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Systematic Investigation of Iridium-Based Bimetallic Thin Film Catalysts for the Oxygen Evolution Reaction in Acidic Media

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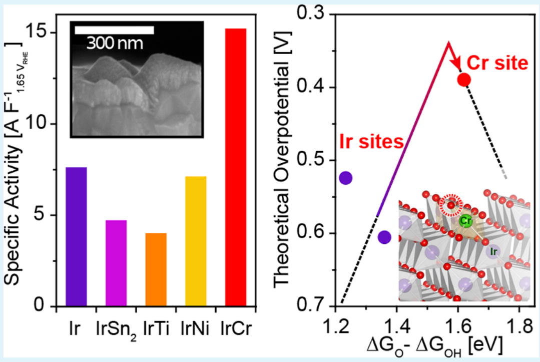
Supporting Information



ABSTRACT: Multimetallic Ir-based systems offer significant opportunities for enhanced oxygen evolution electrocatalysis by modifying the electronic and geometric properties of the active catalyst. Herein, a systematic investigation of bimetallic Ir-based thin films was performed to identify activity and stability trends across material systems for the oxygen evolution reaction (OER) in acidic media. Electron beam evaporation was used to co-deposit metallic films of Ir, $IrSn_2$, IrCr, IrTi, and IrNi. The electrocatalytic activity of the electrochemically oxidized alloys was found to increase in the following order: IrTi < $IrSn_2$ < Ir ∼ IrNi < IrCr. The IrCr system demonstrates two times the catalytic activity of Ir at 1.65 V versus RHE. Density functional theory calculations suggest that this enhancement is due to Cr active sites that have improved oxygen binding energetics compared to those of pure Ir oxide. This work identifies IrCr as a promising new catalyst system that facilitates reduced precious metal loadings for acid-based OER catalysis.

KEYWORDS: *oxygen evolution reaction, electrocatalysis, acidic media, Cr doping, density functional theory, volcano plot, theoretical overpotential, electrochemical characterization*

■ INTRODUCTION

Water electrolysis is a promising emerging technology for renewable energy storage and sustainable hydrogen production.[1−3] Hydrogen is an essential chemical commodity produced at a rate of 65 million tons annually with a demand that is forecast to increase with the continued growth of the agriculture industry and demand for emissions-free fuels.[4] While currently predominately produced from fossil fuels with substantial CO_2 emissions,[5] hydrogen can also be produced with minimal emissions (depending on the electricity source) through electrochemical water electrolysis. Importantly, water electrolyzers can be paired with variable sources of renewable energy as a means of energy storage to enable further penetration of renewable technologies (i.e., solar and wind) into the energy sector.[6]

For electrolytic hydrogen to become commercially competitive, however, anode catalysts must be improved to increase the efficiency of the kinetically limited oxygen evolution reaction (OER) and reduce electricity and catalyst costs.[1−3] While alkaline water electrolyzer systems allow for a variety of earth-abundant high-performance catalysts,[2,7,8] proton exchange membrane (PEM) electrolyzers currently provide higher current densities, improved efficiencies, and greater product purity.[9] However, the highly acidic and corrosive environment of a PEM electrolyzer places severe limitations on applicable catalyst materials.[2,7] Rare, precious metal Ir-based materials remain the only industrially relevant OER catalysts in acidic media due to their relatively high activity and stability.[2] Still, Ir catalysts lack the performance to yield competitive hydrogen costs compared to fossil-derived hydrogen, requiring large applied voltages and high catalyst loadings.[10,11]

Although Ir oxides exhibit the best balance between activity and stability of known materials, Ir oxide has suboptimal oxygen intermediate binding energetics, quantities that strongly correlate with OER activity.[12] Modulating the electronic structure of Ir oxide to improve the oxygen binding energetics can thus theoretically enhance its intrinsic activity and lower the electricity and precious metal loading requirements of PEM electrolyzers. Alloying is one promising method for tuning catalyst intrinsic activity that has previously led to substantial progress in catalyst development and the

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fundamental understanding of Pt-based catalysts for the oxygen reduction reaction (ORR).[13−20] Recent work has investigated similar strategies to enhance the performance of Ir-based materials as OER catalysts. For example, acid-stable, inert materials such as W, Sn, Nb, and Ti have been added in an effort to dilute and stabilize Ir catalysts;[21−23] however, such materials generally demonstrate a performance similar to that of pure Ir oxide. Unstable transition metals (TMs) like Ni,[24−27] Co,[26,27] Fe,[28] Mn,[29] and Cu[30] have also been incorporated into Ir catalysts in an effort to modify the intrinsic OER activity. Indeed, IrNi bimetallic oxides[25] and IrCo oxide nanowires[27] have recently shown enhanced specific activity compared to that of Ir oxide. Additionally, surface-leached Ir-based crystalline materials such as $SrIrO_3$ have led to substantial improvements in Ir intrinsic activity by stabilizing unique surface site geometries.[31] While well-defined systematic studies of surface-leached alloy systems have led to enhanced activity and fundamental insight into Pt-based ORR catalysts, few analogous studies of Ir-based materials for the OER have been performed.

This work systematically explores the OER activity and stability of electrochemically oxidized Ir alloys in an acidic electrolyte to identify improved chemistries and provide insight into structure−function relationships. Electron beam evaporation was utilized to co-deposit compact thin films of Ir, $IrSn_2$, IrCr, IrTi, and IrNi. The alloy composition was found to impact material performance with the IrCr system demonstrating enhanced specific activity over Ir oxide and the highest stability of the alloys tested. Density functional theory (DFT) modeling indicates that the electrochemical leaching observed experimentally may stabilize highly active Cr dopant sites with near optimal adsorbate energetics leading to enhanced OER activity over pure Ir oxide. Through controlled material synthesis, advanced characterization, and theoretical modeling, this study elucidates material performance trends and highlights the potential for further nanostructuring of the IrCr materials system to improve PEM electrolyzer performance and reduce precious metal requirements.

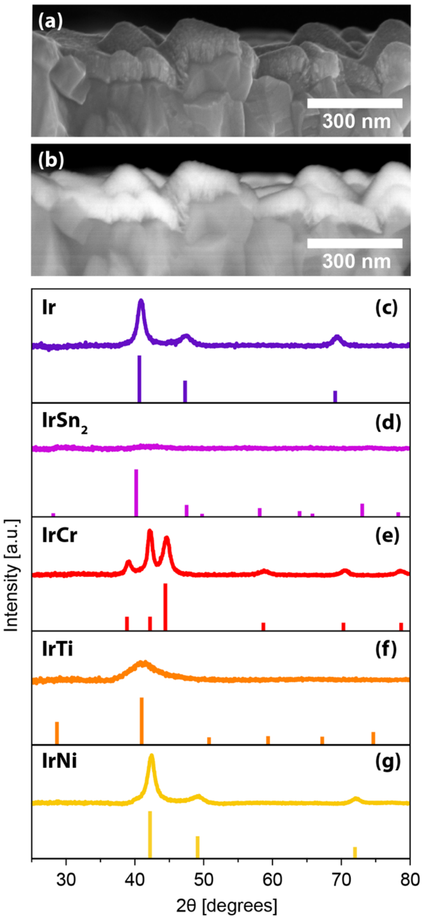

Figure 1. (a) Secondary electron (SE) and (b) backscattered electron (BSE) SEM micrographs of a typical Ir alloy film on an FTO substrate (shown: $IrCr_{ox}$ after quasi-steady state OER electrochemical testing). The Ir-based film is most evident as the bright top layer visible in BSE mode. GI-XRD of (c) Ir, (d) $IrSn_2$, (e) IrCr, (f) IrTi, and (g) IrNi deposited on amorphous glass substrates. Experimental patterns are shown as the top curve, while reference patterns are shown on the bottom of each graph. Reference patterns for the stoichiometric alloys: Ir (00-006-0598), $IrSn_2$ (01-073-2713), IrCr (04-001-1114), IrTi (01-074-5949), and IrNi (04-001-3158).

RESULTS

Film Synthesis and Characterization. Electron beam co-evaporation was used to deposit thin films of Ir, $IrSn_2$, IrCr, IrTi, and IrNi onto fluorinated tin oxide (FTO) substrates (see the Supporting Information for details). Cross-sectional scanning electron microscopy (SEM) (Figure 1a,b) illustrates that the films form dense, conformal 50−60 nm coatings. Grazing incidence X-ray diffraction (GI-XRD) analysis (Figure 1) indicates that electron beam co-evaporation results in catalyst films with no evidence of phase separation, which is commonly observed for other Ir-based catalyst materials.[21,32,33] The Ir, IrCr, and IrNi films are crystalline, matching the reference patterns of their stoichiometric metallic alloys. On the contrary, $IrSn_2$ shows poor crystallinity with no diffraction features, indicating that it is amorphous. The crystal structures corresponding to the matching reference patterns (Figure 1) illustrate that the different alloys impart unique geometric modifications with IrNi forming a strained solid solution of the metallic Ir face-centered cubic structure with 3.5% lattice compression and IrCr forming a hexagonal unit cell. Enhanced (111), (200), and (111) reflections observed for Ir, IrCr, and IrNi, respectively, suggest that crystalline films are preferentially oriented. IrTi displays one broad diffraction peak, consistent with either preferentially oriented IrTi or strained metallic Ir; further differentiation between these possibilities is challenging as there are no additional XRD peaks.

Electrochemical Performance. The electrocatalytic activity of the Ir alloy films for the OER was evaluated in 0.5 M sulfuric acid with quasi-steady state polarization [30 s potential holds at each electrode potential step (see the Supporting Information for details)]. To emphasize that materials are electrochemically oxidized during testing, bimetallic systems are termed IrM_{ox} after electrochemical testing. Figure 2 and Table S2 show the geometric activity (electrode area-based) of the catalyst films, while Figure S10 shows the cyclic voltammograms. Ir_{ox} was found to have an OER activity comparable to that of other Ir films deposited by physical vapor deposition.[34] The geometric activity is highly affected by the material composition, with $IrCr_{ox}$ showing enhanced activity, $IrNi_{ox}$ showing commensurate activity, and $IrSn_{2,ox}$ and $IrTi_{ox}$ showing decreased OER geometric activity compared to that of Ir_{ox}. Table S2 summarizes the activity and Tafel slopes of the materials. $IrCr_{ox}$ was found to outperform Ir_{ox} with >2.2 times the geometric current density at 1.65 V versus RHE and a more desirable Tafel slope (59 and 64 mV

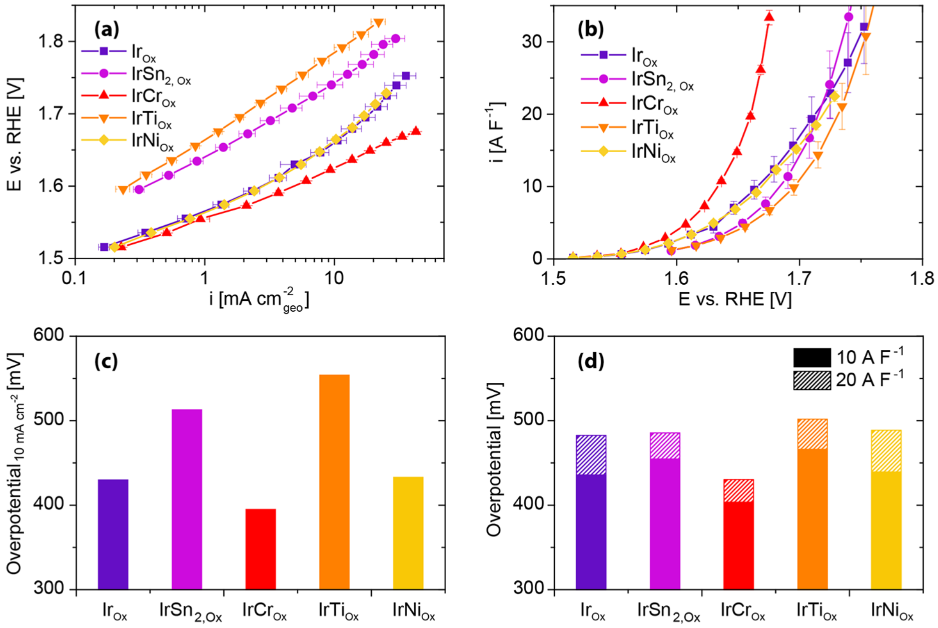

Figure 2. Electrochemical OER activity of electrochemically oxidized Ir, $IrSn_2$, IrCr, IrTi, and IrNi in 0.5 M H_2SO_4. (a) Geometric current density Tafel plot. (b) DLC-normalized specific activity. Overpotential required to achieve (c) 10 mA $cm^{-2}{}_{geo}$ and (d) 10 and 20 A F^{-1}.

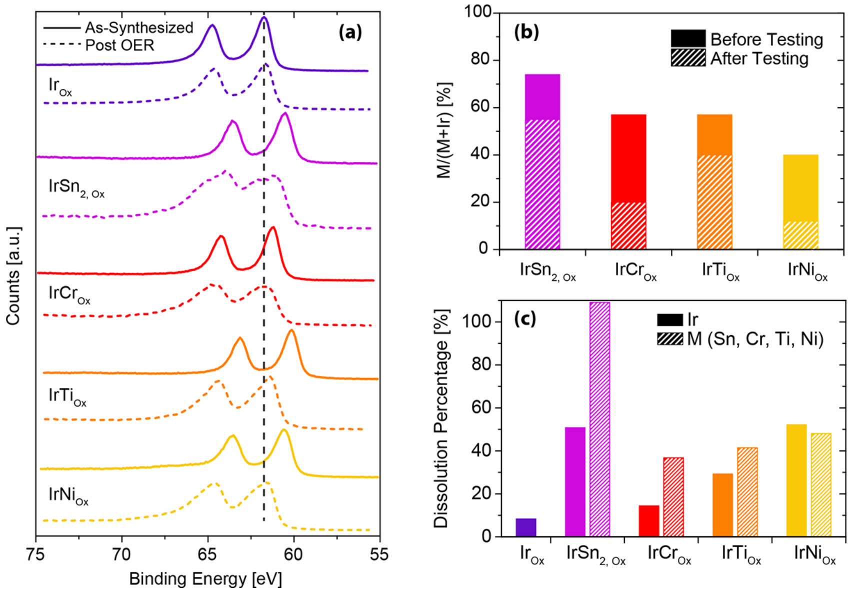

Figure 3. (a) XPS of Ir 4f peaks before (solid lines) and after (dashed lines) OER testing. The black vertical line is provided to guide the eye. (b) XPS-determined surface composition represented as the non-noble alloy metal, M (i.e., Sn, Cr, Ti, or Ni), atomic concentration before (solid bars) and after quasi-steady state OER polarization (striped bars). The concentrations of all non-noble metals decrease, but they are still present in the near-surface region after testing. (c) ICP-MS-measured Ir (solid bars) and non-noble metal (striped bars) dissolution percentage of total loaded amount [determined from quartz crystal microbalance (QCM) measurements during deposition] of each metal after 6 h chronopotentiometric stability tests at 10 mA $cm^{-2}{}_{geo}$ in 0.5 M H_2SO_4. More than 100% Sn loss is reflective of small errors in composition estimation from QCM measurements and electrolyte evaporation during stability testing.

decade^{-1} for $IrCr_{ox}$ and Ir_{ox}, respectively). Additionally, while the Tafel slopes of all of the other tested materials shift to 120−150 mV decade^{-1} at high current densities, often ascribed to a change in the reaction mechanism,[35,36] $IrCr_{ox}$ maintains a low Tafel slope (83 mV decade^{-1}). This suggests that the transition in the rate-determining step observed for the other materials is possibly delayed or prevented in $IrCr_{ox}$ as a result of modifications to the surface structure, electronic properties, or reaction mechanism.

To determine trends in the intrinsic activity, OER measurements must be normalized to the electrochemically active surface area (ECSA). Unfortunately, no ECSA measurement technique exists for Ir-based materials that is without considerable limitations. Redox peak integration, CO stripping, and hydrogen and mercury underpotential deposition either lead to significant errors, are inappropriate for Ir oxides, or involve hazardous materials.[37] As the most appropriate method given current knowledge and limitations for the material systems studied here, non-faradaic capacitance was used to estimate the catalyst ECSA from the double-layer capacitance.[7] To avoid errors and enable more straightforward comparisons to the literature, a general specific capacitance was not assumed, and thus, values are reported in amperes per farad instead of amperes per square centimeter of catalyst. For the sake of simplicity, the double-layer capacitance (DLC) per geometric surface area is henceforth termed the catalyst DLC.

Capacitive measurements and DLCs after OER polarization are shown in Figure S3 and Table S2, respectively, while DLC-normalized specific activities are shown in Figure 2. Upon surface area normalization, the specific activities of the catalyst materials show the same general trend as geometric activity ($IrTi_{ox}$ < $IrSn_{2,ox}$ < Ir_{ox} ∼ $IrNi_{ox}$ < $IrCr_{ox}$). Along with similar activities and Tafel slopes, Ir_{ox} and $IrNi_{ox}$ have comparable DLCs and thus exhibit nearly identical specific activities. In contrast to previously explored Ir−Ni mixed oxides,[25,38] the absence of enhanced activity for $IrNi_{ox}$ in this study may be due to differences in the synthesis route and thus resulting structures. Although $IrTi_{ox}$ and $IrSn_{2,ox}$ show significantly reduced geometric activity compared to that of Ir_{ox}, their DLCs are a factor of 4 lower and thus their intrinsic activities are commensurate with that of Ir_{ox}. At higher current densities, $IrTi_{ox}$ and $IrSn_{2,ox}$ demonstrate commensurate if not enhanced activity compared to those of Ir_{ox} and $IrNi_{ox}$ due to their lower Tafel slopes. It is interesting to note that Sn and Ti, which typically form insulating oxides under OER potentials, do not appear to have a significant impact on the OER activity of $IrSn_{2,ox}$ and $IrTi_{ox}$, respectively (i.e., $IrSn_{2,ox}$ and $IrTi_{ox}$ have intrinsic activities similar to that of Ir_{ox}). Film conductivity, however, does not appear to directly correlate to activity as Ir_{ox} is expected to be the most conductive film, but it is not the most active of the materials tested. $IrCr_{ox}$ was found to have a DLC approximately 15% greater than that of Ir_{ox} but a significantly greater surface area normalized specific activity with a >50 mV reduction in overpotential to achieve a value of 20 A F^{-1} and 2 times the specific current density at 1.65 V versus RHE compared to Ir_{ox}. In other words, after normalization by the 15% greater capacitance (which is proportional to the electrochemically accessible surface area), $IrCr_{ox}$ still has a specific activity two times greater than that of Ir_{ox}. This improvement in specific activity suggests that Cr is playing an important role in enhancing the OER catalytic activity.

Pre- and Post-Electrochemistry Characterization. Prior to electrochemical testing, X-ray photoelectron spectroscopy (XPS) shows that the as-synthesized films have near stoichiometric surface compositions with slight surface enrichment of the non-precious metal for $IrSn_2$, IrTi, and IrCr (Figure 3b). Through shifts in the Ir 4f peaks, XPS analysis illustrates that alloying alters the Ir electronic environment (see Figure 3a, Figure S2, and Table S1). While the Ir catalyst film has an Ir $4f_{7/2}$ peak (61.8 eV) consistent with an IrO_2-like surface oxide,[39] the Ir $4f_{7/2}$ peaks of the majority of the alloyed materials are shifted to substantially lower energies; IrCr, $IrSn_2$, IrNi, and IrTi have Ir $4f_{7/2}$ peaks at 61.2, 60.5, 60.5, and 60.1 eV, respectively. These values are near or even slightly below that of metallic Ir^0 at 60.8 eV.[40] While binding energy shifts to values below the metallic reference are not commonly reported for Ir materials, similar 4f XPS shifts have been observed for Pt in Pt−Cu alloys.[41] XPS spectra for Sn, Cr, Ti, and Ni from the Ir-based alloys (Figure S2) show that these elements have varying degrees of oxidation, with the spectra for most elements shifted to binding energies higher than those expected for the pure metallic materials (Table S1).

To provide insight into material evolution after electrochemistry and identify structure−function relationships, materials characterization post-OER quasi-steady state polarization was performed. GI-XRD illustrates that the synthesized materials maintain their original bulk crystallinity (Figure S4), while XPS evidences changes in the catalyst surface. All materials undergo Ir surface enrichment following OER testing (Figure 3b) with $IrSn_{2,ox}$, $IrTi_{ox}$, $IrCr_{ox}$, and $IrNi_{ox}$ having non-noble metal surface concentrations of 55, 40, 20, and 12 atom %, respectively. Angle-resolved XPS indicates that these compositions are constant for incident angles from 10° to 90° (see Figure S11); however, film roughness may decrease the reliability of these measurements. The relatively high concentration of the non-noble metal component in $IrTi_{ox}$ and $IrSn_{2,ox}$ at the catalyst surface observed by XPS may result in decreased conductivity or specific capacitance compared to that of electrochemically oxidized Ir, resulting in the low DLCs observed for these alloys.[23] In contrast, the relatively low near-surface Ni content in $IrNi_{ox}$ compared to the non-noble metal surface content of the other films and the similarity of its bulk crystal structure to that of Ir may explain the near-identical geometric and specific activity of $IrNi_{ox}$ and Ir_{ox}. For $IrCr_{ox}$, the notable Cr surface concentration after electrochemical testing suggests that Cr could play an influential role in catalysis by altering the Ir electronic structure, crystal structure, or OER active site (see theoretical results and discussion below).

In addition to changes in surface composition, the electronic structures of the Ir films are significantly altered after electrochemical quasi-steady state testing (Figure 3a, Figure S2, and Table S3). XPS analysis indicates that the Ir 4f peaks of all of the catalysts shift to higher binding energies after OER polarization due to the applied oxidative potentials. While the Ir 4f peaks of most materials resemble those of an IrO_2-like oxide, the peaks of $IrSn_{2,ox}$ and $IrTi_{ox}$ remain at binding energies lower than would be expected for a typical rutile IrO_2 or amorphous IrO_x.[40] These shifts are consistent with electronic modifications of the Ir due to the higher non-noble metal surface content observed for these materials. XPS analysis of the non-noble metal components of the catalyst films (Figure S2) reveals that they are in predominately oxidized states following OER testing with the Cr in $IrCr_{ox}$ resembling a CrO_2- or Cr_2O_3-type oxide (see the Supporting Information for details).[42,43]

To further probe material changes during the OER, inductively coupled plasma mass spectroscopy (ICP-MS) was used to quantify dissolution of the catalysts into the electrolyte during electrochemical stability measurements. Specifically, the dissolution was quantified after 2 and 6 h chronopotentiometric stability tests at 10 mA cm^{-2}_{geo} as the percentage dissolved relative to the starting amount in each catalyst film (Figure 3c and Figure S6). Chronopotentiometry (Figure S5) illustrates activity degradation for all catalyst films, with $IrCr_{ox}$ and $IrTi_{ox}$ showing the smallest increase in overpotential over the 6 h stability test (9 and 5 mV h^{-1}, respectively, compared to 22 mV h^{-1} for Ir_{ox}). Non-noble metal dissolution increases in the order Cr < Ti < Ni < Sn and occurs more rapidly during the first 2 h of testing (Figure S6). For $IrCr_{ox}$ and $IrTi_{ox}$, non-noble metal dissolution after the first 2 h of stability testing proceeds at a rate equivalent to the Ir dissolution rate, consistent with the formation and maintenance of an Ir-rich surface layer as was observed in XPS. Complete Sn dissolution

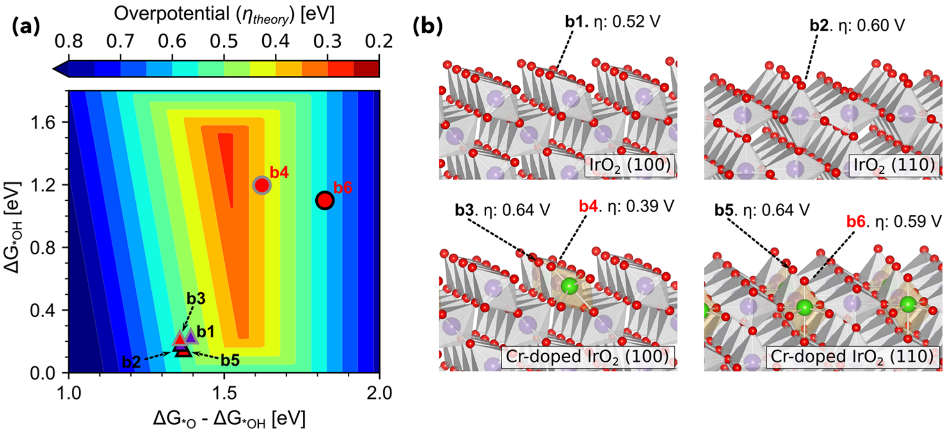

Figure 4. (a) OER activity volcano plot constructed with $\Delta G_{*O} - \Delta G_{*OH}$ and ΔG_{*OH} descriptors and with the *OOH vs *OH scaling fit shown in Figure S8. Sites from pure rutile IrO_2 are colored purple, while sites from Cr-doped IrO_2 are colored red. Circles and triangles correspond to Cr and Ir active sites, respectively. Theoretical overpotentials corresponding to surfaces cut along the (110) plane are represented by black borders, while gray borders correspond to the (100) facet. Additional calculated sites are provided in Figure S7. (b) Corresponding structures and overpotentials of active sites from panel a. Atom color: purple for Ir, green for Cr, and red for O. The structures and corresponding energies are also available at Catalysis-Hub.org.[59,60]

observed via ICP-MS is consistent with the complete loss of activity of $IrSn_2$ during the 6 h stability test. For all materials, the level of Ir dissolution is generally lower than that of the corresponding non-noble metal, consistent with Ir surface enrichment observed in XPS, and increases in the following order: Ir_{ox} < $IrCr_{ox}$ < $IrTi_{ox}$ < $IrNi_{ox}$ ∼ $IrSn_{2,ox}$. The bimetallic materials potentially experience enhanced Ir dissolution compared to the pure Ir_{ox} film as a result of the formation of less stable Ir sites during non-noble metal leaching. Due to the initial metallic nature of these materials, all Ir dissolution rates observed here are greater than those expected for preoxidized Ir materials.[44,45] Of the alloys tested, $IrCr_{ox}$ demonstrates the highest activity and stability to dissolution under OER conditions with further improvements in stability possible through oxidative pretreatments.[44−46]

Theoretical Activity of $IrCr_{ox}$. The origin of the OER activity enhancement in $IrCr_{ox}$ over Ir_{ox} was investigated using DFT calculations. Consistent with post-electrochemistry XPS and as the most stable Ir oxide phase,[47] rutile IrO_2 was used as the catalyst model structure. Given the low surface concentration of Cr after OER testing (20 atom %), $IrCr_{ox}$ was modeled as Cr-doped IrO_2 with Cr atoms replacing Ir at different positions in the rutile IrO_2 crystal. This type of Cr-doped structure is consistent with our post-electrochemistry XPS analysis that shows that Cr resembles a CrO_2-type oxide (see Figure 3, Figure S2, and Table S3 for XPS analysis). By simulating pristine surfaces, we neglect any surface reconstruction effects, which along with maintaining a uniform crystal structure between the IrO_2 and $IrCr_{ox}$ systems, allows us to isolate the effect of doping from other structural effects, as well as reduces the computational expense considerably. The Cr-doped IrO_2 structure studied herein is similar to surface-doped structures employed to model other rutile systems.[48−51] The (110) and (100) surfaces of these materials were modeled due to their high activity and stability for the OER.[31,52,53]

Catalyst activity was assessed by computing the thermodynamic overpotential, η_{theory}, the overpotential beyond which all reaction steps are thermodynamically favorable. Specifically, the theoretical overpotential for the commonly utilized associative OER mechanism[12,54−58] (using *OH, *O, and *OOH as the OER intermediates) can be computed by evaluating the following equation:

$$\eta_{\text{theory}} = \max(\Delta G_{*\text{OH}}, \Delta G_{*\text{O}} - \Delta G_{*\text{OH}}, \Delta G_{*\text{OOH}} - \Delta G_{*\text{O}}, 4.92\text{ eV} - \Delta G_{*\text{OOH}}) - 1.23\text{ V} \qquad (1)$$

Using this methodology, the activity was computed for several Ir- and Cr-substituted sites in the IrO_2 structure (see Table S5 for a full list of modeled sites and energies; for further details about calculating the adsorption free energies, see the Computational Details in the Supporting Information).

The predicted theoretical overpotentials for various sites in IrO_2 and Cr-doped IrO_2 are compared on an OER activity volcano plot using $\Delta G_{*O} - \Delta G_{*OH}$ and ΔG_{*OH} descriptor energies in Figure 4a. A linear scaling relation between *OOH and *OH intermediates was used to account for the *OOH dependence of η_{theory} (see Figure S8). The theoretical overpotentials of the pure rutile IrO_2 (100) and (110) surface sites are 0.52 and 0.6 V, respectively, and lie on the strong binding side of the OER activity volcano (see Figure 4b for corresponding structures). These overpotentials differ from the results of Seitz and co-workers[31] due to our more physical inclusion of spin polarization, which changes the adsorption energies by ∼0.2 eV (see the Supporting Information for further discussion).

OER intermediates bind slightly stronger on the (110) facet than on the (100) facet due to the lower average oxidation state of the active surface metal atoms on the (110) facet (see Bader charge analysis in Table S6). When the surfaces are doped with Cr, the activity and oxygen adsorbate binding energies of Ir sites remain relatively unchanged (<0.15 eV change), indicating strong metallic screening at the surface. Interestingly, the Cr sites in Cr-doped IrO_2 have significantly weakened binding of the OER intermediates relative to the Ir sites (weakened on average by 1.3 eV for *O and 0.9 eV for OH* compared to Ir sites). More importantly, ΔG_{*O} is weakened more than ΔG_{*OH} (see Figure S8), which results in the effective increase in the $\Delta G_{*O} - \Delta G_{*OH}$ energy (shown in Figure 4a). This combined effect lowers the predicted theoretical overpotentials on the Cr dopant sites compared to the Ir sites in pure IrO_2 with the overpotential decreasing from 0.52 to 0.39 V on the (100) surface and from 0.60 to 0.59 V on the (110) surface (see Figure 4b for corresponding structures). The calculated Bader charge of the Cr dopant in bulk rutile IrO_2 (+1.72 e^-) is nearly identical to the charge of the Cr^{4+} cation in bulk rutile CrO_2 (+1.77 e^-), and therefore, it effectively resembles a Cr^{4+} site in the conductive environment of IrO_2 (see Table S6 for full Bader charge analysis). Additional calculations on Ir sites with subsurface Cr dopants (Figure S7) yielded theoretical overpotentials similar to those calculated for the other Ir sites. These results suggest that surface Cr atoms are predominately responsible for the experimentally observed enhancement in the specific activity of $IrCr_{ox}$ compared to Ir_{ox}. The identification of highly active Cr sites is consistent with the enhanced OER activity observed for other Cr-based systems[48,50,51,61,62] and motivates optimization and nanostructuring of the $IrCr_{ox}$ system.

■ CONCLUSION

In conclusion, Ir alloys of $IrSn_2$, IrCr, IrTi, and IrNi were synthesized via electron beam co-evaporation and evaluated for OER catalysis in acid. OER activities were found to be highly dependent on catalyst film composition with geometric and specific activity increasing as follows: $IrTi_{ox} < IrSn_{2,ox} < Ir_{ox} \sim IrNi_{ox} < IrCr_{ox}$. The $IrCr_{ox}$ catalyst outperforms pure Ir_{ox} with over 2 times greater activity based on both the geometric and specific current density at 1.65 V versus RHE. Post-electrochemical characterization of the catalyst films illustrates that metal leaching results in an Ir-enriched surface that still contains a significant amount of non-noble metal species. Of the mixed metal oxides, the $IrCr_{ox}$ catalyst also showed the highest electrochemical and material stability. To identify the origin of the enhanced catalytic performance of $IrCr_{ox}$, DFT was utilized to calculate the theoretical OER activity of Cr-doped IrO_2 and pure IrO_2. Cr^{4+} dopant sites were found to have weaker and more optimal oxygen binding energies compared to those of Ir sites in both the pure and doped IrO_2, potentially accounting for the observed enhanced activity of $IrCr_{ox}$ compared to that of Ir_{ox}. The identification of such highly active dopant sites with near optimal oxygen binding energies in the Cr-doped IrO_2 structure illustrates the potential of the $IrCr_{ox}$ system for further optimization and nanostructuring and motivates a search for other materials as potential hosts for active Cr^{4+} sites. The synthesis of high-surface area $IrCr_{ox}$ is an important future direction for improving geometrically based OER activity. Through systematic studies of controlled materials, promising OER catalysts such as $IrCr_{ox}$ can be identified, optimized, and analyzed computationally to elucidate structure−function relationships and motivate chemistries toward improved water electrolysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b13697.

Experimental methods, computational methods, and additional material and electrochemical characterization (PDF)

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Notes

The authors declare no competing financial interest.

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