

Transition Metal Arsenide Catalysts for the Hydrogen Evolution Reaction

Joseph A. Gauthier,^{†,‡,§,||} Laurie A. King,^{†,‡,§,||} Faith Tucker Stults,^{†,‡} Raul A. Flores,^{†,‡} Jakob Kibsgaard,[§] Yagya N. Regmi,^{||} Karen Chan,[‡] and Thomas F. Jaramillo^{*,†,‡,§,||}

[†]SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States

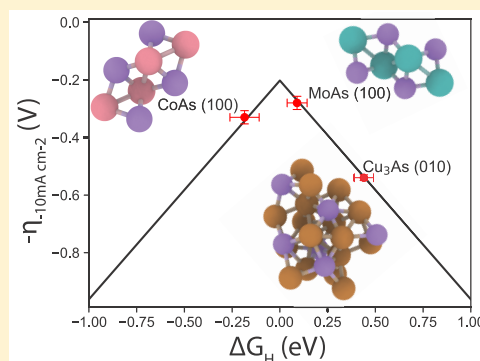
[‡]SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

[§]Department of Physics, Technical University of Denmark, Fysikvej, Building 312, Dk-2800 Kongens Lyngby, Denmark

^{||}Energy Technologies Area, Lawrence Berkeley National Laboratories, 1 Cyclotron Road, MS 0700108, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: We report, to our knowledge for the first time, a combined experimental and density functional theory (DFT) investigation into the activity and stability of cobalt, molybdenum, and copper arsenides as catalysts for the hydrogen evolution reaction (HER). We find CoAs and MoAs to be the most active arsenide materials. We discuss the trends between calculated surface vacancy formation energies and catalyst stability. Using a simple thermodynamic model of HER activity, we find consistent trends between hydrogen binding free energy and the experimentally observed activity.



INTRODUCTION

Hydrogen is an essential chemical feedstock produced globally at over 60 million tons per year for use in a wide variety of processes, including oil refining and thermochemical ammonia synthesis via the Haber–Bosch process.¹ Furthermore, hydrogen offers a sustainable pathway for the storage of renewable energy via technologies such as polymer electrolyte membrane fuel cells (PEMFC).^{2–4} However, 96% of hydrogen is currently produced from fossil fuels⁵ through processes such as the steam reforming of methane, which introduces large amounts of carbon dioxide into the atmosphere. One promising route for the sustainable production of hydrogen is through the coupling of renewable sources (e.g., wind and solar) with electrochemical water splitting.

Electrolytic hydrogen production proceeds via the hydrogen evolution reaction (HER) coupled with the oxygen evolution reaction (OER). Whereas alkaline-based electrolyzer technologies can utilize highly active earth-abundant catalysts, proton exchange membrane (PEM) electrolyzers require precious metal-based catalysts due to the highly corrosive acidic conditions.³ The most active electrocatalysts for the HER are platinum based materials, which require overpotentials of <50 mV to reach -10 mA cm^{-2} .^{6–8} However, due to the high cost and scarcity of platinum,⁹ alternative nonprecious metal based catalysts are being investigated, such as transition metal

dichalcogenides,^{10–15} carbides,^{16–18} and borides.¹⁷ More recently, transition metal phosphides have received significant attention as excellent nonprecious metal HER catalysts.^{19–22} Anion mixing, such as forming molybdenum phosphosulfide, has been proven as another route toward designing more active catalysts.²¹ Just as transition metal selenides have been found to be active for the HER following the success of MoS₂,^{15,23} with selenium one period beneath sulfur, one period beneath phosphorus lies arsenic. Transition metal arsenides (TMAs) are an unexplored family of materials for HER catalysts.

In this paper, we investigate the performance of transition metal arsenides for the HER using a combined experimental and computational approach. In this exploratory work, we synthesized and characterized three thin film transition metal arsenides, specifically, CoAs, MoAs, and Cu₃As. The films are shown to be crystalline and nanostructured. Using density functional theory (DFT), we identify the thermodynamically stable surface facets and surface terminations of these transition metal arsenides. We find trends in the experimental activities to be consistent with a simple thermodynamic picture of HER activity, where the binding free energy of hydrogen,

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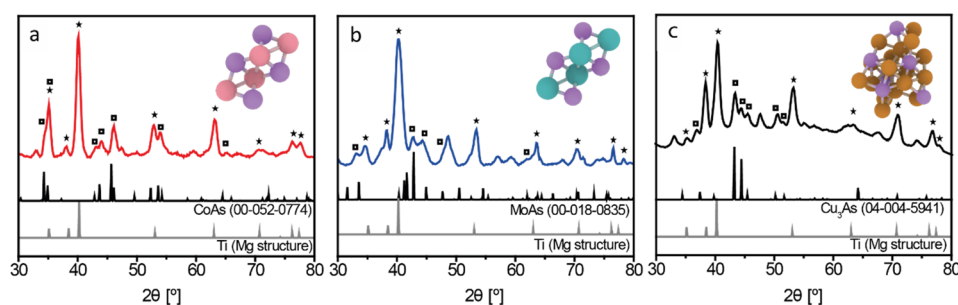


Figure 1. Physical characterization of the transition metal arsenides. X-ray diffraction spectra of the synthesized (a) CoAs, (b) MoAs, and (c) Cu_3As thin films. Reference XRD spectra for the relevant arsenide and titanium support are also shown. The titanium substrate peaks (00-054-1294) are labeled with stars; the predominant TMAs phases are labeled with squares. The inserts show the crystal structures.

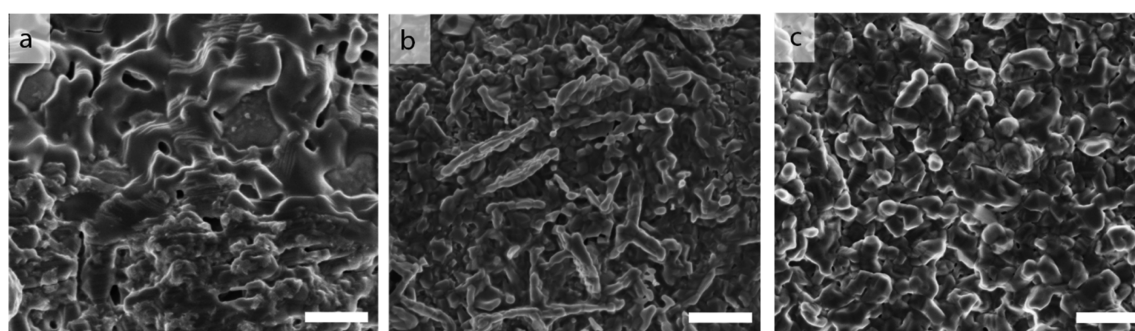


Figure 2. Scanning electron microscopy (SEM) micrographs of the synthesized (a) CoAs, (b) MoAs, and (c) Cu_3As thin films. The scale bar is 1 μm for all of the images.

ΔG_{H} is a descriptor of HER activity, as has been found previously with metals,^{24–26} metal alloys,⁷ as well as a wide variety of ionic compounds.^{10,11,16,19}

EXPERIMENTAL SECTION

The general synthesis of transition metal arsenides was analogous to work previously published for the synthesis of transition metal phosphides.^{19,21} In brief, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich), ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Fluka Analytical), copper nitrate ($\text{Cu}(\text{NO}_3)_2$, Sigma-Aldrich) and sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, Sigma) were dissolved in Millipore water to make stoichiometric 0.0625 M of transition metal arsenides in the general formula of MoAs, Cu_3As , and CoAs. Where necessary, a few drops of nitric acid (6 M) were added to the solution to ensure complete dissolution of the metal salts. To prepare the films, the solutions were drop cast onto titanium foil (0.5 cm \times 0.5 cm) on a hot plate at approximately 50 $^\circ\text{C}$ to prepare samples with a final loading of 0.25 $\text{mg} \cdot \text{cm}^{-2}$ transition metal arsenide. The foils were subsequently annealed at 750 $^\circ\text{C}$ in a forming gas atmosphere.

Materials Characterization. X-ray diffraction (XRD) was performed using a Bruker D8 Venture with a Cu ($K\alpha$) source. Electrochemical testing was performed in a standard 3-electrode configuration. A graphite carbon rod was used as a counter electrode and a mercury/mercury sulfate reference (Hache) electrode was used with 0.5 M sulfuric acid (Aldrich, 99.999%) electrolyte with an H_2 purge for all testing. The reference electrode was calibrated to the reversible hydrogen electrode (RHE). All CVs were iR -corrected using electrochemical impedance spectroscopy to calculate the uncompensated resistance.

Computational Methods. Density functional theory (DFT) in conjunction with the computational hydrogen electrode²⁷ (CHE) was used to determine hydrogen adsorption and surface energies. All calculations were performed using the Bayesian Error Estimation Functional²⁸ (BEEF) in Quantum Espresso²⁹ interfaced through the Atomic Simulation Environment³⁰ (ASE). The core electrons of copper, molybdenum, cobalt, arsenic, oxygen, and hydrogen are represented in this work by ultrasoft pseudopotentials,^{31–33} while the valence electrons have been expanded as plane waves with a kinetic energy cutoff of 600 eV and a charge density cutoff of 6000 eV. Further details of the simulation cells can be found in the [Supporting Information](#).

Predominant surface facets and terminations of Cu_3As , MoAs, and CoAs were determined using the Bravais–Friedel–Donnay–Harker (BFDH) algorithm³⁴ along with surface energy calculations. For MoAs and CoAs, the most stable facets were (001), (010), and (100), while for Cu_3As , the most stable facets were (001) and (110). The surface energies for these facets were all within a range of 0.1 eV, so we considered the activity on all of them. The surface energies are shown in [Figure S1](#). Vacancy formation energies for each surface and facet were determined, using bulk metal as the reference for metal atoms, and AsH_3 (g)³⁵ as the reference for As atoms, shown in eq 1:

$$E_{\text{vac}} = E_{\text{surf,vac}} - (E_{\text{surf}} - E_{\text{ref}}) \quad (1)$$

Here E_{vac} refers to the vacancy formation energy, $E_{\text{surf,vac}}$ refers to the energy of the surface with a vacancy, E_{surf} refers to the energy of the surface without a vacancy, and E_{ref} refers to the reference energy of the atom removed to create the vacancy.

Formation energies of various arsenide compounds were calculated and compared with tabulated literature values,³⁶ and

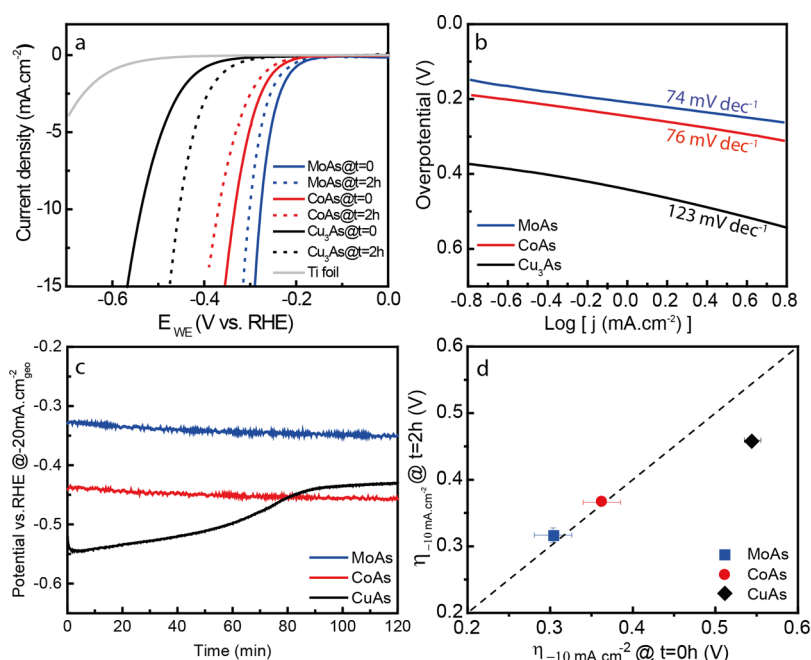


Figure 3. Electrochemical characterization of the TMA catalysts. (a) Initial (solid lines), and postchronopotentiometry hold (dashed lines) *iR*-corrected linear sweep voltammograms with current normalized by geometrical surface area. (b) Tafel plots for the synthesized TMA catalysts. (c) Chronopotentiometry measurements at $-20 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$. (d) Initial overpotential ($@ -10 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$) plotted as a function of the postchronopotentiometry hold overpotential ($@ -10 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$). The average performance of three sibling samples is plotted with error bars representing the standard deviation. The diagonal dashed line is the response for a stable catalyst.

were found to be in reasonable agreement (Figure S2 in the Supporting Information), suggesting the use of GGA-DFT to be appropriate for these systems. Following Kibsgaard et al.,¹⁹ we assume that the HER activity arises predominantly from sites where hydrogen adsorption energies, ΔG_{H} , are closest to zero.

RESULTS AND DISCUSSIONS

Drop casting was used to prepare thin films of CoAs, MoAs, and Cu_3As on Ti foil substrates. The transition metal arsenide (TMA) catalysts synthesized in a forming gas environment at 750°C . X-ray diffraction (XRD) patterns in Figure 1 and Table S1 show that crystalline metal arsenides were obtained. The predominant phases synthesized were CoAs, MoAs, and Cu_3As . CoAs and MoAs adopt orthorhombic crystal structure while Cu_3As is hexagonal. In each diffractogram the Ti substrate peaks are clearly visible (see Supporting Information for further details). The morphology of the synthesized TM-As films was probed by scanning electron microscopy (SEM) (Figure 2a–c). The thin films appear relatively dense, with a nanostructured surface. Feature sizes are generally consistent across the three films, with no distinct difference in morphology observed.

Catalytic Activity and Stability. A 3-electrode electrochemical cell was used to assess the catalytic activity of the synthesized TMA films as well as the Ti-foil substrate. All three TMA showed good activity for the HER (Figure 2a). MoAs demonstrated the best geometric current density with 303 mV overpotential required to reach $-10 \text{ mA}\cdot\text{cm}^{-2}$. The overall order of geometric activity for the TMA films was $\text{MoAs} > \text{CoAs} > \text{Cu}_3\text{As}$. The Ti foil substrate demonstrated poor activity for the HER, reaching $-10 \text{ mA}\cdot\text{cm}^{-2}$ at -0.767 V vs RHE. It is of note that due to the conductive nature of our Ti substrate, 4-point probe measurements on the as-

synthesized catalysts could not be conducted to assess the conductivity of the TMA catalysts. Although we did not measure the conductivity of the synthesized catalysts, Figure 2a clearly demonstrates that the films are sufficiently conductive for this application, reaching current densities of up to $-15 \text{ mA}\cdot\text{cm}^{-2}$ at reasonable overpotentials. This matches what would be expected given literature electrical conductivity values for transition metal arsenides.^{37,38}

To further investigate the activity of the catalysts, Tafel slopes were calculated for the synthesized TMA catalysts (Table S2, Figure S3). The average Tafel slopes were 74 , 76 , and $123 \text{ mV}\cdot\text{dec}^{-1}$ for MoAs, CoAs, and Cu_3As , respectively. These values are higher than that for the transition metal phosphides (typically $50\text{--}60 \text{ mV}\cdot\text{dec}^{-1}$) and platinum ($30 \text{ mV}\cdot\text{dec}^{-1}$). The higher Tafel slopes indicate that the Volmer step may be the rate-determining step rather than Tafel and Heyrovsky steps. However, while these values can be used as a guide for the identification of HER mechanisms, the Tafel analysis is based on a set of assumptions that do not universally hold. Indeed, factors such as conductivity, solvent environment, and surface defects are known to complicate analysis of the Tafel kinetics. The electrochemical surface area (ECSA) for each of the synthesized TMA films was also estimated (details provided in the Supporting Information). The HER activity normalized by the ECSA showed similar trends to the geometric activities (Figure S3) whereby MoAs and CoAs are shown to be more active than Cu_3As .

Toward understanding the experimental trends observed in the HER activity, we performed DFT calculations to determine the differential hydrogen adsorption free energies, ΔG_{H} . This method has previously shown that ΔG_{H} is a good descriptor for HER activity on transition metals,²⁶ transition bimetallic alloys,⁶ transition metal sulfides,^{10,11} and transition metal phosphides.¹⁹ Specifically, ΔG_{H} values that are closest to 0 eV

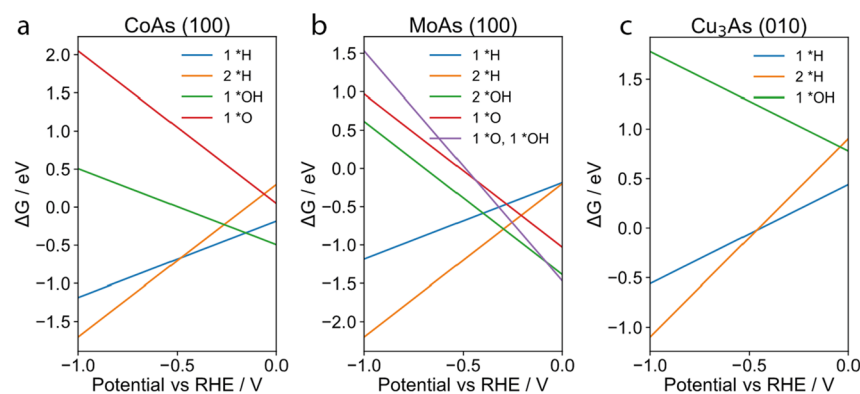


Figure 4. Pourbaix diagram for most active TMA facets: (a) CoAs (100); (b) MoAs (100); (c) Cu₃As (010). Each line in the legends denote the surface coverage. For example, 2*H corresponds to two bound hydrogens in the unit cell, while 1*O, 1*OH corresponds to having both a bound oxygen and a bound hydroxyl in the unit cell.

have previously shown to demonstrate the highest intrinsic activity for the HER. Details regarding the calculation of ΔG_{H} can be found in the [Supporting Information](#). In brief, we use the theoretically determined limiting potential U_{L} as an estimate of activity, defined as the potential where all steps in the HER mechanism become exergonic. For the HER, a two coupled proton–electron transfer process, this is simply defined as $U_{\text{L}} = -\frac{|\Delta G_{\text{H}}|}{e}$, and so activity is maximized at $U_{\text{L}} = 0$, $\Delta G_{\text{H}} = 0$. U_{L} has been shown to correlate well with experimental trends in activity for a number of processes.^{6,7,10,11,19,26} We utilized a Pourbaix analysis to determine the likely surface coverage and arrive at a U_{L} that accounts for *O or *OH poisoning of active sites, since some of the surfaces investigated interact strongly with water.

The BFDH algorithm³⁴ was used to determine likely crystal facets, based on the geometry of the primitive unit cell. Calculated surface energies, seen in [Figure S1](#), were all within 0.1 eV and so every facet was tested for activity. Initial calculations screened the various crystal facets for each TMAs catalyst to determine the most active facet (CoAs (100), MoAs (100), and Cu₃As (010)). Pourbaix diagrams were then calculated for these identified active facets ([Figure 3](#)). Lattice parameters and images of the surface termination for each material and facet are shown in [Table S3](#).

[Figure 4a](#) shows the calculated Pourbaix diagram for the CoAs (100) facet. At 0 V vs RHE, the dominant coverage on CoAs (100) is a single *OH bound to the surface. However, as the potential is made increasing negative and reaches -0.18 V vs RHE, the bound *OH species is displaced by *H, which then becomes active for HER through a Volmer–Heyrovsky mechanism. The binding energy of H* on this surface is $\Delta G_{\text{H}} = -0.18$ eV. Overall, this gives a corresponding limiting potential $U_{\text{L}} = -0.18$ V. As the potential is made even more negative, the dominant surface coverage shifts to having two bound *H in the unit cell.

Parts b and c of [Figure 4](#) show the calculated Pourbaix diagram for the most active facets of MoAs and Cu₃As, respectively. A limiting potential of $U_{\text{L}} = -0.09$ V vs RHE for MoAs (100) and $U_{\text{L}} = -0.44$ V vs RHE for Cu₃As (010) was calculated.

The stable coverage on MoAs (100) is an oxygen terminated surface illustrated in [Figure 5](#). There, hydrogen adsorbs onto *O forming *OH, from which HER occurs. Cu₃As does not strongly bind oxygen containing compounds, where HER occurs at a relatively low coverage of hydrogen. The Pourbaix

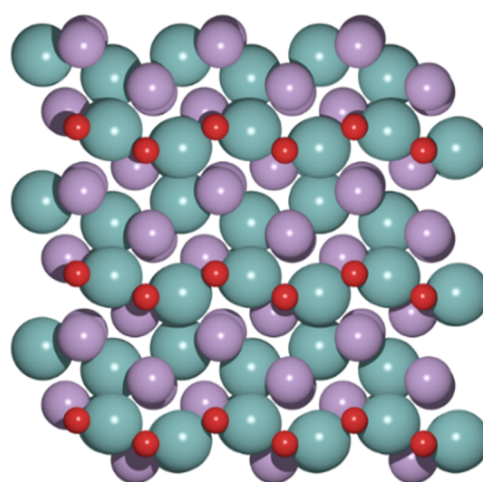


Figure 5. Stable surface termination of MoAs (100) surface. Purple spheres represent arsenic atoms, with blue-green representing molybdenum and red, oxygen.

diagram for Cu₃As shows a simpler case, where the surface is fairly weak binding, meaning no competition with bound oxygen species occurs, and HER occurs at a low coverage.

Calculated Pourbaix diagrams and U_{L} for the remaining facets of the three materials can be found in the [Supporting Information Figure S4](#) and [Table S4](#). [Figure 6](#) shows the comparison between experiment and theoretically determined descriptors. On the y-axis are (cf. [Figure 3c](#)) the experimentally measured overpotentials required to reach a current density of $-10 \text{ mA}\cdot\text{cm}^{-2}$, and on the x-axis are the theoretically determined binding free energies of hydrogen. Volcano plots were also prepared for current densities of -2.5 and $-15 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$ revealing similar trends between the three materials ([Figure S5](#)). A volcano shape emerges from the three points (the solid black line is a line of best fit to guide the eye), suggesting the consistency between experimental and theoretical activities.

To evaluate the stability of the TMAs catalysts, 2 h chronopotentiometry holds at current densities of $-20 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$ were performed ([Figure 3c](#)). The potential required to reach $-10 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$ was assessed before and after the chronopotentiometry hold by LSVs ([Figure 2d](#)). Both the MoAs and CoAs are found to be relatively stable, with just a 4 and 13 mV loss in potential required to reach $-10 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$.

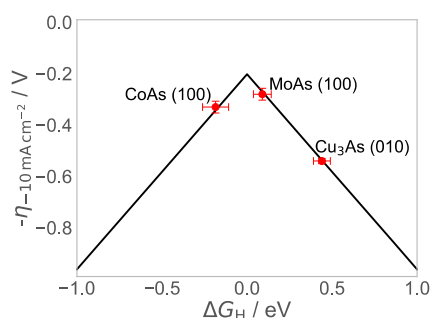


Figure 6. HER volcano plot for transition metal arsenides plotting the experimentally measured overpotential required to reach -10 mA cm^{-2} as a function of the calculated binding energy of hydrogen on the catalyst surface (ΔG_{H}). Error bars on the x -axis represent the standard deviation as estimated by the BEEF ensemble. Error bars on the y -axis represent the standard deviation among three repeated experiments. The solid line is shown to guide the eye.

respectively. We speculate that one of the following factors could lead to an improvement such as this: (1) the reductive removal of a surface oxide resulting in a more conductive surface; (2) the roughening of the catalyst surface during electrochemical testing resulting in an increased surface area. A calculation was performed to confirm that the amount of current passed during the 2 h stability test is 2 orders of magnitude greater than that required to electrochemically corrode the films during the durability measurement (see [Supporting Information](#) for details). Conversely, the Cu_3As samples on average gain 85 mV in the potential required to reach $-10 \text{ mA cm}^{-2}_{\text{geo}}$. These differences in stability observed for the three TMAs catalysts is indeed an intriguing observation. SEM was performed post electrochemical testing ([Figure S6](#)) and revealed that surface rearrangements/morphological changes did occur during the stability measurements. In particular, Cu_3As showed the appearance of smaller nanoparticle features (50–100 nm) post stability testing. This finding is supported by theory, where only Cu_3As was found to have favorable vacancy formation energies (about 1 eV downhill when moving two copper atoms from the (010) unit cell to bulk copper); the vacancies were included in the investigation of HER activity.

CONCLUSIONS

In conclusion, we investigated a previously unexplored class of materials for the HER, using a combined theoretical and experimental approach. Consistent with previous studies of similar ionic compounds, we find that trends in experimental activity agree with trends in the hydrogen binding energy, a simple descriptor for HER activity. We find that two of the synthesized transition metal arsenides, MoAs and CoAs, exhibit a moderate overpotential on a normalized electrochemical surface area basis. We further find that CoAs binds hydrogen too strongly, while MoAs is on the weak binding side of the volcano, which suggests an alloy may lie closer to the peak of the volcano and show higher HER activity. On MoAs, the poisoning of the surface by $^*\text{O}$ indicates that HER proceeds through the oxidized surface. Cu_3As exhibits a large overpotential, due to a relatively weak binding energy of H, and likely undergoes some surface reconstruction due to the instability of the surface relative to bulk copper.

Our analysis here was based on a purely thermodynamic approach, which implicitly assumes the associated activation

barriers to scale similarly with binding energies regardless of binding site. This work was exploratory in nature and does not represent an exhaustive investigation of this class of materials. Future work will investigate trends in activation energies on additional arsenide candidates, and a broad spectrum of ionic materials

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcc.9b05738](https://doi.org/10.1021/acs.jpcc.9b05738).

Details of the Tafel slopes, electrochemical active surface area methods, and the DFT calculated formation energies, surface energetics, Pourbaix diagrams, theory determined limiting potentials, and SEM micrographs post electrochemical testing, and the raw data plotted in [Figures 1–6](#). (PDF)

AUTHOR INFORMATION

Corresponding Author

*(T.F.J.) E-mail: jaramillo@stanford.edu.

ORCID

Joseph A. Gauthier: 0000-0001-9542-0988

Laurie A. King: 0000-0002-0772-2378

Raul A. Flores: 0000-0001-5047-2530

Jakob Kibsgaard: 0000-0002-9219-816X

Yagya N. Regmi: 0000-0001-6588-7683

Karen Chan: 0000-0002-6897-1108

Thomas F. Jaramillo: 0000-0001-9900-0622

Author Contributions

[†]These authors contributed equally to this work

Notes

The authors declare no competing financial interest.

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