

Redefining the Stability of Water Oxidation Electrocatalysts: Insights from Materials Databases and Machine Learning

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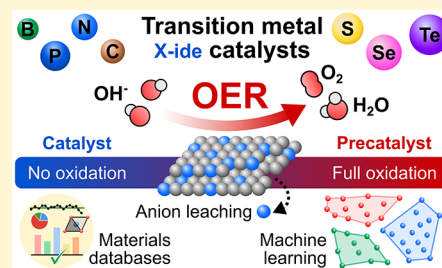


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ABSTRACT: Research on electrochemical water splitting has experienced significant growth in interest in transition metal borides, carbides, pnictides, and chalcogenides, owing to their notable catalytic performance. These materials, collectively called X-ides, are often considered promising electrocatalysts for the oxygen evolution reaction (OER). However, under the strongly oxidizing conditions of the OER, transition metal X-ides often act as precatalysts, undergoing in situ reconstruction to a different, catalytically active phase. Discrepancies exist in the literature, with some studies claiming the absence of such transformations. Building upon previous efforts to elucidate catalytic performance trends in the community, this Perspective discusses a more nuanced approach to X-ide research, emphasizing the need to reassess our understanding of their chemical stability and the significance of the in situ reconstruction process. By discussing the role of experimental and computational databases, we present strategies for predicting X-ide stability and stress the importance of thorough experimental validation. Moreover, we highlight the use of machine learning to extract meaningful insights from these data and urge the community to adopt a standardized, systematic reporting of X-ide performance. Finally, we provide strategic guidelines and directions to advance transition metal X-ide research, ultimately enhancing their future application for a sustainable hydrogen economy.



To achieve global decarbonization, developing technologies and materials for hydrogen gas production from water has taken center stage. Worldwide, researchers have focused on studying electrocatalytic materials to enhance water-splitting reactions, namely, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).^{1,2} The four-electron OER is especially critical as it largely restricts the overall efficiency of water splitting due to its slow kinetics.³ Furthermore, obtaining stable electrocatalysts is a significant challenge under the highly oxidizing conditions of the OER.^{4,5} Despite the challenges, conducting low-temperature electrochemical water splitting in alkaline media—known as alkaline water electrolysis (AWE)—stands out as a promising method. This approach benefits from the use of earth-abundant, transition metal-based catalysts, which exhibit enhanced stability in alkaline conditions.^{3,6,7}

Several transition metal (TM) oxide and (oxy)hydroxide OER catalysts have been thoroughly researched and are now established benchmarks in the field. Nonetheless, there has been a particular interest in investigating TM-based covalent compounds with nonmetals to improve electronic conductivity

and catalytic performance.^{5,8–10} TM borides, carbides, pnictides, chalcogenides, and related TM-based polyanion compounds/composites are commonly referred to as TM X-ides.^{1,4,11} Between 2013 and 2019, the volume of publications on this novel class of OER electrocatalysts skyrocketed, following an exponential-like trend.¹ Are we witnessing a revolutionary change in catalytic materials that will reshape AWE research?

Despite the frequent claims of “outstanding” electrocatalytic activity and stability attributed to these materials, many in the AWE community urge a shift toward a more pragmatic view, recognizing that these materials inevitably undergo significant transformations and oxidation under OER conditions.^{1,4,5,11,12}

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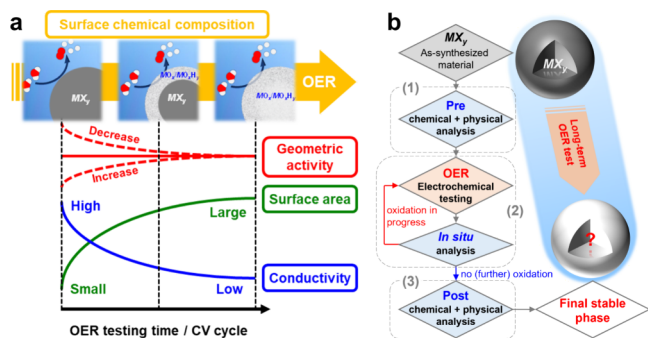


Figure 1. (a) Transformations of TM X-ide electrocatalysts during OER testing and the effects on their performance. (b) Proposed workflow for examining the stability of TM X-ide electrocatalysts. Reprinted with permission from ref 1. Copyright 2023 American Chemical Society.

Acknowledging this reality is crucial to avoid misleading results and to foster an increased understanding of material transformations in this rapidly expanding field. In 2023, our group published a review article offering an in-depth analysis of the latest research on TM X-ide electrocatalysts to assess their significance within the AWE community.¹ Drawing from existing stability characterization data, we categorized hundreds of reported TM X-ide electrocatalysts into three primary groups: catalysts exhibiting no oxidation, precatalysts undergoing partial oxidation, and precatalysts experiencing complete oxidation. Our group embraced the term *precatalyst* to describe a TM X-ide material that, initially not serving as a catalyst, transforms into the active OER phase during testing.^{4,13} Adopting the *precatalyst* terminology in TM X-ide research is essential, as it acknowledges the in situ reconstruction occurring during the OER. Confirming whether the studied material behaves as a precatalyst is crucial because transformations can be correlated to changes in geometric activity, intrinsic activity, surface area, and electronic conductivity observed during the OER (Figure 1a). This confirmation

requires meticulous electrochemical, chemical, and structural analyses before, during, and after OER testing (Figure 1b).

Despite our concerted efforts to elucidate the true nature of TM X-ides in AWE research, we have yet to arrive at a definitive conclusion regarding our primary inquiry: Do all TM X-ides function as precatalysts? We attribute this uncertainty to an alarmingly high number of reports claiming “excellent” stability, which often lack comprehensive characterization or fail to assess catalytic stability appropriately. This is a serious concern, as findings that inaccurately report stability or falsely deny oxidation can quickly proliferate, leading to widespread misinformation within the field. This situation is further

Without solid evidence to rule out structural and compositional changes, assertions of high stability are difficult to support.

compounded by the prevalence of so-called “sandwich” papers, which do not substantially contribute to advancing our understanding of these materials.¹⁴

In this Perspective, we outline essential approaches to highlight the relevance of this topic and provide clear guidelines to enhance the research on TM X-ide electrocatalytic materials. Building upon our findings from existing TM X-ide research in the past decade, we aim to describe specific aspects and challenges for significantly advancing the field. Furthermore, we provide examples to assist researchers in predicting the stability of TM X-ides using materials databases and machine learning, enabling them to identify and focus on the most promising material compositions for OER electrocatalysis. Finally, we summarize essential considerations and new research directions for guiding TM X-ide research. Ultimately, we aim to stimulate rigorous research and inspire new endeavors in TM X-ide OER catalysis research.

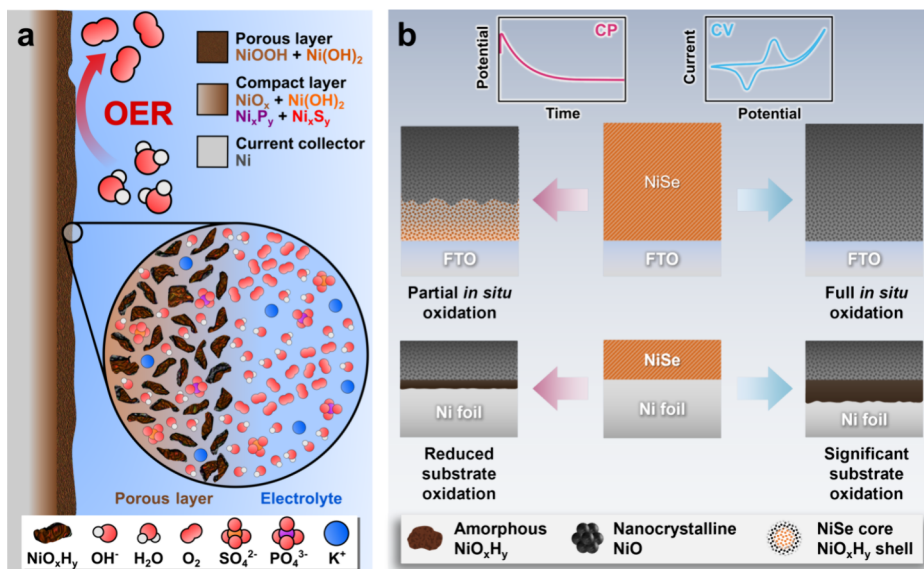


Figure 2. (a) Schematic of the dynamic reconstruction process of TM sulfide and phosphide OER catalysts. Adapted with permission from ref 18. Copyright 2021 Royal Society of Chemistry. (b) Degrees of in situ oxidation for NiSe films on Ni foil and FTO substrates after electrochemical conditioning using cyclic voltammetry or chronopotentiometry techniques. Adapted with permission from ref 6. Copyright 2022 American Chemical Society.

■ STABILITY OR ILLUSION? UNCOVERING THE OXIDATION OF TM X-IDES

Stability, a crucial property for any catalyst, has been extensively examined, with numerous studies claiming the compositional and structural integrity of TM X-ides.³ However, these claims of high stability often clash with the highly oxidizing conditions prevalent during the OER. Without solid evidence to rule out structural and compositional changes, assertions of high stability are difficult to support.⁴ It is worth noting that electrochemical stability testing (e.g., CV cycling, chronoamperometry, chronopotentiometry) may not directly correlate with the chemical stability of the initial TM X-ide. Thus, a stable long-term response does not necessarily mean the material has not undergone a chemical or structural transformation. If the original TM X-ide catalyst oxidizes during the reaction, it fails to meet the definition of a catalyst, raising questions about the material's actual composition during testing and the identity of the active catalytic site.⁴

An essential question becomes evident: Is it possible to predict the stability of TM X-ides before conducting any experiments? Before diving into evidence, we can draw upon thermodynamics and solid-state chemistry to understand the dynamic nature of TM X-ides. Thermodynamically, TM oxides represent the most stable form for most oxidative processes in water.^{1,4,15–17} This fact suggests that the original anions in TM X-ide are replaced with O^{2-} , which is smaller and more electronegative than other nonmetals (i.e., B, C, N, P, S, Se, Te), leading to significant leaching of the nonmetal, morphological and compositional changes, and structural reorganization.^{3,4,18–21} This process results in a porous structure with increased surface area, as depicted in Figure 2a, showcasing a porous film transitioning from a TM X-ide to an oxide/oxyhydroxide phase with leached oxyanions.¹⁸ This newly formed phase differs from the initial TM X-ide and exhibits a new variety of potential catalytic active sites, adsorbates, and TM cations with varying oxidation states. The

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reconstruction of the starting material results in new characteristics and alterations to the local environment, manifesting as changes in the electronic conductivity of the catalyst and the ionic conductivity at the electrode–electrolyte interface.^{1,22}

The hard and soft acid–base (HSAB) theory supports the in situ reconstruction process. High-valent TM cations (e.g., Fe^{3+} , Ni^{3+}), considered hard acids, have stronger interactions with hard bases like O^{2-} or oxyanions, while larger anions (Se^{2-} , Te^{2-}) are soft bases and show weaker interactions.^{12,23} This framework of hard–hard or soft–soft interactions offers a simplistic yet logical explanation for OER catalyst stability. Nonetheless, there are conflicting experimental results in the literature. Chen and co-workers observed that the electro-

chemically active surface area (ECSA) decreases with increasing chalcogenide size ($S > Se > Te$), suggesting a more significant reconstruction for TM sulfides over tellurides.²⁴ In contrast, El-Refaei and co-workers reported faster leaching rates for larger nonmetals.¹¹ Their results suggest that the identity of the nonmetal and the reconstruction process of the TM X-ide do not directly relate to the OER activity enhancement in the absence of Fe impurities, which are known to boost the OER.^{25,26} However, the nonmetal does affect the degree of structural disorder during oxidation and reconstruction.¹¹ These findings support the notion that larger nonmetals are more prone to leach out, leading to more substantial structural changes when replaced by smaller oxide and hydroxide anions.⁴

Predicting instability of TM X-ides could also be supported by the reconstruction observed in other OER catalysts. It is well-known that perovskites (ABX_3) are unstable under OER testing conditions and undergo elemental leaching due to the instability of alkaline-earth metals in the A-site.²² Metal–organic frameworks (MOFs) also serve as a case study in OER research for this instability. Although MOFs exhibit advantageous properties for electrocatalysis, such as large surface area and structural flexibility, these materials also suffer from low conductivity and poor stability.²³ The HSAB theory can also explain these properties, as the covalent bonding between metal centers and organic linkers (hard–soft) is generally weaker than the ionic bonding in inorganic solids (hard–hard). Recent research has questioned the structural robustness of MOFs under electrochemical environments, and the electrocatalytic stability of MOFs remains unproven in many cases.^{12,23} These findings position TM X-ides, perovskites, and MOFs as precatalysts that act as sacrificial templates, transforming into materials with a metal oxide/oxyhydroxide phase.²³ It is worth noting that TM X-ides can oxidize rapidly, similar to perovskites and MOFs. Thus, the initial current drop/increase associated with the reconstruction process would be obscured, and the long-term electrocatalytic response would stem from the phase formed after reconstruction.¹²

The electrochemical conditioning method is also essential to determine the extent of oxidation of a precatalyst. Our group evaluated the influence of chronopotentiometry (CP) and cyclic voltammetry (CV) conditioning techniques on the extent of oxidation of NiSe catalytic films supported on different substrates.⁶ As shown in Figure 2b, while CP conditioning results in partial oxidation, CV conditioning yields a higher degree of in situ oxidation, creating a thicker nanoporous film and transforming the NiSe precatalyst fully into NiO_xH_y . Moreover, through film characterization using time-of-flight secondary ion mass spectrometry (ToF-SIMS), we also found that the presence of an interstratified structure with dissolved cations, anions, and porous NiO_xH_y is limited to a few nm after CP conditioning.²⁷ These results highlight that specific experimental conditions strongly determine precatalyst reconstruction and the observed stability. Selecting different conditioning methods also complicates the interpretation of OER performance, as both techniques result in different material and electrochemical characteristics.⁶ Thus, it is critical to perform electrochemical conditioning before collecting performance data, ensuring that the local equilibrium of the active oxyhydroxide phase is established.^{3,28} This observation raises a second question: are TM X-ides truly stable under all environments?

Theoretical and experimental research converge to challenge the conventional portrayal of TM X-ides as *stable* catalysts. The distinction between chemical and electrochemical stability needs a precise definition, as it does not truly support long-term stability claims.¹² In addition, the lack of standardized protocols and the misuse of conditioning methods further complicate the accurate classification of TM X-ide materials as catalysts or precatalysts, a decision influenced by both the chemical composition of the initial materials and the testing environment. Given these challenges, how does this apparent discrepancy in stability claims align with the trends made by experimental and computational materials databases?

LEARNINGS FROM COMPREHENSIVE MATERIALS DATABASES

A significant challenge lies in the inability to predict the true stability of materials before synthesis.²⁹ Despite this limitation, researchers have moved forward and synthesized TM X-ide OER catalysts, leading to a significant surge in publications in the field over the past decade. Many TM X-ide catalysts exhibiting various chemical compositions, morphologies, catalytic supports, and synthetic approaches have been documented. Thus, with the accumulation of experimental data to this point, it seems plausible that meaningful empirical trends could be revealed, giving clear direction to future research in this field.

In 2023 our group published an experimental database encompassing over 890 TM boride, carbide, pnictide, and chalcogenide OER electrocatalysts, documented in peer-reviewed studies from 2013 to 2022.¹ Through a thorough review of material characteristics, experimental conditions, stability tests, and postcharacterization results, we categorized these materials into *precatalysts* and *catalysts* based on their oxidation status: fully oxidized, partially oxidized, and unoxidized. As displayed in Figure 3, most of the TM X-ides

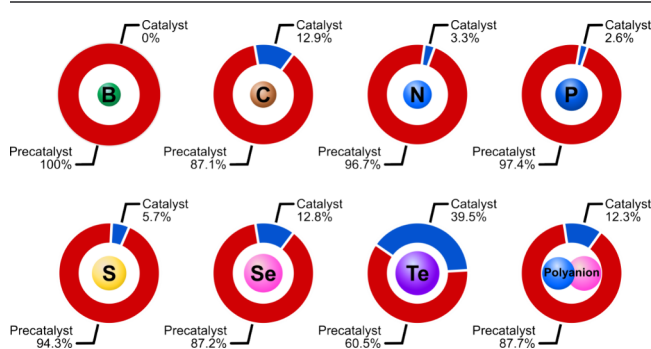


Figure 3. Distribution of TM X-ides categorized as OER precatalysts and catalysts across different groups. Adapted with permission from ref 1. Copyright 2023 American Chemical Society.

documented in the literature are identified as precatalysts based on the experimental evidence provided by the authors. Nonetheless, some TM X-ides, especially TM selenides and tellurides, are still considered catalysts. To uncover explanations for the observed experimental patterns, we employed analysis of variance (ANOVA) tests to detect significant correlations between OER performance metrics and material properties. However, the significant statistical variability in the data prevented us from discerning any clear trends. These

results showcase a critical limitation in *experimental* databases: Is the reported OER performance data *reliable*?

Besides interpreting empirical trends, modern computational tools unlock new avenues for assessing the viability of TM X-ides as OER catalysts. A great example is the Materials Project, an open-access database providing extensive computational data on real and hypothetical materials.^{30–33} Among the tools made available by the Materials Project, our group has exploited Pourbaix diagrams to forecast the stability of TM X-ides.^{1,4,27} These diagrams represent the thermodynamically stable phases of materials within an aqueous electrochemical system, serving as a valuable predictor for potential elemental leaching and phase transformation of catalytic materials.²² After leveraging our comprehensive database of TM X-ide OER catalysts, we observed that Ni- and Co-based X-ides are prevalent in existing research.¹ Thus, we generated and refined a series of Pourbaix diagrams for Ni and Co TM X-ides using the Materials Project, detailed in the Supporting Information (Figures S2–S14). We encourage the community to use these diagrams as a predictive tool to evaluate the stability of TM X-ides. These can be used to tune the synthetic goals or adjust operating conditions.

Although studies often focus on highly alkaline or acidic conditions, this consideration is far from trivial, given the observable shifts in local pH and the variable operational conditions characteristic of actual water electrolysis systems.^{28,34} Therefore, it is essential to consider the dynamic environment when testing water-splitting electrocatalysts. Figure 4 shows the Pourbaix diagrams of Co₂P and CoTe compositions to illustrate some notorious characteristics of the stability of TM X-ides. First, these diagrams reveal that Co-based phosphides and tellurides exhibit a variety of chemical states across different pH and electrode potentials. These states remain stable within relatively narrow regions, meaning that even minor pH and electrode potential changes could trigger transitions to new chemical compositions. Second, only CoTe exhibits solid Te species (i.e., CoTeO₄ and CoTe₂) under narrowly defined conditions of near-neutral pH and electrode potentials adjacent to the OER and HER stability lines. Third, the diagrams illustrate that OER conditions predominantly lead to the formation of cobalt oxyhydroxide and aqueous oxanions (e.g., PO₄^{3–}, TeO₄^{2–}). In contrast, HER conditions favor the emergence of metallic Co and reduced aqueous nonmetal species (e.g., H₂Te, H₂Se, PH₃). These transformations during the HER have been observed experimentally, including the formation of a metallic Co-rich phase and dissolution of reduced P and Se species,^{35,36} as well as the emergence of surface PH_x-enriched phases from Ni and Fe phosphides.^{37,38} Similar patterns are observed across other Ni- and Co-based X-ides, as detailed in the Supporting Information.

Using computed Pourbaix diagrams also reveals essential insights for TM X-ide OER research. Although computed Pourbaix diagrams offer a valuable prediction of material stability, these primarily account for bulk, thermodynamic properties, not the actual corrosion kinetics.²⁷ The low solubility of certain species, such as metal oxyhydroxides, selenates, and tellurates, may lead to the precipitation of segregated phases or sedimentation in the electrolyte rather than on the catalyst surface, adversely affecting stability.^{22,27} Researchers should carefully weigh these considerations when proposing and assessing TM X-ide compositions, especially in claims of high stability. Nevertheless, although computed

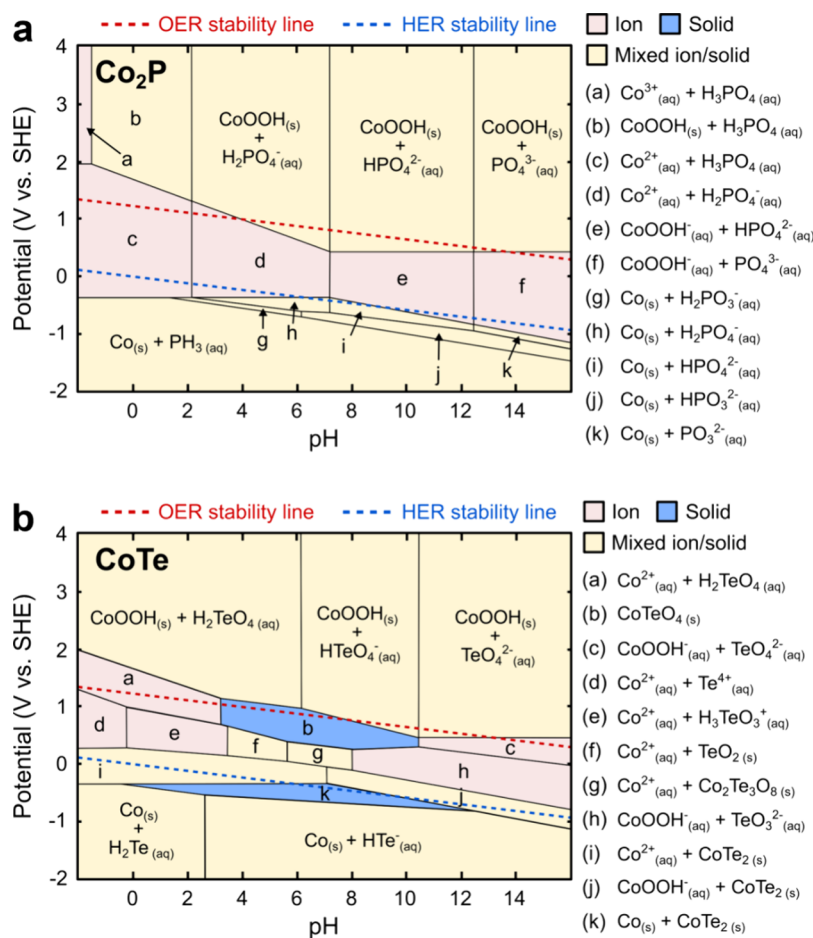


Figure 4. Pourbaix diagrams for (a) Co_2P and (b) CoTe X-ides. The plots were adapted from the diagrams generated using the Materials Project.^{30–33} Ion concentration: $10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

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Pourbaix diagrams offer a valuable prediction of material stability, these primarily account for bulk, thermodynamic properties, not the actual corrosion kinetics.²² Furthermore, the density-functional theory (DFT) method significantly influences the generated Pourbaix diagrams, which may not always align with electrochemical observations. Building upon previous findings on the theoretical and experimental stability of transition metal oxides,^{39,40} it is essential to correlate the theoretical predictions of computational Pourbaix diagrams with accurate and direct experimental observations of the electrochemical stability of TM X-ides. Additional research is necessary to validate the stability trends suggested by these computational approaches, and caution is advised when making stability claims based solely on theoretical data.

Based on these observations, experimental materials databases highlight a critical issue: the accuracy of the available

experimental data is a serious concern. While computed databases, such as Pourbaix diagrams, contribute valuable insights into the true stability of TM X-ides, OER research still requires precise and reproducible experimental data to establish reliable stability–structure correlations. However, if further studies confirm the high stability for specific X-ide compositions, a better understanding of why these materials deviate from expected thermodynamic trends and computed stability properties should be provided. These two situations highlight the need for more rigorous and systematic investigations into TM X-ide OER electrocatalysts.

■ UNDERSTANDING PERFORMANCE TRENDS USING MACHINE LEARNING

After identifying a significant gap in the rigor of experimental investigations into TM X-ides, another question arises: How can we extract meaningful insights from experimental reports? Machine learning (ML) applies mathematical principles to learn from training data sets and extract meaningful insights beyond the initial data set.^{41,42} We employed ML to unravel separability between the catalysts and precatalyst classes of TM X-ide OER electrocatalysts. The compiled materials were grouped into distinct spaces based on specific features. By understanding the specific feature combinations that define each group, we can reveal those features indicative of catalysts or precatalysts that warrant further investigation.

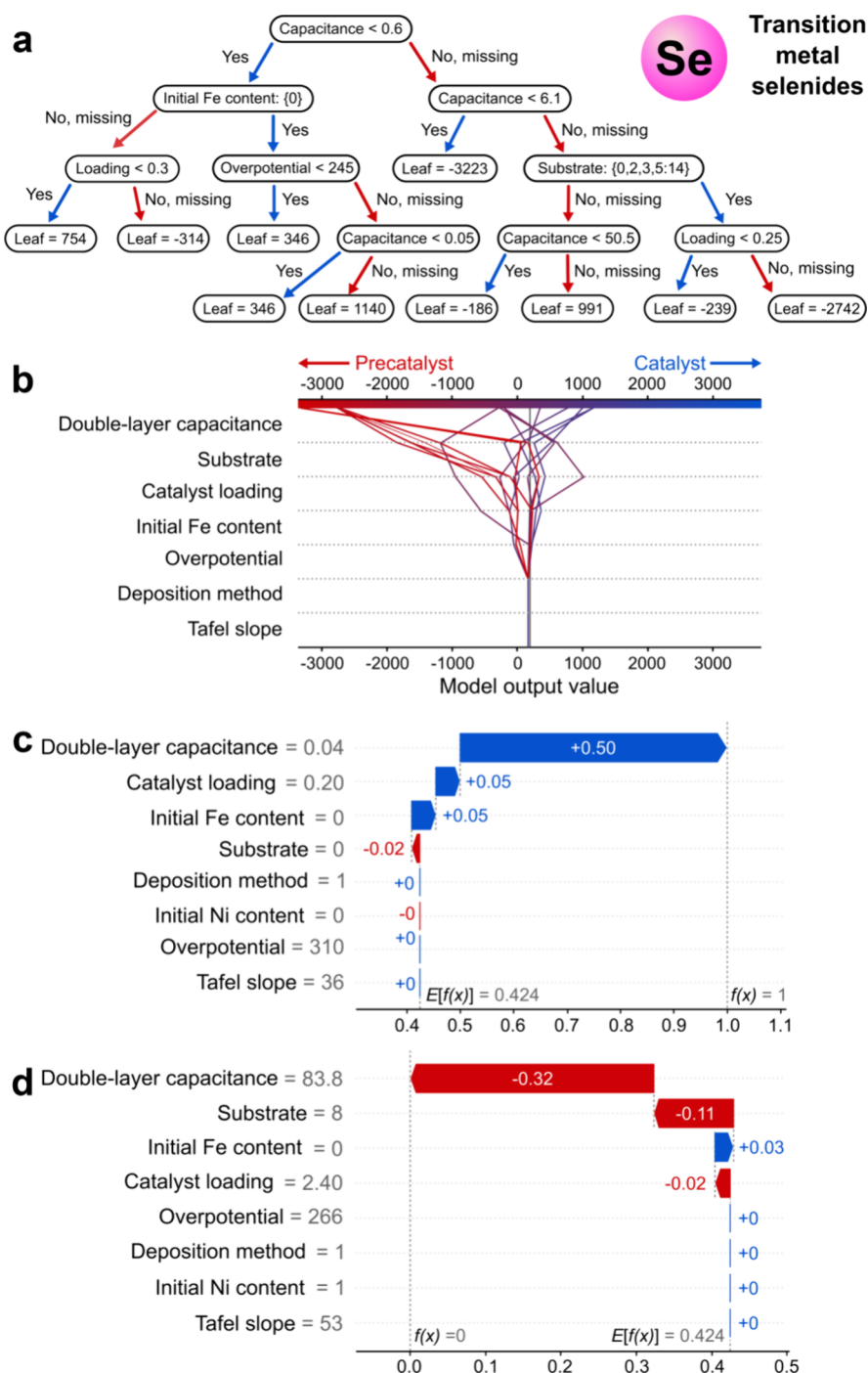


Figure 5. Using ML to reveal insights from the TM X-ide database compiled by our group: (a) Tree-based assessment using the XGBoost algorithm to classify TM selenides as catalysts or precatalysts. (b) Decision plot describing the relationships between different TM selenide features and its reconstruction outcome (catalyst vs precatalyst). Force plot examples for a (c) catalyst and (d) precatalyst from the TM selenide data set. Codes for categorical variables (e.g., substrate, deposition method) are shown in the [Supporting Information](#).

Using the TM X-ide database compiled from our previous work,¹ we employed decision tree-based models to classify the reported materials as catalysts and precatalysts. The XGBoost algorithm, which implements gradient-boosting decision trees to analyze large data sets, reveals specific catalyst groups defined by a set of shared features. Based on the availability of data reported in the literature, we considered the OER overpotential, Tafel slope, double-layer capacitance, catalyst loading, type of electrode substrate, deposition method, and the presence of Fe in the initial material composition. [Figure](#)

[5a](#) shows the decision tree structure generated from the XGBoost algorithm for the TM selenide database. Each node represents a decision point where the algorithm examines data set features to identify the feature and its corresponding value that split the data. The goal is to obtain groups that are as pure as possible. A pure node denotes a group where the materials possess identical features, and no further division is needed. In this case, we aim to segregate the data into two groups: catalysts and precatalysts, denoted by blue and red arrows, respectively. As shown in [Figure 5a](#), the decision tree reveals

that the double-layer capacitance, the initial Fe content, the specific loading, the overpotential, and the type of substrate are the features selected by the algorithm that produce the cleanest groups of catalysts and precatalysts. Catalysts from the TM selenide group are defined by a specific set of features. Studies designating TM selenides as catalysts reported double-layer capacitance values lower than $0.6 \text{ mF}\cdot\text{cm}^{-2}$, catalyst loadings below $0.3 \text{ mg}\cdot\text{cm}^{-2}$, the initial presence of Fe, overpotentials below 245 mV, and avoided the use of carbon cloth and foam substrates. Figures S13 and S14 show additional decision trees for TM phosphides and sulfide, respectively.

Next, we employed decision plots to better understand the relationships between TM X-ide features and the reconstruction outcomes. The Shapley additive explanations (SHAP) Python library leverages Shapley values reflecting the average of all the marginal contributions of a specific feature to the prediction.^{43,44} We used this approach to measure the importance of each feature relative to others once all possible

combinations have been considered. Figure 5b shows a decision plot generated using the TM selenides data. This decision plot lends insights into how this machine learning model makes decisions based on the TM selenide data set. The plot shows a series of colored lines, with each line representing a single TM selenide electrocatalyst from the compiled data set. The color indicates the model's final classification: blue for catalyst and red for precatalyst. Starting from the bottom of the

Future investigations must prioritize the use of more reliable data sets, as the quality of data fed into ML models critically determines their output's accuracy.

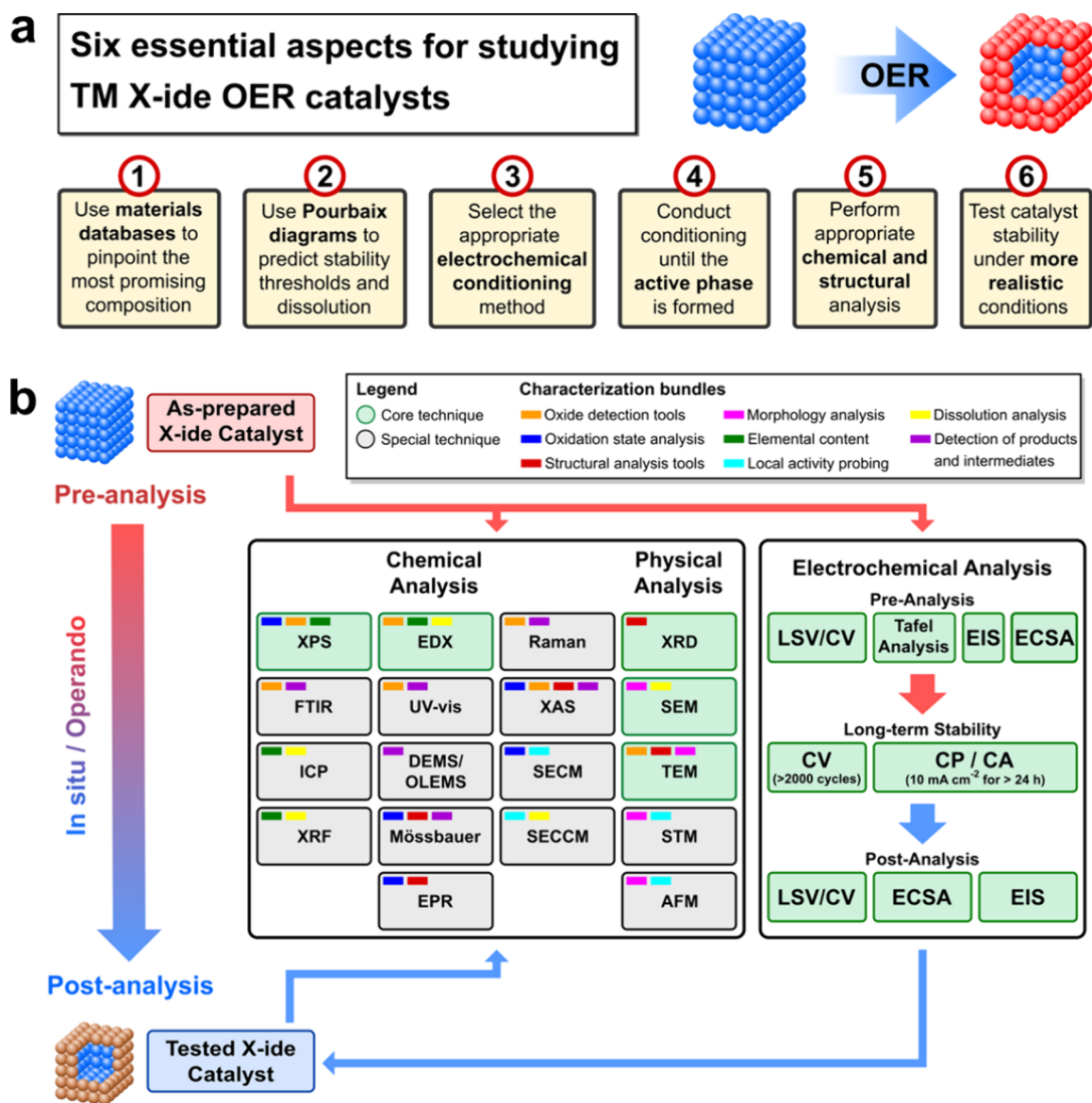


Figure 6. (a) Suggested experimental design considerations for evaluating TM X-ide OER electrocatalysts. (b) Characterization workflow for examining the physical and chemical transformations of TM X-ide electrocatalysts before, during, and after OER testing. Panel (b) reprinted with permission from ref 1. Copyright 2023 American Chemical Society.

plot, the line shows how different features of the electrocatalyst influence the model's classification. The line moves toward more positive values when a feature's value indicates a catalyst and toward negative values when it suggests a precatalyst. The features are ranked in descending order based on their importance to the model, with the most influential feature at the top. Specifically for the TM selenide data set (Figure 5b), the substrate type and the double-layer capacitance, a proxy of the ECSA, are significant features impacting the outcome as a precatalyst. However, note that these rankings can vary depending on individual model training. Therefore, this order is not absolute, and these results are specific to this model and the data set on which it was trained. From our compilation of TM X-ide data, only the data sets for TM sulfides, selenides, and phosphides are sufficiently large to enable meaningful predictions. Figures S15 and S16 show additional decision plots for TM phosphides and sulfides, respectively.

In machine learning, force plots can be utilized to reveal how individual features influence the prediction of a specific data point, acting like forces that pull the prediction toward either catalyst or precatalyst classification. Figure 5c shows a force plot for a TM selenide from the compiled library classified as a catalyst, in which the double-layer capacitance significantly influences its outcome as a catalyst. In contrast, Figure 5d shows a force plot in which the double-layer capacitance and the substrate type are the main pulling forces that explain the precatalyst outcome. Additional force plots for single catalysts and precatalysts from the TM phosphide and sulfide databases can be found in Figures S17 and S18.

This assessment illustrates how researchers can leverage ML models to identify potential predictors of TM X-ide stability. However, it is crucial to acknowledge that these examples do not intend to suggest that any particular feature dominantly influences the observed classification. Building upon our discussion in the previous section, it is essential to note that inconsistencies and a lack of reproducibility of experimental results in the field significantly hamper the predictive capability of these models. Thus, this approach should be viewed merely as a preliminary exercise for TM X-ides. While these ML approaches are robust and have been extensively utilized to derive significant insights into the catalytic performance of various materials,^{43,45–50} researchers must exercise caution when making claims about the relevance and impact of specific descriptors. Future investigations must prioritize the use of more reliable data sets, as the quality of data fed into ML models critically determines their output's accuracy. Simply put, the efficacy of ML outcomes is directly proportional to the quality of the input data. Researchers keen on integrating ML models into their studies must ensure the data's integrity, preferably by relying on systematically analyzed, well-controlled experiments or credible, reproducible literature sources. Finally, while ML models are excellent in interpolating information within large data sets, the ability to extrapolate information beyond the scope of the data provided is significantly limited. Caution is therefore recommended within the research community when applying ML-derived insights to justify claims or endorse specific characteristics (e.g., substrates, catalyst loadings, and material compositions). Please refer to the Supporting Information file for instructions on utilizing the machine learning methods described in this Perspective.

■ GUIDELINES FOR TM X-IDE OER ELECTROCATALYSIS RESEARCH

Leveraging the insights from our comprehensive literature review, computational material databases, and machine learning, it becomes evident that future research on TM X-ides should prioritize stability rather than just examining catalytic activity. As depicted in Figure 6a, we identify six critical aspects researchers must consider when investigating TM X-ide OER catalysts. Before synthesizing any material, researchers must define the objectives of their study clearly and utilize existing literature and materials databases to select the most suitable X-ide composition. For instance, future studies might explore whether selenides and tellurides act as catalysts, as suggested by a notable number of reports in our literature review (Figure 3).¹ Next, researchers are advised to use Pourbaix diagrams and other computational analyses to predict the stability of their chosen TM X-ide composition. The scientific community should use these tools to scrutinize “outstanding” performance claims for compositions predisposed to significant transformations, demanding further evidence to substantiate such claims.

Future research on TM X-ides should prioritize stability rather than just examining catalytic activity.

Moving forward, researchers must design experiments appropriately, including selecting the electrochemical conditioning method, considering potential impurity incorporation, and following recommendations to conduct electrochemical measurements appropriately.^{6,25,51–58} Comprehensive details regarding conditioning, testing, and characterization conditions should be provided to improve reproducibility within the field. Importantly, claims of activity and stability should only be made after a stable local equilibrium of the active phase has been achieved after conditioning.²⁸ It is essential to distinguish between conditioning and long-term testing; conditioning seeks to establish a stable “baseline” phase of the material, while long-term testing challenges this phase with prolonged or variable currents. The initial conditioning step is crucial for eliminating potentially unstable phases, ensuring that long-term testing focuses solely on the most promising compositions.

Next, appropriate physical and chemical characterizations are necessary to (i) identify the material's composition postconditioning (i.e., catalyst vs precatalyst) and (ii) investigate in detail the reconstruction processes during conditioning or long-term testing. Figure 6b outlines a characterization workflow that can be utilized to investigate TM X-ides depending on the goals of the study. It is worth noting that, despite the growing interest in advanced in situ and operando techniques, their use should be adaptable, not mandatory, for all studies, particularly those not aimed at detailed reconstruction analysis. Core characterization techniques should be the foundation of TM X-ide studies, with specialized methods applied as the research focus dictates. For instance, inductively coupled plasma (ICP) methods are invaluable for investigating elemental leaching.^{25,27,59} X-ray absorption spectroscopy is ideal for examining stability–structure relationships. Raman and X-ray photoelectron spectroscopies (XPS) are highly recommended for analyzing

surface/interface processes,^{1,2,12,60} while microscopic techniques can reveal surface and morphological changes.^{3,60} Caution is advised with simulations, especially those performed on pristine TM X-ides, which may not represent the material's true active phase. Thus, identifying this "baseline" phase after surface reconstruction is essential before conducting simulations. Nevertheless, it is important to emphasize that neither computational nor experimental characterization alone can provide a complete and accurate depiction of the dynamic nature of catalytic active sites. Therefore, researchers need to carefully select these tools based on the specific scope of their research and the conditions under which testing is conducted.

Recent theoretical advances in atomic simulations assisted by ML methods offer promising avenues for understanding complex catalytic systems.^{61,62} For instance, machine learning interatomic potentials (MLIPs) can parametrize the potential energy surface of atomic systems based on local environment descriptors, achieving accuracy comparable to ab initio methods but at speeds orders of magnitude faster.^{63,64} Electronic-structure data from DFT data sets can train MLIPs to predict energies and forces for larger ensembles of atoms, thereby making more complex structural problems computationally manageable.^{65,66} MLIPs have been used to study complex catalytic scenarios, such as the nucleation and crystallization of Pt nanoparticles⁶⁷ and the solvation of adsorbates at metal-water interfaces.⁶⁸ We believe that MLIPs could be extremely valuable for understanding the dynamics of TM X-ide catalysts and encourage further research in this area. However, it is important to note that the accuracy and robustness of MLIPs depend on the quality of the training data, so researchers must carefully select materials and reaction environments.

Lastly, we encourage the community to investigate the performance of the most promising materials under more industrially relevant conditions. Water electrolysis on a large scale is subjected to more rigorous conditions, including high temperatures, concentrated electrolytes, and fluctuating currents.³⁴ Therefore, scaling up TM X-ides for evaluation under these demanding conditions is essential once a material demonstrates efficacy on a laboratory scale. Our group has described a practical and robust electrolyzer setup for examining electrocatalytic stability in such environments.²⁸ We invite the community to replicate or modify this setup to advance TM X-ide research toward practical water electrolysis applications. Consistently applying this benchmark will further enhance accuracy and reproducibility within the field.

The concept of stability within TM X-ide research warrants a more nuanced understanding. The community needs to recognize that the reconstruction process is not detrimental but rather a necessary and potentially advantageous outcome. Reconstruction strategies such as in situ metal incorporation and electrochemical dealloying can be used to tune and refine electrocatalytic interfaces, thereby enhancing performance.^{27,69} Promoting surface reconstruction does not necessarily compromise stability; it can activate the catalyst until a more stable and active phase is achieved. For instance, Zhao and co-workers provide an interesting reflection regarding the stability of perovskite OER catalysts.²² Utilizing a stability level descriptor to assess perovskite surface stability, they linked the extent of surface transformation with OER catalytic performance. Overly stable materials lack high activity due to insufficient active sites, whereas excessive reconstruction and leaching result in structural instability and complete failure of

the perovskite. Therefore, optimal stability is critical for generating active sites and improving OER catalytic performance without entirely deactivating the catalyst. This concept could be expanded to TM X-ides, wherein the precatalyst acts as the precursor to the optimal catalytic material. Labeling a material as a precatalyst is not inherently negative but somewhat indicative of a material's dynamic pathway to optimization.

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PERSPECTIVES AND RESEARCH DIRECTIONS

TM X-ide research continues to pose numerous questions that can deepen our understanding of electrocatalytic processes. We encourage the community to explore the following areas to advance TM X-ide research further:

Understanding the Reconstruction Process. The mechanisms and impacts of reconstruction processes remain poorly understood. Critical considerations include the role of the nonmetal, chemical composition, morphology, initial crystallinity, and catalytic support in influencing leaching rates and their effects on the local environment (e.g., changes in local ionic conductivity and pH due to dissolved anions), electronic conductivity, and the relationship between the HSAB theory and TM X-ide stability. Our group has investigated these aspects for specific compositions, such as TM carbides and nitrides.^{19,70–72} Moreover, previous studies suggest that processes like metal incorporation heavily influence X-ide reconstruction.^{6,11,27,58,71,73,74} Furthermore, we encourage the community to advance the development of computational methods and utilize these tools to explore the reconstruction of catalytic sites under dynamic conditions. Notable examples include the replica-exchange algorithm for simulating surfaces and clusters in reactive atmospheres,⁷⁵ the Wang–Landau Monte Carlo algorithm for deriving thermodynamic properties and studying phase transitions,⁷⁶ the nested sampling algorithm for computing surface thermodynamic properties at finite temperatures,⁷⁷ and the use of MLIPs to address more complex catalytic scenarios.^{63–66}

Deriving Performance Correlations Systematically. Instead of examining TM X-ides separately, it is crucial to establish structure–activity and stability correlations through systematic examination of different compositions under identical conditions. Comprehensive studies across various TM X-ide compositions have provided valuable insights.^{11,24} Controlling variables such as the catalytic support, morphology, and catalyst loading allows for focused investigation of specific parameters, for example, the impact of nonmetal size on the reconstruction and OER performance. Furthermore, researchers can draw on previous efforts to develop materials databases for other classes of materials, such as halide perovskites,⁴¹ transition-metal dichalcogenides and oxides,¹⁶ catalysts for electrochemical CO₂ reduction,^{78,79} and the Open Catalyst 2022 (OC22) data set for oxide electrocatalysts.⁸⁰

Considering Extrinsic Properties. Future research should also consider the effects of extrinsic properties—those dependent on the environment rather than inherent to the

material.⁵⁹ As noted previously, results for the TM selenide data set (Figure 5b) indicate that the surface area, via the double-layer capacitance, and the type of substrate significantly influence the outcome as precatalyst, suggesting a link to the reconstruction of precatalysts and enhancement of catalytic activity. Previous works have linked substrate effects to OER activity enhancement in transition metal oxyhydroxide catalysts.^{81–83} More experimental and computational studies are necessary to explore the role of these extrinsic properties on the performance and transformation of TM X-ides. Furthermore, studies could explore how postreconstruction morphologies affect bubble removal, which is crucial for industrial water electrolysis, along with the reconstruction's impact on mechanical stability, surface roughness, and corrosion over time.^{3,59,84} Investigations at higher and fluctuating currents are also pertinent.²⁸

Bifunctionality of TM X-ides. While TM X-ides may show potential as bifunctional materials, claims to this effect should be backed by solid evidence. According to Pourbaix diagrams, the HER and OER conditions may lead to divergent reconstruction outcomes, highlighting the need to identify each reaction's active phase and understand how each influences the reconstruction process.

Scaling up TM X-ides. Once a promising composition is determined, researchers are encouraged to test the materials under more realistic conditions to favor scale-up and technological development in water electrolysis research.^{3,28} As previously discussed, the electrochemical conditioning technique significantly influences the reconstruction process and the resulting material properties. Therefore, it is expected that reconstruction might also vary in drastically different environments. Potential future research aspects include testing at higher currents, high temperatures, different pH conditions, reverse currents, high mechanical stress, and vigorous bubble evolution.

Appropriate Use of Machine Learning. Machine learning has become an invaluable tool in materials research, and its capabilities should be exploited whenever possible. However, researchers should exercise caution in data selection from previous studies. We recommend constructing experimental libraries systematically using well-controlled environments to train machine learning models properly. ML tools such as decision tree models and SHAP analysis can provide valuable insights into how descriptors like catalytic properties and synthesis conditions impact catalytic performance. However, researchers must ensure that these descriptors are measured accurately, adhering to established standards and fully disclosing the measurement conditions. For instance, researchers can utilize the characterization workflow shown in Figure 6b to measure critical descriptors of catalytic performance with complementary techniques and confirm the observed trends. Researchers are also referred to data acquisition, storage, and use guidelines.⁸⁵ Lastly, exercise caution when extrapolating results, as predictions for one set of materials may not apply to others, necessitating further experimental validation.

Standard Practices and Benchmarks. TM X-ide research needs standardized guidelines and testing protocols to allow for fair comparisons in the literature. The lack of consistency and reproducibility hampers the ability to discern clear trends or utilize experimental databases effectively. We urge the community to conduct systematic studies to define optimal stability testing conditions for various TM X-ides, as

We urge the community to conduct systematic studies to define optimal stability testing conditions for various TM X-ides, as the appropriate duration of OER exposure remains undetermined.

the appropriate duration of OER exposure remains undetermined. So, how long should TM X-ides be tested to accurately claim full or partial oxidation for a given set of standard experimental conditions? Additionally, identifying benchmark materials that are simple to synthesize, reproducible, and exhibit defined performance is crucial for advancing the field. Future research should aim to establish these materials and offer detailed guidelines for their characterization. Researchers are urged to follow essential guides in the literature.^{4,25,28,53–55,85–89}

We aim to reinvigorate TM X-ide research, directing future studies toward unresolved questions. The insights gained from this field hold significant potential for electrocatalysis research, with possible applications extending to other reactions that undergo similar catalytic transformations. We hope this Perspective brings more innovation and exciting strategies to TM X-ide research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c00544>.

Additional information on machine learning models and supporting figures, tables, and schemes (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. CRediT: **Raul A. Marquez**: conceptualization, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing – original draft; **Erin Elizabeth Oefelein**: conceptualization, data curation, formal analysis, investigation, methodology, software, validation, visualization, writing – original draft; **Thuy Vy Le**: formal analysis, validation, visualization, writing – review & editing; **Kenta Kawashima**: conceptualization, supervision, writing – review & editing; **Lettie A. Smith**: supervision, writing – review & editing; **C. Buddie Mullins**: funding acquisition, project administration, resources, supervision, writing – review & editing.

Notes

Views expressed in this Perspective are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

Biographies



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