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Catalyst or Precatalyst? The Effect of Oxidation on Transition Metal Carbide, Pnictide, and Chalcogenide Oxygen Evolution Catalysts

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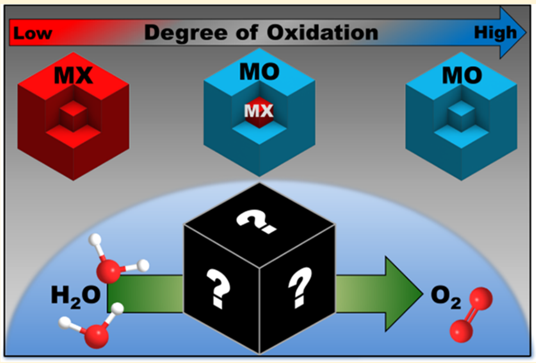
Supporting Information

ABSTRACT: Metal chalcogenides, pnictides, and carbides, labeled collectively as metal X-ides, have become an exciting new class of water oxidation electrocatalysts, but there is a lack of agreement regarding the composition of the "true" catalyst. The most prominent theories are that the X-ides are either completely oxidized, left unoxidized, or transformed into core@shell particles upon testing. Here, we examine examples of each conjecture, summarizing the conflicting viewpoints on catalyst identity and offering guidelines for more rigorous identification in the future. Most studies indicate that at least partial oxidation of the catalyst surface is critical to high performance, likely caused by an increased catalyst surface area upon oxidation or improved charge transfer in the X-ide cores. Therefore, more thorough and uniform long-term testing and nanoscale chemical analysis are essential to determine how these factors relate to catalyst performance.



As interest in intermittent renewable energy sources like solar and wind power has grown, so too has interest in techniques to store this energy for later use. Among the most promising of these is the electrocatalytic splitting of water to produce hydrogen gas as a chemical fuel that can be stored and used to provide energy after dark or during periods of low wind.[1−4] The full implementation of a so-called "hydrogen economy" will require significant investment in infrastructure, but the development of technology and materials to produce raw hydrogen from water has been underway for many years.

Most work on the electrocatalytic generation of hydrogen gas focuses on total water splitting, a combination of the hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$, V_{HER} = 0.0 V vs RHE) and the oxygen evolution reaction (OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, V_{OER} = 1.23 V vs RHE) occurring simultaneously at two electrodes. The four-electron OER is the more difficult reaction of the two; thus, there has been considerable research toward finding catalysts to reduce the electric potential required for this half-reaction. Researchers have previously used RuO_2 in basic solution and IrO_2 in acidic solution as benchmark OER catalysts, both with an overpotential at 10 mA/cm^2 (η_{10}) of ~380 mV,[5] but their high cost has spurred the search for more earth-abundant catalysts like Fe or Ni.[6−14] Complicating this search are the highly oxidizing conditions under which these catalysts must function. Under these conditions, many candidate catalysts, including IrO_2 and RuO_2,[15] physically and chemically degrade within a relatively short period of time, making them unsuitable for widespread use. In their place, materials such as NiFe layered double hydroxides have risen to prominence[8] as a result of their increased resistance to degradation. This gradual change in benchmark choice shows that both activity and stability are essential to judge the applicability of an electrocatalyst for total water splitting.

In this Perspective, we will focus on the interaction between these two concepts for a large family of materials that are known to be active for the OER, the metal X-ides, where "X" refers to counteranions from Groups 4−6 including the elements C, N, P, S, Se, and Te.[10,16−20] For the sake of conventional clarity, we will be excluding metal oxides and hydroxides from the term "X-ide". The distinction is important because, for many years, metal oxides and hydroxides have been the most-studied earth-abundant catalysts for the OER, and significant effort has been directed toward modifying the

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elemental composition,[14,21] nanostructure,[22,23] and synthesis of these catalysts.[24,25] Much of this work was conducted to circumvent inherent limitations in the metal oxides, such as low conductivity and poor catalytic kinetics. Many of the X-ides lack such limitations and have come into greater prominence as more researchers report their catalytic ability and stability for water splitting.

However, the reported chemical composition and electrochemical stability of many X-ide catalysts are in conflict with the highly oxidizing conditions in which these materials operate. Previous calculations on 2D monolayers have shown that within the chalcogenide family oxides have the most negative values for enthalpy of formation, with the overall order following O < S < Se < Te.[26] Researchers have also shown that for a few examples of X-ides (Al, Cd, Cu, Ga, and In) with known nitride, phosphide, and oxide enthalpy values the nitrides and phosphide enthalpies were typically more positive than those of the oxide.[27] It is also well-accepted that the oxide is the thermodynamically stable end-point of most oxidative chemical processes in water. From this standpoint, almost any metal X-ide has a high probability of transforming into an oxide or (oxy)hydroxide during sufficiently extended periods of OER testing. Therefore, it can be inferred that the electrochemical stability may not directly correlate with the chemical stability of the starting material and that a lack of change in electrolysis potential or current density does not necessarily mean that the starting material is the active catalyst. This has been illustrated in several previous works on metal chalcogenides, which all showed significant oxidation despite demonstrating electrochemical stability.[11,19,28] To further illustrate this, we have provided Pourbaix diagrams for a variety of Ni X-ides in the Supporting Information (Figures S1 and S2), which show the speciation and stability of a selection of different catalysts across a range of pHs and potentials, generated using the Materials Project.[29−31] It is readily apparent that the chalcogenides are generally more stable than the pnictides or carbides, but regardless of the initial catalyst, the "true" active form of the catalyst during alkaline OER (pH > 12.0, $V > 1.23$ V vs RHE) will be some form of oxidized material. Recently, there has been a push in the wider electrocatalysis community to better understand the "true" nature of OER catalysts in the case of the various metal X-ides and to also develop better standards for reporting this data in publications.[32−35]

Therefore, it can be inferred that the electrochemical stability may not directly correlate with the chemical stability of the starting material and that a lack of change in electrolysis potential or current density does not necessarily mean that the starting material is the active catalyst.

Three Possible Catalyst Structures. Unambiguous assignment of the active catalyst for what many researchers describe as an OER-active metal X-ide is made more difficult by the possible chemical oxidation mentioned above. In the context of water oxidation, a catalyst is a material that lowers the energy required to perform the chemical reaction without being consumed itself or undergoing a nonreversible chemical change. If the catalyst under study is itself oxidized during the reaction, it does not meet this technical definition, raising questions regarding the "true" composition of the electrocatalyst and the nature of the catalytic site. Broadly speaking, most research in the field currently places these materials into one of three broad categories (Figure 1). The first category simply states that the X-ide does not undergo oxidation, is stable under alkaline oxidative conditions, and is itself the active OER catalyst in its pristine, original state. The second category involves X-ides that are completely oxidized upon sufficient exposure to OER conditions, resulting in an amorphous metal oxide/(oxy)hydroxide that is the active OER catalyst. Finally, the third category covers the more moderate position in which the surface of the X-ide is converted to an amorphous oxide/(oxy)hydroxide while the core of the material remains unoxidized. Here, the oxide/(oxy)hydroxide is recognized to be the OER catalyst, with the unoxidized core serving as a support. Each category has evidence for its assignment, and it is using these categories that we will examine metal X-ides as OER electrocatalysts in this Perspective.

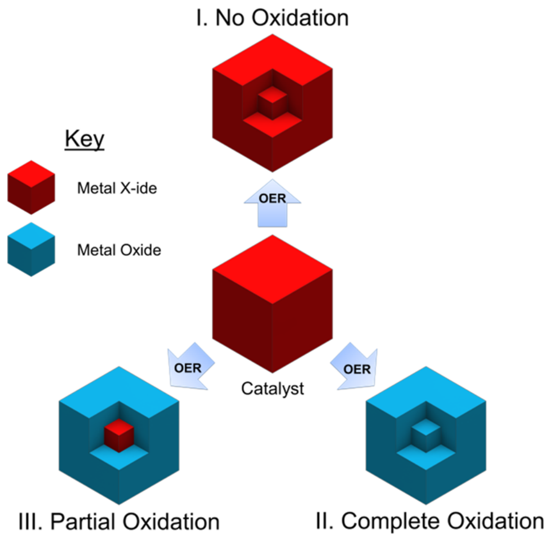

Figure 1. Possible reaction pathways for a hypothetical metal X-ide catalyst during water oxidation. (I) No oxidation to the outer surface or the core. (II) Oxidation of both the outer surfaces and the inner core. In many cases, the oxidized portions will be more porous than the initial X-ide. (III) Oxidation of the outer surface to some finite depth while retaining an unoxidized core.

Before doing so, we will briefly introduce another complicating factor in measuring and evaluating catalytic performance: the support. Most OER catalysts are distributed on electrically conductive, high surface area supports that facilitate electron transport to the external load and increase the effective surface area of the catalyst. Typical supports include vulcanized carbon, carbon nanotubes (CNTs), carbon paper, carbon cloth, and nickel foam. While most studies either assume or show that the support itself has little to no activity for the OER by itself, there is a precedent from more traditional gas-phase catalysis that shows that catalyst−support interactions are extremely important for catalyst performance.[36−38] As a result, disentangling the catalyst performance from its support is likely important but is in many cases very difficult. It also again raises the question of how tightly to limit the term "catalyst" while discussing metal X-ides for water oxidation.

Individual members of the community tend to draw a line between the catalyst and the support differently, depending on which of the three above categories they most frequently use. For this Perspective, we will limit the term to describe only that material directly involved in water oxidation. Given the example of a generic metal phosphide (M_xP) on nickel foam, if the phosphide is unoxidized, we will consider the phosphide itself the catalyst and the foam the support. If the phosphide is completely oxidized (MO_x), we will consider the oxide/(oxy)hydroxide the catalyst and again the foam as the support. Finally, if the phosphide is an $M_xP@MO_x$ system, we will consider the MO_x shell the active catalyst and both the unoxidized M_xP core and the Ni foam the support.

No Oxidation of Metal X-ide Catalyst. The earliest and simplest explanation of the nature of the OER catalyst for metal X-ides is that the X-ide itself is the active catalyst and, if stable, does not undergo transformation.[20,32,39−44] Frequently, researchers use elemental analysis like X-ray photoelectron spectroscopy (XPS), electron dispersive X-ray spectroscopy (EDX), and X-ray absorption fine structure spectroscopy (XAFS) to investigate the chemical stability of the catalysts before and after OER testing. Given the previously mentioned thermodynamic arguments favoring chalcogenide and pnictide oxidation, such results are surprising and should be well-supported. Often, the high activity toward the OER is ascribed to the superior kinetics of the X-ide surface for the reaction as opposed to a native metal or oxide/(oxy)hydroxide phase.[20,32,41,45,46] For instance, De Silva et al. recently reported that due to the unique crystallographic structure of Ni_3Te_2 the material possesses several unique Ni sites where −OH adhesion could occur.[20] For each site, the cohesive energies for −OH on the telluride surface were lower than the cohesive energy on nickel oxide. Thus, they propose that the material requires less energy to achieve −OH coverage, and it is by this mechanism that the catalyst surpasses the performance of nickel hydroxide. Catalyst stability was determined after both XPS and EDX analysis of the material showed a lack of oxidized species. If correct, the unexpected stability and high activity of the material (η_{10} = 180 mV/cm^2) indicate that it is an exciting new catalyst and deserves further study to determine the mechanism behind its anomalous stability and how it relates to the superior OER performance. Liu et al. show that $CoSe_2$ nanosheets show significantly lower binding energies for water molecules on Co vacancies in the material.[41] This likewise leads to superior binding of H_2O molecules, reducing the energy required to begin water splitting and indicating that metal X-ides may possess sites that are more catalytically active than metal oxides.

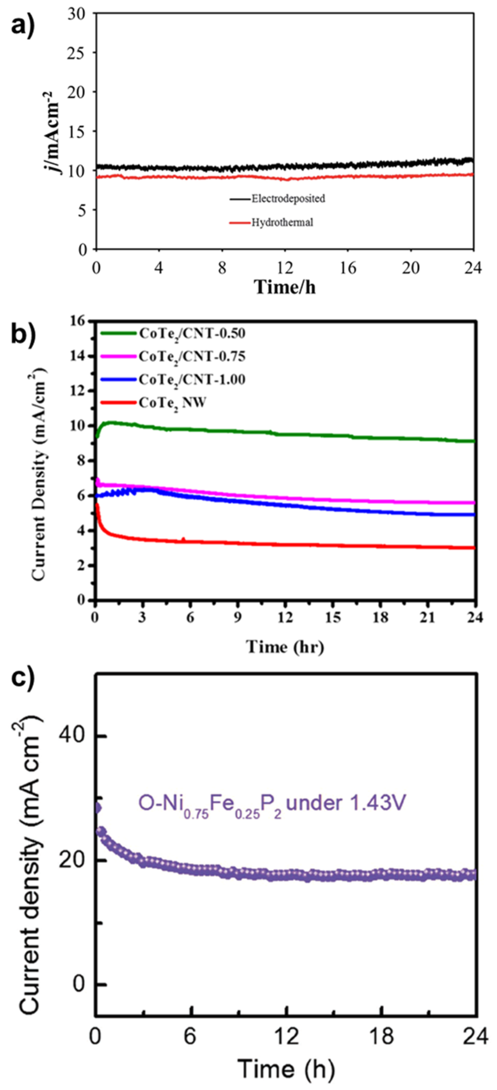

Figure 2. Chronopotentiometry plots for (a) Ni_3Te_2, (b) $CoTe_2$, and (c) NiFeP OER catalysts under overpotentials required to generate roughly 10 mA/cm^2 of current density. In each case, the relative stability of the electrochemical performance is used as a proxy for the overall stability, chemical and electrochemical, of the catalyst in question. Panel (a) shows the results from both electrodeposited (black) and hydrothermally synthesized (red) Ni_3Te_2, while panel (b) shows the results from a variety of $CoTe_2$/CNT composites. Panel (c) shows the stability of a mixed Ni−Fe phosphide with active oxygen species on the surface. (a) Adapted with permission from ref 20. Copyright 2018 Royal Society of Chemistry. (b) Reprinted with permission from ref 39. Copyright 2016 American Chemical Society. (c) Reprinted with permission from ref 32. Copyright 2018 John Wiley Sons, Inc.

In addition to showing superior kinetics, the catalysts also frequently show excellent stability under reaction conditions. Figure 2 shows the chronoamperometric results of long-term stability testing for several catalysts, clearly showing little loss of performance with time. Frequently, the electrochemical stability of the catalyst is used as evidence to show that these materials are chemically and compositionally stable over long time periods.[20,39,41] This must be done carefully, however, as electrochemical and chemical stability are not identical. A close observation of Figure 2a shows a roughly 10% increase in current density for the electrodeposited sample, which could potentially indicate dissolution and increased surface area. Conversely, Figure 2c shows a clear 8% decrease in current density, which may indicate excessive oxidation and catalyst damage. In Figure 2b, Lu et al. showed that when loaded on the surface of CNTs $CoTe_2$ showed superior stability due to the enhanced electrical conductivity of the composite system, which reduced charge buildup in the material and increased its stability.[39] This also highlights another important feature of the metal X-ides, their superior electrical conductivity. The increased metallic nature of most metal X-ides results in faster charge conduction and extraction, although in this case it is only notable when the material is supported on highly conductive CNTs. As such, it is important to consider substrate effects when studying this family of materials. Liu et al. also demonstrate the metallic nature of the X-ides with their calculations of the density of states for a series of Fe— and Co—P materials. Here, they show that the mixed Fe—Co—P alloys show a more metallic nature when compared to metal oxides.[45] Likewise, two separate NiFeN$_x$ materials both showed reduced electrical resistance in the active catalyst materials, which the authors used to help explain the improved performance of the catalysts.[40,47]

In each of the above cases, the authors use electrochemical and spectroscopic data to determine that the metal X-ide catalyst upon which they are reporting does not experience significant oxidation. Given the more positive formation energies of most non-oxide X-ides when compared to their oxide counterparts, this apparent lack of oxidation in these catalysts is surprising and very interesting. Oxide formation would be expected given the harsh oxidative conditions present during the OER, if not in the bulk, and then at least on the surface of the catalyst. Unfortunately, the surface of the catalyst during reaction must have water in a variety of transition states bound to surface catalytic sites, many of which may be very similar to a metal oxide/(oxy)hydroxide. This can blur the lines between an oxidized catalyst and a catalytic transition state on the X-ide surface.

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Some studies theorize that the catalyst forms temporary hydroxy-X-ides rather than more permanent (oxy)-hydroxides.[20] Still others show that the catalysts may undergo incomplete oxidation, i.e., the formation of small numbers of catalytic (oxy)hydroxides on the largely X-ide surface. In the previously mentioned study from Liu et al., this is the case for their Co—Fe—P catalyst, where XPS shows that the surface Fe atoms are primarily oxidized after OER tests while both the Co and P remain relatively unchanged. Similar work from He et al. showed using density functional theory (DFT) that the presence of Fe in NiP$_2$ results in lower free energy costs for the various steps in the OER when compared to a pure NiP$_2$ sample.[32] They attribute this to the presence of Fe-(oxy)-hydroxide species on the surface, which help to bind OOH to the surface and act as the active site for the OER. These studies suggest that the presence of oxygen species on the metal X-ide catalyst is favorable for improving the overall performance of the catalyst.

Complete Oxidation of the Metal X-ide Catalyst. In contrast to the studies that show that X-ides do not oxidize at all, several other works have suggested that some metal X-ides are unstable under OER conditions and transform completely to their corresponding oxide or (oxy)hydroxide upon catalysis.[11,13,18,19,28,48,49] Viewed through this lens, the metal X-ide is not itself the catalyst but is instead a "precatalyst" that can be transformed electrochemically to the active OER catalyst.[11] As previously noted, it has been well-established that (oxy)-hydroxides are highly efficient catalysts for the OER[5,6,8,14,24,25,34] and that many of the metal X-ides are more stable as oxides.[26,50] Thus, there is good reason to believe that an oxidized X-ide could be the active OER catalyst.

Early work from the Cui lab,[19,28] the Hu lab,[48] and our lab[11] showed that a variety of chalcogenide materials can be easily oxidized under OER conditions to form amorphous (oxy)-hydroxides. As shown by Chen et al., oxidation of the initial X-ide typically results in a product with a notably higher surface area than an "as-synthesized" metal oxide/(oxy)hydroxide.[19] Figure 3 shows similar results from a number of other studies. Indeed, many researchers argue that this degradation of the catalyst to form a more amorphous (oxy)hydroxide is one of

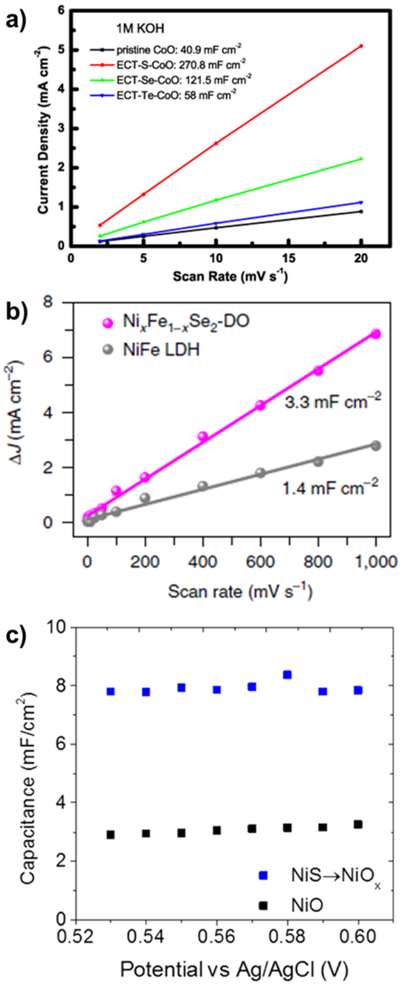

Figure 3. Current density vs CV scan rate for (a) a series of converted cobalt chalcogenides compared to a pristine oxide and (b) an oxidized NiFe selenide catalyst compared to a pristine layered double hydroxide. In each case, the oxidized X-ide catalyst shows a significantly higher slope than the pristine oxide or hydroxide, indicating a larger capacitance and thus surface area. This is in agreement with SEM images that frequently show roughening of tested X-ide catalysts. In panel (a), the legend refers to electrochemically transformed (ECT) cobalt oxides, based on different initial chalcogenides. (c) Capacitance of an oxidized NiS catalyst derived by impedance spectroscopy at a variety of potentials is always roughly twice as large as that of an as-synthesized NiO film. (a) Reprinted with permission from ref 19. Copyright 2016 American Chemical Society. (b) Reprinted with permission from ref 48. Copyright 2016 Nature Research. (c) Reprinted with permission from ref 11. Copyright 2016 American Chemical Society.

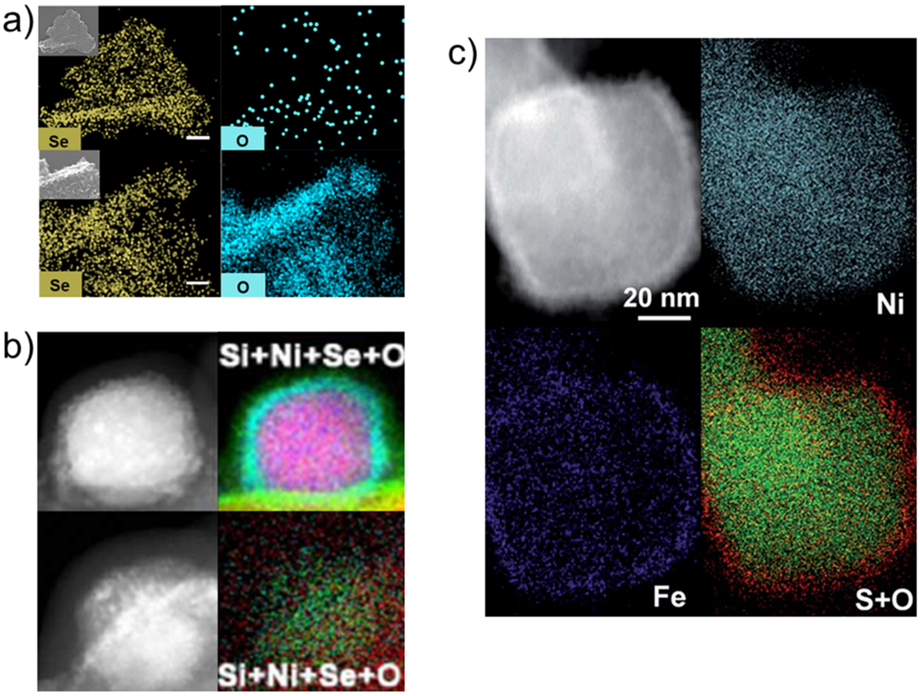

Figure 4. TEM/EDX mapping for (a) $NiCo_2Se_4$ nanosheets, (b) $NiSe_2$ nanoparticles, and (c) $(NiFe)S_2$ nanoparticles showing clear X-ide@oxide structure. Panel (a) shows the difference in the O content of a $NiCo_2Se_4$ particle before (top) and after (bottom) 100 CV cycles, indicating that the increase of O on the particle surface is due to OER-induced surface oxidation. The insets in the corners show SEM images of the particles; scale bar = 200 nm. Likewise, panel (b) shows a $NiSe_2$ catalyst supported on a Si nanowire at 4 (top) and 6 h (bottom) of chronoamperometric testing. The O (green) in the top image shows a clear shell around the Se-rich core (red), while Ni (blue) is present throughout. The bottom image shows that this Se-rich (orange) core is eventually completely degraded and oxidized (blue) where Ni (green) is present. Panel (c) shows the oxidation of a pristine $(NiFe)S_2$ nanoparticle after 100 CV cycles, with a S-rich (green) core surrounded by an O-rich (red) shell. Interestingly, while Ni (blue) is present throughout, Fe (purple) appears to segregate to the surface. (a) Adapted with permission from ref 46. Copyright 2017 American Chemical Society. (b) Adapted with permission from ref 18. Copyright 2016 American Chemical Society. (c) Adapted with permission from ref 35. Copyright 2017 Royal Society of Chemistry.

the leading causes for the superior performance of metal X-ide water oxidation catalysts. As the X-ide is oxidized, it undergoes significant leaching of the nonmetal component (S, P, etc.), which results in structural reorganization and increased surface area from the newly porous structures that form.[11,19,28,48] The increased surface area of the final catalyst results in an increased number of active sites for the OER and thus better catalytic performance. This is supported by studies that show that the Tafel slope of the oxidized X-ide product is almost identical to an as-synthesized oxide, indicating that the active catalytic species is the same for both.[19,28] The native oxides and (oxy)hydroxides, even those that are synthesized to be high surface area, frequently cannot match the level of surface roughness and therefore do not perform as well when measured using the projected geometric surface area as a comparison.

The increased surface area of the catalyst following oxidation has been observed in most cases of total oxidation reported in the literature. Chen et al. showed that when comparing cobalt chalcogenides that had been completely electrochemically oxidized the electrochemically active surface area (ECSA) of the materials, determined using capacitance as a proxy, followed the order S > Se > Te.[19] Because all of the metal chalcogenide catalysts were created using thermal transformation of an identical electrodeposited oxide film to the final chalcogenide film for testing, the researchers ensured that differences between catalysts were due to surface area and not catalyst quantity. This result, in addition to scanning electron microscope (SEM) images of the materials before and after oxidation, shows that the sulfide-derived oxides undergo a greater degree of physical rearrangement upon oxidation; the resulting increase in surface area significantly improves the performance of the final oxide. The result is interesting because it means that materials that undergo a large degree of physical degradation when oxidizing should result in better catalysts, but this is directly refuted by the data. One would expect that $CoTe_2$, containing a Te^{2-} anion much larger than that of either O^{2-} or OH^- (0.221,[51] 0.14,[51] and 0.11 nm[52]), would be much more likely to undergo significant structural changes and roughening upon oxidation. Instead, it appears that it exhibits very little change, while the sulfide (ionic radius = 0.184 nm[51]) shows a much more pronounced change in morphology. A closer study of the exact oxidation mechanism for the various X-ides (chalcogenide, pnictide, and others) must be made to understand how the chemistry of the precatalyst plays into the performance of the active catalyst.

Partial Oxidation of the Surface of the Metal X-ide Catalyst. The final class of metal X-ide water oxidation electrocatalysts that we will examine could easily be considered a composite of the first two and is composed of X-ide materials that exhibit only partial oxidation on their surface without oxidation of the bulk. By far, this has become the most widely used categorization of X-ide OER electrocatalysts in the past few years as more researchers begin to explore the effect of OER on the catalysts after testing.[10,17,18,32,35,45−47,53−62] Materials in this class are frequently labeled as "core@shell" particles, and

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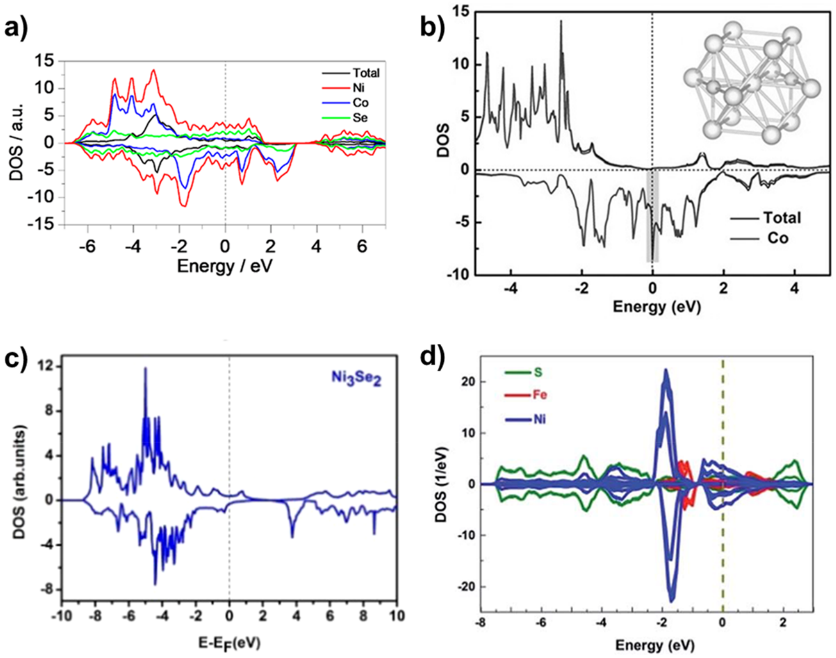

Figure 5. Density-of-states (DOS) plots calculated for (a) $NiCo_2Se_4$, (b) Co_4N, (c) Ni_3Se_2, and (d) $Ni(Fe)S_2$ electrocatalysts for the OER. In each case, there are nearly continuous states without evidence of a band gap, indicating a metallic nature rather than a semiconducting nature for these catalysts. Being metallic, these catalysts are expected to possess greater conductivity, which has been suggested as a possible reason for their superior catalytic performance. (a) Reprinted with permission from ref 46. Copyright 2017 American Chemical Society. (b) Reprinted with permission from ref 57. Copyright 2015 John Wiley Sons, Inc. (c) Reprinted with permission from ref 62. Copyright 2017 American Chemical Society. (d) Reprinted with permission from ref 35. Copyright 2017 Royal Society of Chemistry.

they include both chalcogenides and pnictides, suggesting that there is some commonly conserved oxidation mechanism between Groups 15 and 16. These materials typically exhibit excellent performance and electrochemical stability, which are frequently ascribed to increased surface area due to the formation of amorphous (oxy)hydroxides,[10,46,54−57,59] the beneficial effect of increased electronic conductivity through the metallic metal X-ide core,[10,17,18,35,45,47,55−57,62] and other cooperative interactions between the elements that make up the catalyst compounds.[32,45,46,59,62] Because many of these features are related to each other, it is extremely difficult to determine if any single one is primarily responsible for the performance of core@shell metal X-ide catalysts. Thus, while we will attempt to distinguish them individually here, we cannot definitively state which factor is most important for efficient OER catalysis.

As noted before, the oxidation of a metal X-ide is expected to result in significant structural reorganization and roughening as the generally larger X-ide anions are replaced with smaller oxide and hydroxide anions.[51] Indeed, the core@shell materials often show ECSAs that are notably larger than the oxide or (oxy)hydroxide as-synthesized counterparts.[10,46,57] As suggested by Cui and co-workers, the oxidized surfaces of the metal X-ide catalyst are doubly beneficial in that oxidation creates the metal (oxy)hydroxides that act as the active catalysts while simultaneously increasing their apparent loading by increasing the surface area exposed to solution.[19] Yu and co-workers showed a much higher ECSA for their NiCoSe holey nanosheets, which correlated well with increased OER performance.[46] This is also combined with clear oxidation of the surface of the particles after testing, as shown by EDX mapping, which taken together suggests the formation of a high surface area (oxy)hydroxide coating that serves as the active catalyst. Furthermore, their research suggests that this coating acts similarly to the oxide coating that forms on Al metal and actively prevents further oxidation of the underlying material, preserving the inherent conductivity of the nanosheet. Figure 4 shows the clear core@shell structure of this catalyst in panel (a), as well as several other examples of this structure. Zhou et al. also noticed similar oxidation when studying a $NiFeS_2$ OER catalyst.[35] After testing the material for 12 h under OER conditions, the researchers found that the catalyst had developed a shell of NiFeOOH around the sulfide. This shell served both as the active catalyst and as an impermeable barrier to prevent further oxidation of the sulfide core. On the basis of earlier research,[63] the authors speculated that the presence of Fe in the oxide caused it to form the crystalline NiFeOOH phase, which proved to be a durable catalyst. This material therefore appears to benefit from all three of the features previously listed.

As briefly mentioned in our earlier discussion of the unoxidized metal X-ides, the metallic core of these particles can be viewed as an extension of the conductive substrate upon which the catalyst is loaded. Several groups have investigated the band structure of metal X-ide catalysts, as can be seen in Figure 5, and show that the band structure is significantly more continuous and therefore the materials are more metallic.[35,45,46,57,58,62] The increased metallic nature therefore results in better electrical conductivity within the X-ide catalyst materials and helps electrons move from the site of catalysis on the surface to the external circuit. This path of conduction is important because, as previous research has shown in the case of FeOOH films, even extremely thin (oxy)hydroxide films (<10 nm) can exhibit significant overpotential due to their poor conductivity.[64] Some researchers use electronic software to automatically compensate for the *iR* drop from both the catalyst and the solution,[46,53] but others do not.[35,60] By accounting for this resistance, researchers can level the playing field for all catalysts and provide a more uniform analysis of the "real" catalyst without support effects. Conversely, testing without *iR* compensation allows for engineering of the catalyst system, both catalyst and support, to be studied. Care must be taken, however, to prevent inaccurate resistances from being used during correction. Impedance spectroscopy can be used to measure the series resistance of some catalysts, but in the case of porous catalysts, contributions from the underlying substrate may be very significant and skew the results. Likewise, direct measurements based on Ohm's law can be rendered inaccurate if the conductivity of the catalyst changes under OER conditions. If these considerations are taken into account, it would be beneficial to provide both *iR*-corrected and uncorrected data for new catalysts and allow any improvements in intrinsic catalytic ability to thus be differentiated from catalyst engineering. In this way, new systems can be evaluated on both a fundamental and practical level.

Several groups have observed interplay between the various metallic components of mixed metal X-ide catalysts, which results in improved stability or performance.[17,32,40,45] While not unique to metal X-ide catalysts, as traditional metal oxide OER catalysts with dopants have long been studied for their effects on improving water splitting,[64−68] the additional interplay of the dopant with the X-ide anion appears to be important. Notably, Liu et al. used XPS to show selective oxidation of Fe atoms at the surface of their Co/Fe phosphide during OER.[40] When they examined a Co−Fe−P alloy, the researchers found that the Fe $2p_{3/2}$ peak showed significant growth near 711.1 eV that indicates the formation of FeOOH on the surface, while the Co $2p_{3/2}$ shows no such shift. While the intensity of the Co peak at 778 eV does seem to decrease after OER, there is significantly less oxidation than is shown in the Fe spectra. Additionally, they see little to no change in the line shape of the X-ray absorption near-edge structure (XANES) spectra, indicating that the bulk of the material remains a phosphide. This is in sharp contrast to either of the pure Co−P and Fe−P catalysts, which showed conversion to the (oxy)hydroxide during OER testing. Their results suggest that selective oxidation of the X-ide materials, in this case, the Fe−P bond, can result in improved stability of the catalyst and prolonged lifetimes for water splitting.

In contrast, Wang et al. showed in another Co−Fe−P OER catalyst that significant oxidation occurred during testing, including oxidation of the Co and P species on the surface.[17] XPS from this study very clearly shows that the Fe is in the form of a phosphate both before and after testing, while the Co transforms from a phosphide phase to a phosphate/hydroxide phase upon testing. Likewise, the P 2p spectrum shows complete loss of the phosphide and formation of a phosphate layer on the surface of the catalyst. The authors show that the presence of Fe in the material does improve catalytic performance but does not stabilize the Co−P material as was reported by Liu et al.[40] One significant deviation between the two works is the relative Co/Fe ratio of the two phosphides; Liu et al. used a 1:1.5 ratio, while Wang et al. used a 3:1 ratio that was much more cobalt rich, suggesting that the elemental composition has a significant effect on chemical stability and that there may be a critical concentration of iron required to protect the Co−P material in the catalyst. The interplay of Fe, Co, and Ni in metal X-ides promises to be an area of interesting chemistry in the coming years.

He and co-workers also showed that the presence of Fe(oxy)hydroxide moieties on the surface of a NiFeP catalyst improved OER performance without preserving the stability of the X-ide core.[32] Using DFT, the group showed that the binding of O species to the Fe−Fe sites on the surface reduces the activation energy of the rate-determining oxygen desorption step in the OER while limiting side reactions that would make the process less efficient. This takes place specifically on the mixed X-ide oxide-phosphide phase, however, and their post-OER EDX and XPS measurements show that a significant portion of the initial phosphorus on the surface has been oxidized away during reaction. It is also observed that the catalyst develops a significant degree of amorphous nature following testing, as can be seen in the X-ray diffraction (XRD) and transmission electron microscope (TEM) results. This suggests that here the core is accessible for further oxidation, in contrast with the previous cases, where the oxide coating protected the underlying material.

This can be seen more clearly in another example from the Park lab in their study on Co and Ni diselenides as OER catalysts.[18] The authors show initially that the $NiSe_2$ core is stable via XRD after OER testing and that the surface is likely an (oxy)hydroxide via XPS. This is confirmed by TEM/EDX mapping, which shows a significant concentration of O on the surface of the particles after 4 h of OER testing, when supported on Si nanowires as a photocatalytic co-catalyst. As a result, they propose that the catalyst forms a core@shell structure that provides a conductive selenide core for electrical conductivity and an (oxy)hydroxide shell for efficient OER. However, when the catalyst is run for 6 h, EDX mapping shows a complete transformation to the oxide and complete loss of the selenium. This is further confirmed by XPS, which shows a significant increase in binding energy for the Ni 2p region, which is in agreement with oxidation of the catalyst. In the case of this material, it seems that assignment of the catalyst to the fully oxidized or core@shell categories is a matter of experiment time rather than intrinsic chemical stability. We believe that this may be likewise true of many of the materials that are studied today.

Future Directions. The discrepancies in the studies described above, and summarized in Table S1, highlight the need for a more standardized testing regime for metal X-ide OER catalysts. Surveying the literature, a general consensus leans toward the presence of a metal (oxy)hydroxide on the surfaces of the OER catalysts serving as the active catalyst and that most metal X-ides can be best thought of as precatalysts that are oxidized to yield this layer. The extent of oxidation then becomes important as we work to determine the role, if any, of the unoxidized core of the core@shell catalysts. In the case of Jang et al., two additional hours of OER testing were enough to convert a $NiSe_2$-derived core@shell catalyst into a completely oxidized NiO_x catalyst.[18] If the selenide core that provides improved electrical contact with the current collector is completely oxidized, should we still refer to the catalyst as a core@shell particle, or should we refer to it as an oxide catalyst derived from an X-ide precatalyst? More importantly, how long should we as researchers expose these catalysts to OER conditions in order to make this determination? One of the major challenges facing the field today is a lack of consistency in reporting the full physical characteristics of catalysts before *and* after testing.

Here we propose a preliminary set of guidelines for how metal X-ide materials should be benchmarked and charac-

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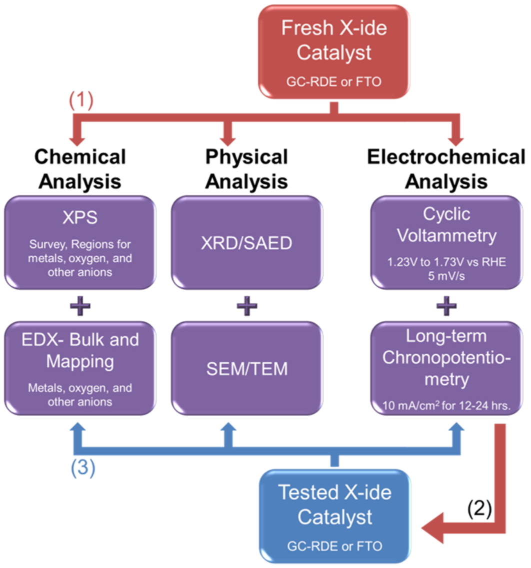

Figure 6. Chart outlining the suggested workflow for accurately analyzing metal X-ides for use as OER catalysts. Following the chemical, physical, and electrochemical analysis of the pristine catalyst (1), the catalyst after long-term stability testing (2) should undergo the same testing (3). Comparisons of chemical makeup, structure, and performance can then be more accurately made.

terized, based in part on the thorough work of the Jaramillo group on similar oxide systems.[69] We have highlighted the proposed workflow in Figure 6. Briefly, to eliminate variations in substrate effects where possible, a glassy carbon rotating disk electrode (GC-RDE) should be used for all powder catalyst studies, while an inert substrate like fluorine-doped tin oxide (FTO) or a GC-RDE should be used for all electrodeposition studies. Following synthesis, full physical characterization of the material (XRD, XPS, SEM, TEM, EDX) should be performed to determine the initial state of the catalyst. Then, the catalyst should be tested for OER performance using both *iR*-corrected CV and chronopotentiometric studies for performance and stability, respectively. The chronopotentiometric testing should proceed for at least 12−24 h in order to detect whether any electrochemical transformation of the active material has occurred. This should be followed by CV to check the overall OER performance. Ideally, results should be reported as the current density based on the true geometric surface area of the catalyst ($mA/cm^2_{catalyst}$), as well as the mass activity of the catalyst ($mA/g_{catalyst}$) where applicable. Finally, the sample used for chronopotentiometric stability should be reanalyzed using physical characterization methods. Accurate measurements of the surface (XPS, TEM+EDX mapping) and bulk (XANES, EDX) elemental composition of the catalysts both before and after electrochemical testing should be provided to show the extent and location of oxidation and should be performed on all samples. To show the presence of a core@shell morphology, TEM+EDX mapping, XPS with Ar sputtering, and/or a technique such as XANES are essential. Finally, mass spectrometry techniques like ToF-SIMS or ICP-MS should be used to determine the presence of residual X in the material that could influence electrocatalytic performance. These experiments would constitute the minimum amount of characterization required to properly analyze the X-ides, and the widespread adoption of such a testing regimen would be inherently beneficial to researchers in the field seeking to compare their results to other groups.

In addition to more consistent characterization, additional attention should be paid to the choice of support for these catalysts and the effect that the support has on apparent catalyst performance. For instance, most studies report their results as a current density based on the projected surface area of a planar substrate. This is valid when the projected and geometric surface areas of the substrate are equal, as is the case for GC-RDEs, but it is less accurate for porous electrodes where the projected surface area is less than the geometric surface area. Porous electrodes like nickel foam are useful for showing the optimized performance of a catalyst, but these results should always be reported alongside the performance on a planar substrate so that accurate comparisons to other catalysts in the literature can be made.

Of related importance, such considerations cannot always account for all variations, and special attention should be paid to finding an accurate, widespread way to measure the "intrinsic" catalytic ability of an OER catalyst, divorced from surface area. Tafel slope analysis and use of the ECSA as a normalization factor are currently used, but both techniques suffer limitations. Most notably, in the case of ECSA, it has been shown that metal (oxy)hydroxides are frequently poor electronic conductors under the low potential conditions used to measure ECSA.[64,70] Because these nonconductive materials are very porous, however, they can allow electrolyte to penetrate to the underlying substrate, and thus, the ECSA measurements may instead measure the surface area of the conductive substrate alone. If this ECSA is used as a normalization factor, the catalyst will then appear to have a much higher performance than it possesses in reality due to the misrepresentation of the surface area. Instead of ECSA, one viable alternative for catalyst normalization is to report electrochemical performance on the basis of mass activity (A/g). While it may be potentially difficult to measure the mass of electrodeposited thin films, such a standard would be ideal for particle-based electrocatalysts and provide a fair comparison between different metal X-ides. Additional research should be directed to finding ways to more accurately determine electrochemical turnover frequencies (TOFs) for OER catalysts, which would help provide a fairer comparison between catalysts and highlight those most active for further study.

Finally, looking ahead, the effect of mixed X-ide systems, such as phosphide-nitrides or seleno-tellurides, for the OER will likely be an interesting area to direct further research. Given that previous research has shown that differences in anion choice can dramatically influence the stability of the active catalyst,[19,62] great opportunities exist to engineer catalysts with higher surface areas,[19] improved conductivity,[62] or selective catalytic active sites.[20] Careful investigation of these materials should then be undertaken to determine which, if any, of these benefits exist.

To conclude, metal X-ides are a large family of materials that show great promise as catalysts and/or precatalysts for the OER. While the initial reports and current article titles seem to indicate that the active catalysts are X-ides, more recent research suggests that these materials are partially or fully oxidized to yield metal (oxy)hydroxides that serve as the active OER catalyst. Oxidation of the parent material frequently results in increased exposed surface area for catalysis, while the presence of remaining underlying metal X-ide may result in improved electrical conductivity between the catalyst and the current collector. The result is that these materials are among the best-performing OER catalysts to date and show high potential for eventual application. However, a more complete and nuanced understanding of these catalysts will be essential to the field as we move forward. Determining how surface area, conductivity, and elemental composition affect performance and stability will help guide future material design and produce more efficient, stable, and economic catalysts in the future.

> Determining how surface area, conductivity, and elemental composition affect performance and stability will help guide future material design and produce more efficient, stable, and economic catalysts in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b01774.

> Table providing information about catalysts discussed in the text, including oxidation type, catalyst form, overpotential, stability, loading, analytical techniques, electrolyte pH, and testing potential, and Pourbaix diagrams and Gibbs free energy overlays for a series of nickel-based X-ide samples (PDF)

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■ REFERENCES

(1) Zou, X.; Zhang, Y. Noble Metal-Free Hydrogen Evolution Catalysts for Water Splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148−5180.

(2) Yao, T.; An, X.; Han, H.; Chen, J. Q.; Li, C. Photoelectrocatalytic Materials for Solar Water Splitting. *Adv. Energy Mater.* **2018**, *8*, 1800210.

(3) Moniz, S. J. A.; Shevlin, S. A.; Martin, D. J.; Guo, Z. X.; Tang, J. Visible-Light Driven Heterojunction Photocatalysts for Water Splitting-a Critical Review. *Energy Environ. Sci.* **2015**, *8*, 731−759.

(4) Shi, Y.; Zhang, B. Recent Advances in Transition Metal Phosphide Nanomaterials: Synthesis and Applications in Hydrogen Evolution Reaction. *Chem. Soc. Rev.* **2016**, *45*, 1529−1541.

(5) Gorlin, Y.; Jaramillo, T. F. A Bifunctional Nonprecious Metal Catalyst for Oxygen Reduction and Water Oxidation. *J. Am. Chem. Soc.* **2010**, *132*, 13612−13614.

(6) Wang, H.; Lee, H.-W.; Deng, Y.; Lu, Z.; Hsu, P.-C.; Liu, Y.; Lin, D.; Cui, Y. Bifunctional Non-Noble Metal Oxide Nanoparticle Electrocatalysts through Lithium-Induced Conversion for Overall Water Splitting. *Nat. Commun.* **2015**, *6*, 7261.

(7) Suntivich, J.; May, K. J.; Gasteiger, H. a.; Goodenough, J. B.; Shao-Horn, Y. A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles. *Science* **2011**, *334*, 1383−1385.

(8) Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J. Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. An Advanced Ni-Fe Layered Double Hydroxide Electrocatalyst for Water Oxidation. *J. Am. Chem. Soc.* **2013**, *135*, 8452−8455.

(9) Wygant, B. R.; Jarvis, K. A.; Chemelewski, W. D.; Mabayoje, O.; Celio, H.; Mullins, C. B. Structural and Catalytic Effects of Iron- and Scandium-Doping on a Strontium Cobalt Oxide Electrocatalyst for Water Oxidation. *ACS Catal.* **2016**, *6*, 1122−1133.

(10) Yu, F.; Zhou, H.; Zhu, Z.; Sun, J.; He, R.; Bao, J.; Chen, S.; Ren, Z. Three-Dimensional Nanoporous Iron Nitride Film as an Efficient Electrocatalyst for Water Oxidation. *ACS Catal.* **2017**, *7*, 2052−2057.

(11) Mabayoje, O.; Shoola, A.; Wygant, B. R.; Mullins, C. B. The Role of Anions in Metal Chalcogenide Oxygen Evolution Catalysis: Electrodeposited Thin Films of Nickel Sulfide as “Pre-Catalysts. *ACS Energy Lett.* **2016**, *1*, 195−201.

(12) Wang, Q.; Dastafkan, K.; Zhao, C. Design Strategies for Non-Precious Metal Oxide Electrocatalysts for Oxygen Evolution Reactions. *Curr. Opin. Electrochem.* **2018**, *10*, 16−23.

(13) Xu, J.; Li, J.; Xiong, D.; Zhang, B.; Liu, Y.; Wu, K.-H.; Amorim, I.; Li, W.; Liu, L. Trends in Activity for the Oxygen Evolution Reaction on Transition Metal (M = Fe, Co, Ni) Phosphide Pre-Catalysts. *Chem. Sci.* **2018**, *9*, 3470−3476.

(14) Smith, R. D. L.; Prévot, M. S.; Fagan, R. D.; Trudel, S.; Berlinguette, C. P. Water Oxidation Catalysis: Electrocatalytic Response to Metal Stoichiometry in Amorphous Metal Oxide Films Containing Iron, Cobalt, and Nickel. *J. Am. Chem. Soc.* **2013**, *135*, 11580−11586.

(15) Cherevko, S.; Geiger, S.; Kasian, O.; Kulyk, N.; Grote, J. P.; Savan, A.; Shrestha, B. R.; Merzlikin, S.; Breitbach, B.; Ludwig, A.; et al. Oxygen and Hydrogen Evolution Reactions on Ru, RuO_2, Ir, and

IrO_2 Thin Film Electrodes in Acidic and Alkaline Electrolytes: A Comparative Study on Activity and Stability. *Catal. Today* **2016**, *262*, 170−180.

(16) Kim, J.-H.; Kawashima, K.; Wygant, B. R.; Mabayoje, O.; Liu, Y.; Wang, J. H.; Mullins, C. B. Transformation of a Cobalt Carbide (Co_3C) Oxygen Evolution Precatalyst. *ACS Appl. Energy Mater.* **2018**, *1*, 5145−5150.

(17) Wang, T.; Wang, C.; Jin, Y.; Sviripa, A.; Liang, J.; Han, J.; Huang, Y.; Li, Q.; Wu, G. Amorphous Co-Fe-P Nanospheres for Efficient Water Oxidation. *J. Mater. Chem. A* **2017**, *5*, 25378−25384.

(18) Kwak, I. H.; Im, H. S.; Jang, D. M.; Kim, Y. W.; Park, K.; Lim, Y. R.; Cha, E. H.; Park, J. $CoSe_2$ and $NiSe_2$ Nanocrystals as Superior Bifunctional Catalysts for Electrochemical and Photoelectrochemical Water Splitting. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5327−5334.

(19) Chen, W.; Liu, Y.; Li, Y.; Sun, J.; Qiu, Y.; Liu, C.; Zhou, G.; Cui, Y. In Situ Electrochemically Derived Nanoporous Oxides from Transition Metal Dichalcogenides for Active Oxygen Evolution Catalysts. *Nano Lett.* **2016**, *16*, 7588−7596.

(20) De Silva, U.; Masud, J.; Zhang, N.; Hong, Y.; Liyanage, W. P. R.; Asle Zaeem, M.; Nath, M. Nickel Telluride as a Bifunctional Electrocatalyst for Efficient Water Splitting in Alkaline Medium. *J. Mater. Chem. A* **2018**, *6*, 7608−7622.

(21) Zhang, B.; Zheng, X.; Voznyy, O.; Comin, R.; Bajdich, M.; Garcia-Melchor, M.; Han, L.; Xu, J.; Liu, M.; Zheng, L.; et al. Homogeneously Dispersed Multimetal Oxygen-Evolving Catalysts. *Science* **2016**, *352*, 333−337.

(22) Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan, Y. Efficient Water Oxidation Using Nanostructured α-Nickel-Hydroxide as an Electrocatalyst. *J. Am. Chem. Soc.* **2014**, *136*, 7077−7084.

(23) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S.-Y.; Suib, S. L. Structure−Property Relationship of Bifunctional MnO_2 Nanostructures: Highly Efficient, Ultra-Stable Electrochemical Water Oxidation and Oxygen Reduction Reaction Catalysts Identified in Alkaline Media. *J. Am. Chem. Soc.* **2014**, *136*, 11452−11464.

(24) Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W. Solution-Cast Metal Oxide Thin Film Electrocatalysts for Oxygen Evolution. *J. Am. Chem. Soc.* **2012**, *134*, 17253−17261.

(25) Zhao, B.; Ke, X. K.; Bao, J. H.; Wang, C. L.; Dong, L.; Chen, Y. W.; Chen, H. L. Synthesis of Flower-like NiO and Effects of Morphology on Its Catalytic Properties. *J. Phys. Chem. C* **2009**, *113*, 14440−14447.

(26) Rasmussen, F. A.; Thygesen, K. S. Computational 2D Materials Database: Electronic Structure of Transition-Metal Dichalcogenides and Oxides. *J. Phys. Chem. C* **2015**, *119*, 13169−13183.

(27) Stevanović, V.; Lany, S.; Zhang, X.; Zunger, A. Correcting Density Functional Theory for Accurate Predictions of Compound Enthalpies of Formation: Fitted Elemental-Phase Reference Energies. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 1−12.

(28) Chen, W.; Wang, H.; Li, Y.; Liu, Y.; Sun, J.; Lee, S.; Lee, J. S.; Cui, Y. In Situ Electrochemical Oxidation Tuning of Transition Metal Disulfides to Oxides for Enhanced Water Oxidation. *ACS Cent. Sci.* **2015**, *1*, 244−251.

(29) Persson, K. A.; Waldwick, B.; Lazic, P.; Ceder, G. Prediction of Solid-Aqueous Equilibria: Scheme to Combine First-Principles Calculations of Solids with Experimental Aqueous States. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 1−12.

(30) Singh, A. K.; Zhou, L.; Shinde, A.; Suram, S. K.; Montoya, J. H.; Winston, D.; Gregoire, J. M.; Persson, K. A. Electrochemical Stability of Metastable Materials. *Chem. Mater.* **2017**, *29*, 10159−10167.

(31) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; et al. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1*, 011002.

(32) Liu, K.; Wang, F.; He, P.; Shifa, T. A.; Wang, Z.; Cheng, Z.; Zhan, X.; He, J. The Role of Active Oxide Species for Electrochemical Water Oxidation on the Surface of 3d-Metal Phosphides. *Adv. Energy Mater.* **2018**, *8*, 1703290.

(33) Jin, S. Are Metal Chalcogenides, Nitrides, and Phosphides Oxygen Evolution Catalysts or Bifunctional Catalysts? *ACS Energy Lett.* **2017**, *2*, 1937−1938.

(34) Suen, N.-T.; Hung, S.-F.; Quan, Q.; Zhang, N.; Xu, Y.-J.; Chen, H. M. Electrocatalysis for the Oxygen Evolution Reaction: Recent Development and Future Perspectives. *Chem. Soc. Rev.* **2017**, *46*, 337−365.

(35) Zhou, M.; Weng, Q.; Zhang, X.; Wang, X.; Xue, Y.; Zeng, X.; Bando, Y.; Golberg, D. In Situ Electrochemical Formation of Core−shell Nickel−iron Disulfide and Oxyhydroxide Heterostructured Catalysts for a Stable Oxygen Evolution Reaction and the Associated Mechanisms. *J. Mater. Chem. A* **2017**, *5*, 4335−4342.

(36) Campbell, C. T. Catalyst-Support Interactions: Electronic Perturbations. *Nat. Chem.* **2012**, *4*, 597−598.

(37) Kumar, A.; Ramani, V. Strong Metal-Support Interactions Enhance the Activity and Durability of Platinum Supported on Tantalum-Modified Titanium Dioxide Electrocatalysts. *ACS Catal.* **2014**, *4*, 1516−1525.

(38) Bruix, A.; Rodriguez, J. A.; Ramírez, P. J.; Senanayake, S. D.; Evans, J.; Park, J. B.; Stacchiola, D.; Liu, P.; Hrbek, J.; Illas, F. A New Type of Strong Metal-Support Interaction and the Production of H_2 through the Transformation of Water on Pt/CeO_2(111) and Pt/CeO_x/TiO_2(110) Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 8968−8974.

(39) Lu, T.-H.; Chen, C.-J.; Lu, Y.-R.; Dong, C.-L.; Liu, R.-S. Synergistic-Effect-Controlled $CoTe_2$ /Carbon Nanotube Hybrid Material for Efficient Water Oxidation. *J. Phys. Chem. C* **2016**, *120*, 28093−28099.

(40) Wang, Y.; Xie, C.; Liu, D.; Huang, X.; Huo, J.; Wang, S. Nanoparticle-Stacked Porous Nickel-Iron Nitride Nanosheet: A Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting. *ACS Appl. Mater. Interfaces* **2016**, *8*, 18652−18657.

(41) Liu, Y.; Cheng, H.; Lyu, M.; Fan, S.; Liu, Q.; Zhang, W.; Zhi, Y.; Wang, C.; Xiao, C.; Wei, S.; et al. Low Overpotential in Vacancy-Rich Ultrathin $CoSe_2$ nanosheets for Water Oxidation. *J. Am. Chem. Soc.* **2014**, *136*, 15670−15675.

(42) Zhang, B.; Xiao, C.; Xie, S.; Liang, J.; Chen, X.; Tang, Y. Iron-Nickel Nitride Nanostructures in Situ Grown on Surface-Redox-Etching Nickel Foam: Efficient and Ultrasustainable Electrocatalysts for Overall Water Splitting. *Chem. Mater.* **2016**, *28*, 6934−6941.

(43) Chen, Q.; Wang, R.; Yu, M.; Zeng, Y.; Lu, F.; Kuang, X.; Lu, X. Bifunctional Iron−Nickel Nitride Nanoparticles as Flexible and Robust Electrode for Overall Water Splitting. *Electrochim. Acta* **2017**, *247*, 666−673.

(44) Swesi, A. T.; Masud, J.; Nath, M. Nickel Selenide as a High-Efficiency Catalyst for Oxygen Evolution Reaction. *Energy Environ. Sci.* **2016**, *9*, 1771−1782.

(45) Liu, K.; Zhang, C.; Sun, Y.; Zhang, G.; Shen, X.; Zou, F.; Zhang, H.; Wu, Z.; Wegener, E. C.; Taubert, C. J.; et al. High-Performance Transition Metal Phosphide Alloy Catalyst for Oxygen Evolution Reaction. *ACS Nano* **2018**, *12*, 158−167.

(46) Fang, Z.; Peng, L.; Lv, H.; Zhu, Y.; Yan, C.; Wang, S.; Kalyani, P.; Wu, X.; Yu, G. Metallic Transition Metal Selenide Holey Nanosheets for Efficient Oxygen Evolution Electrocatalysis. *ACS Nano* **2017**, *11*, 9550−9557.

(47) Fu, G.; Cui, Z.; Chen, Y.; Xu, L.; Tang, Y.; Goodenough, J. B. Hierarchically Mesoporous Nickel-Iron Nitride as a Cost-Efficient and Highly Durable Electrocatalyst for Zn-Air Battery. *Nano Energy* **2017**, *39*, 77−85.

(48) Xu, X.; Song, F.; Hu, X. A Nickel Iron Diselenide-Derived Efficient Oxygen-Evolution Catalyst. *Nat. Commun.* **2016**, *7*, 12324.

(49) Yu, J.; Cheng, G.; Luo, W. Ternary Nickel-Iron Sulfide Microflowers as a Robust Electrocatalyst for Bifunctional Water Splitting. *J. Mater. Chem. A* **2017**, *5*, 15838−15844.

(50) Schlesinger, M. E. The Thermodynamic Properties of Phosphorus and Solid Binary Phosphides. *Chem. Rev.* **2002**, *102*, 4267−4302.

(51) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta*

Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **1976**, *32*, 751−767.

(52) Marcus, Y. Volumes of Aqueous Hydrogen and Hydroxide Ions at 0 to 200 °C. *J. Chem. Phys.* **2012**, *137*, 154501.

(53) Li, D.; Baydoun, H.; Kulikowski, B.; Brock, S. L. Boosting the Catalytic Performance of Iron Phosphide Nanorods for the Oxygen Evolution Reaction by Incorporation of Manganese. *Chem. Mater.* **2017**, *29*, 3048−3054.

(54) Ren, J. T.; Yuan, Z. Y. Hierarchical Nickel Sulfide Nanosheets Directly Grown on Ni Foam: A Stable and Efficient Electrocatalyst for Water Reduction and Oxidation in Alkaline Medium. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7203−7210.

(55) Yan, F.; Wang, Y.; Li, K.; Zhu, C.; Gao, P.; Li, C.; Zhang, X.; Chen, Y. Highly Stable Three-Dimensional Porous Nickel-Iron Nitride Nanosheets for Full Water Splitting at High Current Densities. *Chem. - Eur. J.* **2017**, *23*, 10187−10194.

(56) Bai, X.; Ren, Z.; Du, S.; Meng, H.; Wu, J.; Xue, Y.; Zhao, X.; Fu, H. In-Situ Structure Reconstitution of $NiCo_2P_x$ for Enhanced Electrochemical Water Oxidation. *Sci. Bull.* **2017**, *62*, 1510−1518.

(57) Chen, P.; Xu, K.; Fang, Z.; Tong, Y.; Wu, J.; Lu, X.; Peng, X.; Ding, H.; Wu, C.; Xie, Y. Metallic Co_4N Porous Nanowire Arrays Activated by Surface Oxidation as Electrocatalysts for the Oxygen Evolution Reaction. *Angew. Chem.* **2015**, *127*, 14923−14927.

(58) Xu, K.; Chen, P.; Li, X.; Tong, Y.; Ding, H.; Wu, X.; Chu, W.; Peng, Z.; Wu, C.; Xie, Y. Metallic Nickel Nitride Nanosheets Realizing Enhanced Electrochemical Water Oxidation. *J. Am. Chem. Soc.* **2015**, *137*, 4119−4125.

(59) Yu, J.; Li, Q.; Xu, C.-Y.; Chen, N.; Li, Y.; Liu, H.; Zhen, L.; Dravid, V. P.; Wu, J. NiSe $_2$ Pyramids Deposited on N-Doped Graphene Encapsulated Ni Foam for High-Performance Water Oxidation. *J. Mater. Chem. A* **2017**, *5*, 3981−3986.

(60) Tang, C.; Cheng, N.; Pu, Z.; Xing, W.; Sun, X. NiSe Nanowire Film Supported on Nickel Foam: An Efficient and Stable 3D Bifunctional Electrode for Full Water Splitting. *Angew. Chem., Int. Ed.* **2015**, *54*, 9351−9355.

(61) Zhang, J. Y.; Lv, L.; Tian, Y.; Li, Z.; Ao, X.; Lan, Y.; Jiang, J.; Wang, C. Rational Design of Cobalt-Iron Selenides for Highly Efficient Electrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 33833−33840.

(62) Xu, K.; Ding, H.; Lv, H.; Tao, S.; Chen, P.; Wu, X.; Chu, W.; Wu, C.; Xie, Y. Understanding Structure-Dependent Catalytic Performance of Nickel Selenides for Electrochemical Water Oxidation. *ACS Catal.* **2017**, *7*, 310−315.

(63) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **2014**, *136*, 6744−6753.

(64) Burke, M. S.; Kast, M. G.; Trotochaud, L.; Smith, A. M.; Boettcher, S. W. Cobalt-Iron (Oxy)Hydroxide Oxygen Evolution Electrocatalysts: The Role of Structure and Composition on Activity, Stability, and Mechanism. *J. Am. Chem. Soc.* **2015**, *137*, 3638−3648.

(65) Park, H. S.; Kweon, K. E.; Ye, H.; Paek, E.; Hwang, G. S.; Bard, A. J. Factors in the Metal Doping of $BiVO_4$ for Improved Photoelectrocatalytic Activity as Studied by Scanning Electrochemical Microscopy and First-Principles Density-Functional Calculation. *J. Phys. Chem. C* **2011**, *115*, 17870−17879.

(66) Bates, M. K.; Jia, Q.; Doan, H.; Liang, W.; Mukerjee, S. Charge-Transfer Effects in Ni-Fe and Ni-Fe-Co Mixed-Metal Oxides for the Alkaline Oxygen Evolution Reaction. *ACS Catal.* **2016**, *6*, 155−161.

(67) Lu, Z.; Wang, H.; Kong, D.; Yan, K.; Hsu, P.; Zheng, G.; Yao, H.; Liang, Z.; Sun, X.; Cui, Y. Electrochemical Tuning of Layered Lithium Transition Metal Oxides for Improvement of Oxygen Evolution Reaction. *Nat. Commun.* **2014**, *5*, 4345.

(68) Zhang, C.; Fagan, R. D.; Smith, R. D. L.; Moore, S. A.; Berlinguette, C. P.; Trudel, S. Mapping the Performance of Amorphous Ternary Metal Oxide Water Oxidation Catalysts Containing Aluminium. *J. Mater. Chem. A* **2015**, 3, 756−761.

(69) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **2015**, *137*, 4347−4357.

(70) Batchellor, A. S.; Boettcher, S. W. Pulse-Electrodeposited Ni-Fe (Oxy)Hydroxide Oxygen Evolution Electrocatalysts with High Geometric and Intrinsic Activities at Large Mass Loadings. *ACS Catal.* **2015**, *5*, 6680−6689.