential of hydrated IrO_x , further investigations are needed to 1) fully understand the nature of the different iridium soluble species which define the morphology and local environment of Ir in the deposited IrO_x and 2) potentially control the density and nature of the electrodeposited IrO_x active sites. Finally, the nature of the electrolyte and water structure on the stability of OER catalysts is not limited to the case of Ir-based catalysts in acidic conditions but also applies to other catalysts at different pH.

Figure 5. a) Cyclic voltammograms recorded for $\text{Sr}_2\text{IrCoO}_6$ in 1 M HClO_4 and 1 M H_2SO_4 . b) Schematic representation of the electrodeposition of dissolved iridium species. c) Cyclic voltammograms recorded for a bare glassy carbon electrode cycled in electrolytes containing dissolved iridium species in 0.1 M HClO_4 and 0.1 M H_2SO_4 . d) The pseudo-capacitive region of c).

Extending the stability window of OER catalysts in acid by the design of bulk protonated phases

Complex iridium-based perovskites, pyrochlores and mixed metal oxides appear as thermodynamically unstable in the potential-pH window of interest for OER in acidic conditions where only IrO_2 and electrodeposited IrO_x amorphous compounds have been reported stable above 1.23 V vs. RHE (Figure 6a). This observation drastically constrains our landscape for materials exploration in acid and new strategies must be developed to overcome this limitation and design new active and stable crystalline catalysts in these harsh conditions. Aside from the aforementioned strategies including confining the dissolution of iridium by using nanoporous materials or the use of substrates to stabilize the iridium-based catalysts, exploration of novel phases via topochemical synthetic strategies appear as potentially promising. For that, inspiration can be taken from the functioning of hydrous amorphous IrO_x catalysts previously described. Indeed, while only adsorption/desorption events occur on the surface of thermally prepared IrO_2 prior to the OER, continuous oxidation/reduction events associated with proton exchange is observed for hydrous IrO_x catalysts (Figure 5b).

Recently, a series of novel bulk protonated iridium phases H_xIrO_3 and H_xIrO_4 was uncovered via cation exchange in acidic conditions of the lithiated parent phases $\beta\text{-Li}_2\text{IrO}_3$ and Li_3IrO_4 , respectively.^{61,62} For the H_xIrO_4 phase, the cation exchange reaction drives a mild structural transition from the initial O3 stacking in Li_3IrO_4 to a P3 stacking in $\text{H}_{3.4}\text{IrO}_4$, as shown in Figure 6a. In other words, the reaction is topotactic and allows the stabilization of the protonated iridate $\text{H}_{3.4}\text{IrO}_4$ with a well-defined crystal structure (Figure 6b), which is of significant difference to the amorphous hydrated IrO_x with a structure parent to the rutile IrO_2 phase formed on the surface of iridium metal oxides (Figure 3) or the amorphous hydrous IrO_x formed from the oxidation of metallic Ir.⁶³ Furthermore, we could observe by operando XRD that the $\text{H}_{3.4}\text{IrO}_4$ phase remains crystalline in the potential window of 0.24 to 1.64 V vs. RHE in 0.1 M HClO_4 , as shown in the 2D contour plots in Figure 7. The concurrent OER at potential above 1.5 V vs. RHE does not jeopardize the crystallinity of $\text{H}_{3.4}\text{IrO}_4$. More specifically, $\text{H}_{3.4}\text{IrO}_4$ exhibits an excellent structural flexibility to reversibly release/uptake H^+ at this potential range, as seen by the continuous shifting of the (003) diffraction peak at $2\theta \approx 19^\circ$, indicating continuous modification of the interlayer distance as commonly seen for layered compounds upon reversible Li^+ or Na^+ intercalation (Figure 6).^{64,65} Furthermore, as shown in Figure 6c, $\text{H}_{3.4}\text{IrO}_4$ was observed with both stable OER currents and proton exchange redox processes for over 100 cycles. This stability might result from the charge balance phenomenon associated with the proton exchange and the concomitant change of iridium oxidation state before and during the OER. We thus believe that bulk protonated H_xIrO_y phases can offer a good alternative to thermally prepared IrO_2 to design OER catalysts with enhanced and stable OER activities. Furthermore, as suggested by our recent study⁶¹, the iridium dissolution in the bulk protonated phase H_2IrO_3 is largely decreased compared to other crystalline phases such as SrIrO_3 , providing another evidence that bulk protonated H_xIrO_y phases are promising OER catalysts with stable performances. As for any new strategy, more remains to be done in order to fully uncover the real potential of such a family of protonated oxides as OER electrocatalysts. More specifically, one must determine if this stability is thermodynamic or kinetics in nature, as well as compare it with the dissolution rate previously found for amorphous hydrated IrO_x catalysts which are known to be less stable than their crystalline IrO_2 counterpart.⁶³ Furthermore, topotactic cation exchange was successfully achieved starting from layered lithiated phases and a thorough exploration of this synthesis route will be needed to determine if such a strategy can be extended to other families such as tungsten bronze oxides, Ruddlesden-Popper compounds or others.

Figure 6. a) Pourbaix diagram of iridium in HClO_4 solution with the shaded area indicating where stable and crystalline protonated iridates can be explored. On the right shows the structure of the protonated iridate $\text{H}_{3.4}\text{IrO}_4$ that was obtained via a proton exchange reaction from Li_3IrO_4 in acid.⁶² b) Rietveld refinement of the XRD pattern of $\text{H}_{3.4}\text{IrO}_4$ with in red the experimental points, in black the simulated pattern, in green the difference between observed and simulated and the blue ticks are the Bragg reflections. An SEM micrograph of the pristine $\text{H}_{3.4}\text{IrO}_4$ is shown in the inset.⁶² c) The CVs recorded for $\text{H}_{3.4}\text{IrO}_4$ in 0.1 M HClO_4 for 100 cycles at a scan rate of 10 mV/s. The current is normalized by the BET surface area ($2.23 \text{ m}^2/\text{g}$). The inset displays the enlarged capacitive region showing the redox processes associated with H^+/e^- exchange in $\text{H}_{3.4}\text{IrO}_4$. Figure a) and b) adapted with permission from Proton Ion Exchange Reaction in Li_3IrO_4 : A Way to New $\text{H}_{3+x}\text{IrO}_4$ Phases Electrochemically Active in Both Aqueous and Nonaqueous Electrolytes, A. J. Perez et al., *Advanced Energy Materials*, 2019, John Wiley and Sons.

Figure 7. Operando XRD study of $\text{H}_{3.4}\text{IrO}_4$ in 0.1 M HClO_4 suggesting its structural flexibility to reversibly release/uptake H^+ in the potential range of 0.24 to 1.64 V vs. RHE. On the left is shown the electrochemical cycling carried out during continuous XRD measurement. A 2D contour plot of the evolution of resulting patterns aligned with the electrochemistry is shown on the right. Only relevant 2θ ranges are displayed here.

Controlling the water structure in the environment of active sites

From the example of iridium oxides used as OER catalysts in acidic conditions, it appears that the next frontier to conquer regarding the development of water splitting catalysts is the control over the complex equilibrium/ion exchanges occurring

at the interface between the oxide catalysts and the electrolyte. Nevertheless, in order to achieve such fine control, one critical piece of information is cruelly missing: the understanding of the water structure in the environment of the active sites. Even if recent results are slowly uncovering this effect (see the discussion below), our understanding related to water solvation structure on the OER activity of transition metal oxides is certainly less advanced than our comprehension regarding the hydrogen evolution reaction (HER).

Indeed, poised by the observations that Pt performed better in strongly acidic conditions than in either neutral or alkaline conditions,^{23,66–68} researchers have slowly uncovered the effect of pH and of the water solvation structure on the HER performances of Pt. In acidic media, the proton discharge (Volmer step: $\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_{\text{ad}}$) on the electrode is known to be fast and the reaction rate is controlled by the $\text{H}_{2(\text{g})}$ evolution.^{69,70} On the contrary, H_2O dissociation-adsorption was proposed to be the rate-determining step in alkaline media due to the very low concentration of protons, resulting in large penalties for the HER kinetics.^{67,71} This slower kinetics for reducing H_2O when compared to H^+ could arise from both the difficulty to break the O-H bond from water⁶⁷ and the difficulty to evacuate OH^- ions generated during water reduction,²³ thus modifying the reaction pathway. Either way, adding some oxophilic $\text{Ni}(\text{OH})_2$ islands to the surface of Pt(111) has proved to enhance the HER kinetics for Pt in alkaline conditions.⁶⁷ This effect is even more pronounced when alkali cations such as Li^+ are added to the electrolyte, thanks to their interaction with water/hydroxyl ions and $\text{Ni}(\text{OH})_2$ on the surface of the catalyst.⁶⁷ Furthermore, comparing the pH dependence observed for the HER activity of Pt with the one measured for the underpotential deposition of hydrogen (H_{UPD}) that precedes the HER during cathodic

scan, discrepancies could be observed. Indeed, while the HER kinetics for Pt(111) shows pH dependence, the H_{UPD} energy does not show any. This indicates that the HER rate is not solely controlled by the energetics of proton adsorption^{23,67} and is rather governed by the modification of the double-layer structure. Indeed, as the potential of zero free charge (pzfc) is quasi-invariant with pH while the one for the HER is more negative (Nernst equation), the electrical field and so water rigidity at the Pt interface increases with the pH, which slows down water-ions transfer (proton adsorption / hydroxide desorption) across the double layer and hence the HER rate.²³ Overall, the energetics for proton transfer from the bulk of the electrolyte to the catalyst's surface can be schematically expressed as:⁷²

$$\Delta G^* = W_{H^+} + \Delta G_{\text{desolv}} + \Phi^*$$

with W_{H^+} the work to transfer a solvated proton from the outer to the inner Helmholtz plane, ΔG_{desolv} the free energy to partially desolvate a proton which is also the energy to deform the solvation sphere in the electrical field and Φ^* the energy to transfer an electron from the Fermi level of the catalyst to the inner Helmholtz plane of the double layer at the catalyst/solvent interface, each term being interdependent to the others.⁷² Explained in a very intuitive manner, the proton must thus convert entropy into enthalpy when moving from the bulk of the electrolyte to the interface, the entropy being greater at lower pH due to the stronger electric field.⁷³

For the OER, proper comparisons of the electrocatalytic activity in alkaline and in acidic conditions is mainly hindered by the limited stability of most transition metal oxides under both conditions, as discussed above. Consequently, only thermally prepared IrO_2 is stable enough to compare the OER kinetics in both alkaline and acidic media. While an initial report using IrO_2 nanoparticles pointed towards a higher activity in acidic conditions⁴¹, a recent study on an IrO_2 thin-film focusing on the interplay between the OH_{ad} and O_{ad} adsorption energies and the OER kinetics in different electrolytes pointed towards faster kinetics for IrO_2 in alkaline solution than in acidic media²⁶. In this study, two parallel pathways were proposed for the formation of OOH_{ad} (acidic: $\text{O}_{\text{ad}} + \text{H}_2\text{O} \rightarrow \text{OOH}_{\text{ad}} + \text{H}^+ + \text{e}^-$; alkaline: $\text{O}_{\text{ad}} + \text{OH}^- \rightarrow \text{OOH}_{\text{ad}} + \text{H}^+ + \text{e}^-$) and the alkaline pathway was assumed to have greater kinetics than the acidic one. In acidic media, the proton-independent acidic pathway is dominant and thus the OER activity follows the formation energy of OOH_{ad} intermediate which is observed to increase with increasing pH. In strong alkaline media, the alkaline pathway becomes dominant due to the availability of OH^- . As a result, the OER kinetic becomes faster in stronger base, despite the observed increased formation energy of the OOH_{ad} , which is in good agreement with previous observations made for transition metal oxides.^{74–76} Nevertheless, the dependence in the concentration of OH^- was proposed to cause the activity of IrO_2 not to scale linearly with ΔG_{OOH} and therefore to disobey the volcano relationship.²⁶ Given that only the electrolyte composition is modified while keeping the surface of the catalyst unaffected, the authors concluded that other factors must be taken into account to explain such observation. Hence, the solvation structure in the vicinity of the active sites as well as specific interactions with cations on the surface of the OER catalysts⁷⁷ can affect the energetics and the structure of the intermediates and thus break the scaling relationship for the OER intermediates in alkaline conditions.

A similar observation was made for the oxygen reduction reaction (ORR) on different Pt-alloys for which the activation enthalpy remains constant while the ORR activity is drastically improved when compared to pure Pt.⁷⁸ The improvement for the ORR activity on Pt-alloys is proposed to originate from the pre-exponential factor of the rate law which is given by the entropies of activation as well as the number of active sites.⁷⁹ Indeed, following the rate law from the transition-state theory, the rate of a given reaction would be controlled by the free activation energy ΔG^* according to:

$$r \propto A \exp\left(\frac{-\Delta G^*}{RT}\right)$$

with A being the pre-exponential factor. Additionally, the rate of the reaction can be expressed using a derived Arrhenius law in which an entropic term is introduced into the pre-exponential term:

$$r \propto A' \exp\left(\frac{-E_a}{RT}\right)$$

with $A' \propto \exp\left(\frac{-\Delta S^*}{R}\right)$

with E_a the apparent activation energy and ΔS^* the entropy of activation from the transition-state theory.⁸⁰ If following a so-called Bronsted-Evans-Polanyi relation,^{81,82} the activation energy E_a linked to the binding energy of oxygen (ΔG_0) should define the OER kinetics. When extrapolating the results from previous work by Bockris and Otagawa,⁸³ the apparent activation energy for the OER is found to decrease linearly with increasing current density, from 110 kJ/mol for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ and 98 kJ/mol for LaMnO_3 to 75 and 71 kJ/mol for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and LaNiO_3 at 300 mV, respectively (Figure 8a). Therefore, when comparing a large variety of transition metal oxides, the apparent activation energy and therefore the binding energy of the rate-determining intermediate remains a powerful descriptor for the OER activity. Nevertheless, recent studies have highlighted that, for the most active transition metal oxides, the OER kinetics are greatly influenced by the concentration of OH^- for LaNiO_3 ⁸⁴ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ⁷⁵, as shown in Figure 8 b). Interestingly, the activation energy measured for these compounds is very close to the one reported for water autoprotolysis.^{85–87} Both observations raise questions about the interactions that govern the OER kinetics. Similar to what was found for the HER in alkaline conditions, weak interactions such as hydrogen bonding or ion-water interactions that modify the O-H bond dissociation and/or the adsorption of OH^- on the surface of the OER catalysts could be involved.

Recent studies were therefore carried out to investigate the effect of modifying the water composition and/or solvation properties on the OER kinetics.^{85–87} Indeed, the strong interactions between adsorbates on the surface of IrO_2 such as $^*\text{OH}$ and $^*\text{O}$ and cations in solution depending on their Lewis acidity, with for instance Li^+ stabilizing the $^*\text{OH}$ intermediate more than K^+ ^{26,88} and thus modifying the OER activity,²⁶ as recently been suggested. In contrast to this observation based on IrO_2 , large alkali cations ($\text{Cs}^+ > \text{K}^+ \sim \text{Na}^+ > \text{Li}^+$) were found to dramatically enhance the OER activity of Fe-containing NiOOH .^{89,90} Interestingly, only a very weak cation effect was observed ($\text{Cs}^+ \sim \text{K}^+ \sim \text{Na}^+$) for “Fe-free” NiOOH which shows limited OER activity when compared to their Fe-containing counterparts, with the only exception of Li^+ which is found to reduce the OER activity. The question then arises regarding the modification of the intermediates which results from the

competition between the following effects: modification of water hydrogen bonding network in the vicinity of the active site, specific cation/anion interactions with the catalysts surface and finally cation intercalation in the porosity and/or the structure of the catalyst. Furthermore, moving the alkali cations, the use of large hydrophobic organic cations such as tetramethylammonium cations (TMA^+) was found to greatly reduce the OER activity for Fe-containing NiOOH .⁸⁹ Similarly, we observed that the presence of TMA^+ also reduces the OER activity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ while that of the less active LaCoO_3 (compared to $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$) remains unaffected.⁹¹ Altogether, these observations indicate that cation or pH effects on the OER kinetics predominantly appear for the most active catalysts for which the rate of oxygen evolution may not be governed by the energy of the intermediates, as discussed above. Rather, these effects can originate from the hydration enthalpy of cations that controls the proton acidity in water⁹² or from the water structure at the electrochemical interface which is dependent on the nature of the cations, or both. Furthermore, special care must be exercised when studying complex oxides such as perovskites, since A-site cations such as lanthanides leached under OER conditions can also interact with the surface of these catalysts that often reconstruct in the form of an oxyhydroxide film.^{93–95}

Figure 8. a) Apparent activation energies as reported by Otagawa and Bockris for perovskites OER catalysts as a function of the OER current density measured at 300 mV overpotential.⁸³ b) OER current density as a function of pH for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (left) and LaNiO_3 (right).^{75,84}

To gain insight into the origin of these ion/pH dependent effects, the concept of the chaotropy or kosmotropy of an ion can be introduced. As widely discussed in the field of liquid-liquid extraction,^{96–99} ions (cations and anions) in solution can be divided into two categories depending on their ability to structure (kosmotropic) or disorder (chaotropic) the

water hydrogen bond network. Experimentally, the chaotropy or kosmotropy of ions is determined by measuring the evolution of the viscosity of the solution containing the ions of interest as a function of their concentration. Doing so, the so-called Jones-Dole equation:

$$\frac{\eta}{\eta^0} - 1 = Ac^{\frac{1}{2}} + Bc + \dots$$

with η the viscosity of the solution and c the concentration of ions in solution is empirically used to sort out chaotrope and kosmotrope ions based on the B coefficient ($B > 0$ for kosmotrope and $B < 0$ for chaotrope ions). As shown in Figure 9, the B coefficient measured for different cations such as alkaline cations (Li^+ , Na^+ or K^+), organic cations (TMA^+ and other tetraalkylammonium cations) as well as H_3O^+ does not follow the enthalpy of hydration for these cations. Such deviation reveals the entropic nature for the water hydrogen bond network ordering or disordering effect of cations in solution,⁷⁷ with Li^+ and TMA^+ having a structuring effect on the water hydrogen bond network while K^+ has a very weak destructuring effect. Hence, when revisiting the difference in OER kinetics measured for amorphous $\text{NiFe}(\text{OH})_2$ films or for crystalline $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ in KOH and TMAOH , one can conclude that the main effect is most probably not related to the difference of hydration enthalpies between both cations (-203 kJ/mol for TMA^+ compared to -320 kJ/mol for K^+). Instead, it presumably arises from the modification of the water hydrogen bond network in the electric double layer when changing from K^+ to TMA^+ . Furthermore, as previously discussed, the presence of cations can also affect the OER activity by self-insertion into the porous structure of NiOOH in addition to hydration enthalpy which modifies the energetics of the intermediates and the water structuring effect.⁹⁰ Future work is thus needed to fully understand and dissociate all these different effects.

Figure 9. B coefficients from the Jones-Dole equation as obtained by viscosity measurements for different cations and anions plotted against their hydration enthalpy. The inset displays an illustration for the water structure as found around kosmotropic and chaotropic ions.

In light of the effect of ions observed on the performances of the most active OER catalysts, one must therefore consider more than just the binding energy of oxygen intermediates on the surface of the catalyst. Indeed, effects related to the free energy to deform the solvation structure in the electric field, the free energy to transfer hydroxyl ions from the outer to the inner Helmotz plane (in alkaline conditions) as well as the work to transfer protons from the inner to the outer Helmotz plane (in acidic conditions) must be taken into consideration.²³

As discussed for the HER, the stronger the electric field at the interface, the more rigid the water structure.²³ Specific adsorption occurring before any charge transfer with the electrolyte, such as the H_{UPD} , hence quenches the electrical field and renders the water structure less rigid. Nevertheless, the nature of the double layer for OER catalysts is largely unknown and it remains uncertain if such adsorption processes occur prior to the OER on the surface of transition metal oxides. Our understanding on how the structure of the bulk electrolyte translates to the structure of water in the vicinity of the active sites is thus elusive. In order to push our understanding further on how the bulk solvation structure extends to the electrochemical interface, control experiments must therefore be performed. This will only be possible through the use of thin-film electrodes deprived of binder and carbon additives and with well-defined surface areas and active sites. Furthermore, while the control of such weak interactions was so far only achieved by tuning the composition of the electrolyte, and therefore the solvation structure of water, coating strategies could be envisioned to selectively modify the pzfc of transition metal oxides as well as their proton affinity.⁹¹ Moreover, the water structure affects not only the OER activity but may also modify the stability of the catalysts, as illustrated in Figure 5a. Further work will therefore be needed to explore in depth the effect of electrolyte composition in alkaline conditions on the stability of OER catalysts. One can thus foresee the design of OER catalysts to integrate, in addition to bulk properties that have been widely explored in the past few years, even more design principles originating from sol-gel or colloids chemistry. Nevertheless, how these effects will translate into a real water electrolyzer in which a membrane is used remains to be seen as the transport properties of ions will be drastically modified.

Conclusion

Through different examples, we have highlighted recent developments in the field of water splitting catalyst design. Driven by the finding of physical descriptors for the OER activity of transition metal oxides, numerous catalysts were proposed in the past decade and our knowledge about catalysts' operation has certainly advanced when compared to pioneering works made on perovskites or binary oxides. Nevertheless, the field is now facing a major difficulty, which is to design not only very active catalysts, but also solids that show sufficient stability under these very oxidizing conditions. For that, as emphasized by the recent development of iridium-based OER catalysts for acidic conditions, a thorough understanding of the dissolution/precipitation equilibrium is necessary. This understanding relies first on assessing the intermediates responsible for the dissolution of transition metal oxides, then on uncovering the exact nature of the dissolved species and their interactions with the electrolyte which, in turn, controls the electrochemical redeposition of active species on the surface of the catalyst. While most catalysts are not stable under these acidic conditions, we believe that the development of bulk protonated oxides can unlock the design of active and stable electrocatalysts for acidic conditions, owing to the reversible bulk exchange of protons that allows the counter-balancing of charge associated with the iridium oxidation and the chemical reaction with water.⁶¹ Finally, we believe that the next step in achieving enhanced electrocatalytic properties in solids lies within the structure of water in the vicinity of the active sites. We therefore highlight the importance of entropic terms relat-

ed to the ability of ions to structure or destructure the water hydrogen bond that can be tuned to selectively control the OER activity of the most active transition metal oxides.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures for electrochemical measurements, UV-vis, *Operando* X-ray diffraction, and BET measurements. Data extracted for Figure 2 and 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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