II.C.6 Accelerated Discovery of Advanced RedOx Materials for Solar Thermal Water Splitting to Produce Renewable Hydrogen

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Overall Objectives

- Develop a computationally accelerated and experimentally validated materials-by-design approach to design materials with optimum thermodynamic, mass transport, and kinetic properties for solar thermal water splitting (STWS) that can be tailored for materials discovery for other technologies

- Use our accelerated materials discovery approach to screen doped perovskite and spinel metal oxide materials for STWS and provide a rank-ordered list of promising redox active materials

- Address fundamental and broad materials chemistry questions in accomplishing Tasks 1 and 2

- In conjunction with DOE sister project (DE-EE0006671), test promising redox materials identified by our rapid screening process using a stagnation flow reactor (SFR) to validate screening methods

Fiscal Year (FY) 2015 Objectives

- Use density functional theory (DFT) to predict hydrogen production for metal aluminates through different mechanisms; experimentally test materials to establish mechanism for STWS redox reaction

- Develop and utilize a descriptor model [1] to predict the oxygen vacancy formation energy of binary perovskites

- Develop a computational materials screening approach for new materials based on thermodynamics of established mechanism

- Calculate potential energy surface for hydrogen production reaction on a model surface (hercynite)

- Initiate study of the sensitivity of metal oxide water splitting kinetics towards to composition

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(S) High-Temperature Robust Materials

(W) Materials and Catalyst Development

Technical Targets

This project involves conducting fundamental studies of novel perovskite and spinel redox active materials to identify those with high H_2 production capacities (>200 µmol H_2/$g_{material}$ /cycle), low thermal reduction temperatures (<1,400°C), fast kinetics, low cost, and enthalpies of reduction high enough to drive the water splitting reaction, but not so high as to be thermodynamically inefficient. Insights gained from these studies will be applied towards the design of a flowing particle solar water splitting system that meets the following DOE hydrogen production targets:

- Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost: $2/kg

- Annual Reaction Material Cost: $11,000/yr-TPD (metric tons per day) H_2

- Solar to Hydrogen Energy Conversion Ratio: 26%

FY 2015 Accomplishments

- Predicted redox reaction mechanism and H_2 capacity of three metal aluminate materials using DFT calculations; experimentally validated computational results

- Identified a simple criteria and approach for assessing redox capabilities of new materials

- Used oxygen vacancy formation model to screen 1,078 binary perovskites and 590 binary spinels for STWS capabilities

- Characterized atomistic hydrogen formation reaction mechanism on hercynite surface

✦   ✦   ✦   ✦   ✦

INTRODUCTION

Two-step thermochemical redox processes based on metal oxide cycles are a promising route to efficiently capture and store solar energy because they have the potential to operate at high thermal efficiencies, are chemically simple, and require less land and water to operate than competing biomass, artificial photosynthesis and photovoltaic-driven electrolysis. In two-step metal-oxide-based STWS, a metal oxide is heated using concentrated solar thermal energy to a temperature at which it reduces, generating O_2. Subsequently, H_2O is introduced to the system as steam to re-oxidize the material to its initial state and generate H_2. Traditionally, two types of metal oxide redox chemistries are utilized in solar thermochemical H_2O splitting. The first prototypical chemistry utilizes a stoichiometric mechanism. Such materials undergo a phase change to produce a stoichiometric quantity of O_2. The vast majority of simple binary metal oxides previously examined for use as STWS materials have been examined under the assumption that they operate via this mechanism. The most studied of these are ZnO, SnO_2, and Fe_3O_4. While these materials theoretically exhibit high redox potential, in practice deactivation induced by irreversible processes such as sintering or the formation of liquid phases and metal vaporization lead to loss of active oxide. The second chemistry is based on the formation of oxygen vacancies in metal oxides during reduction, as shown in Equations 1 and 2, for which ceria is a representative example. Such redox materials are thermally reduced without undergoing a phase change, as the lattice is able to accommodate the strain induced by oxygen vacancy formation. These materials are thermally stable, although the extent of reduction, and hence H_2 production capacity per cycle, is small compared to other reducible oxides.

$$MO_x \rightarrow MO_{x-\delta} + \delta/2 \ O_2 \qquad (1)$$
$$MO_{x-\delta} + \delta \ H_2O \rightarrow MO_x + \delta \ H_2 \qquad (2)$$
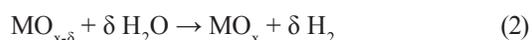
The ideal material for efficiently driving STWS has not yet been identified, although a large number of materials have been examined. To be a STWS material, a candidate material must undergo both reduction and water oxidation; to be a practical STWS material, it must reduce at temperatures which are achievable using concentrated sunlight and at which reactor containment materials do not degrade (<1,700°C). The assessment of STWS materials and cycles has generally been undertaken by one of two approaches: (1) evaluating a set of previously proposed water splitting cycles for their practical viability; (2) identifying novel materials from a broad set of candidates by predicting their ability to drive STWS. Because an optimal STWS material or cycle has not yet been identified, our focus is on the latter of these two approaches, which we call "STWS materials screening."

APPROACH

Our STWS materials screening approach to discover materials for an efficient cost effective H_2 production process involves using computational materials modeling based primarily on DFT quantum mechanical simulations to rapidly predict basic materials properties, which we use as descriptors within a model we will develop for predicting the redox properties of candidate materials. The computational screening will be used to guide an experimental effort to synthesize and validate promising redox materials identified by our rapid screening process.

Although in principle an ab initio approach could predict the redox properties of candidate metals oxides directly, the large number of possible materials (e.g., over 1.3 million possibilities just for earth abundant, non-radioactive, non-toxic, quaternary perovskites with the formula $A^1_{0.75}A^2_{0.25}B^1_{0.75}B^2_{0.25}O_3$), the properties of which are unknown a priori, makes this approach intractable. Thus, we are developing a computationally accelerated STWS material discovery and development method where DFT is used only to predict materials stability relative to melting and phase segregation and to predict basic materials properties. We are developing an advanced descriptor model informed by DFT calculated band gaps, materials heats of formation, and other fundamental properties to predict a material's redox thermodynamics and will apply this descriptor model to screen materials for STWS performance. Materials predicted to possess favorable thermodynamic properties for STWS will be analyzed for their kinetic properties for STWS using a novel descriptor method to quickly predict the kinetics of the rate-limiting step. At each stage of the screening process, the rigor and the associated computational costs of the methods will be increased, and materials not meeting material performance criteria, i.e., possessing a high likelihood of poor STWS performance, will be eliminated. Throughout this process, experiments will be carried out in conjunction with our DOE sister project led by Alan Weimer to validate the computational models, analyze stability and water spitting behavior, and inform the choice of performance criteria for material down-selection. This stage of computational "prototyping" will identify materials that are likely to have high H_2 production capacity (>200 µmol H_2/g/cycle), low thermal reduction temperature (<1,400°C), an enthalpy of reduction sufficiently high to drive the reactions at reasonable rates but not so high as to be thermodynamically inefficient (near the enthalpy of splitting water, 280 kJ/mol), and short reduction and oxidation times (<15 min).

RESULTS

During this fiscal year, active redox material development has focused on establishing and validating a screening criteria for metal oxide materials, using the

screening method to evaluate binary perovskites, and performing kinetics studies on a model surface. In order to assess new materials we first propose a two-step screening method then use this method to predict the redox reaction mechanism and H_2 production capacities for three aluminate materials, pure hercynite ($FeAl_2O_4$), cobalt aluminate ($CoAl_2O_4$), and doped-hercynite ($Co_xFe_{1-x}Al_2O_4$).

Since the enthalpies of both the reduction and oxidation steps together must be greater than the enthalpy of water splitting (Equation 3) and the oxidation of the material must be exothermic (to ensure a spontaneous oxidation reaction (since), the reduction enthalpy must be >286 kJ/mol. Therefore, 286 kJ/mol represents a minimum reduction enthalpy for STWS, and based on this requirement we can assess the viability of candidate STWS materials or reaction mechanisms by comparing their reduction enthalpies to the enthalpy required for water splitting, i.e., if the metal oxide reduction enthalpy is less than the water splitting enthalpy, the suggested material or reaction mechanism is unlikely to drive STWS without the input of external work.

$$\Delta H_{STWS} = \Delta H_{TR} + \Delta H_{OX} \geq 286 \; kJ/mol \qquad (3)$$

Although a reduced material may store sufficient energy to split water, this does not guarantee that it will do so after reduction at a reasonable operating temperature. As the reduction enthalpy of a particular material increases, the driving force for the water splitting reaction also increases, although the extent of reduction and the associated H_2 production capacity at a given reduction temperature decreases. Therefore, the extent of reduction, if any, must be determined at practical reduction temperatures. To do this, we proposed using a benchmark material to predict the H_2 production capacities of candidate materials. We used a method in which a material known to drive water splitting, even if very poorly, was chosen as a standard against which to compare readily obtainable reduction enthalpies of candidate materials within a similar STWS class, i.e., a similar crystal structure and reaction mechanism.

Thus, we assessed the water splitting ability of materials by a two-stage screening: first, we determined if the material or reaction pathway has sufficient energy to split water. If so, then we compared its ability to drive water splitting to previously characterized materials of a similar class as outlined in Equation 4.

$$r_{ben,can}(T) = \frac{e^{\left(\frac{-\Delta G_{can}}{RT}\right)}}{e^{\left(\frac{-\Delta G_{ben}}{RT}\right)}} \approx \frac{e^{\left(\frac{-\Delta H_{can}}{RT}\right)}}{e^{\left(\frac{-\Delta H_{ben}}{RT}\right)}} = e^{\left(\frac{-\Delta\Delta H_{can,ben}}{RT}\right)} \quad (4)$$

Two possible reactions mechanisms, a stoichiometric mechanism and an oxygen-vacancy mechanism, for three aluminates were examined using this screening method. In the stoichiometric reaction mechanism, the active material decomposes to a reduced phase to produce a stoichiometric quantity of O_2. In the O-vacancy reaction mechanism,

materials produce oxygen vacancies within the lattice of the host material without it decomposing into a different phase; these vacancies are subsequently filled during oxidation by the O atoms of split H_2O molecules.

We calculated the reduction energy of the doped-hercynite ($Co_xFe_{1-x}Al_2O_4$) stoichiometric reaction to be 175 kJ/mol, indicating that the stoichiometric doped-hercynite cycle does not possess the reducing power to split water. For the O-vacancy mechanism, we calculated a reduction energy of 384–621 kJ/mol, where the wide range stems from the variation in local environments of the oxygen atom involved in the formation of an O-vacancy. This indicates that reduced $Co_{0.5}Fe_{0.5}Al_2O_4$ has sufficient energy to split water and suggests that the doped-hercynite cycle could operate via an O-vacancy mechanism. Furthermore, the energies of these different structures was calculated to determine the relative number of different sites within the material. Similar calculations were done using pure hercynite and cobalt aluminate and are summarized in Figure 1. This information was then used to predict a H_2 production capacity of 1:0.7:2x10^{-4} for $FeAl_2O_4$:$Co_{0.5}Fe_{0.5}Al_2O_4$:$CoAl_2O_4$ for the O-vacancy mechanism. Alternatively, if the enthalpic minimum for water splitting does not exist, Equation 4 predicts a relative production capacity of 1:0.012:0.004 for $CoAl_2O_4$:$Co_{0.5}Fe_{0.5}Al_2O_4$:$FeAl_2O_4$ for the stoichiometric mechanism.

These predicted H_2 capacities were then tested experimentally by cycling the materials near-isothermally between 1,500°C and 1,350°C in an SFR. The H_2 production ratios of the aluminates were found to be 1:0.6:0 for $FeAl_2O_4$:$Co_{0.5}Fe_{0.5}Al_2O_4$:$CoAl_2O_4$. This agrees with the computationally predicted relative H_2 production capacities for the aluminates operating via an O-vacancy mechanism and suggests that the thermodynamic screening parameters for STWS viability and reaction mechanism are valid.

We used this screening criteria in conjunction with a predictive O-vacancy formation energy model [1] to screen 1,078 binary perovskites and 590 binary spinels. These materials have the general structure and are comprised of all combinations of the elements shown in Figure 2. The results of the screening are shown in Figure 3.

In addition to thermodynamic screening conducted during the past fiscal year, we performed theoretical kinetics studies to characterize the hydrogen formation reaction pathway on the hercynite, $FeAl_2O_4$, (100) surface. We considered the reaction starting from three possible initial states, (1) a defect free surface, (2) a surface oxygen vacancy coordinated to three aluminum and no iron atoms (referred to as O-Al3), and (3) a surface oxygen vacancy coordinated to two aluminum and one iron atom (O-FeAl2). We found that the O-FeAl2 surface was the thermodynamically most prevalent surface at operating conditions.
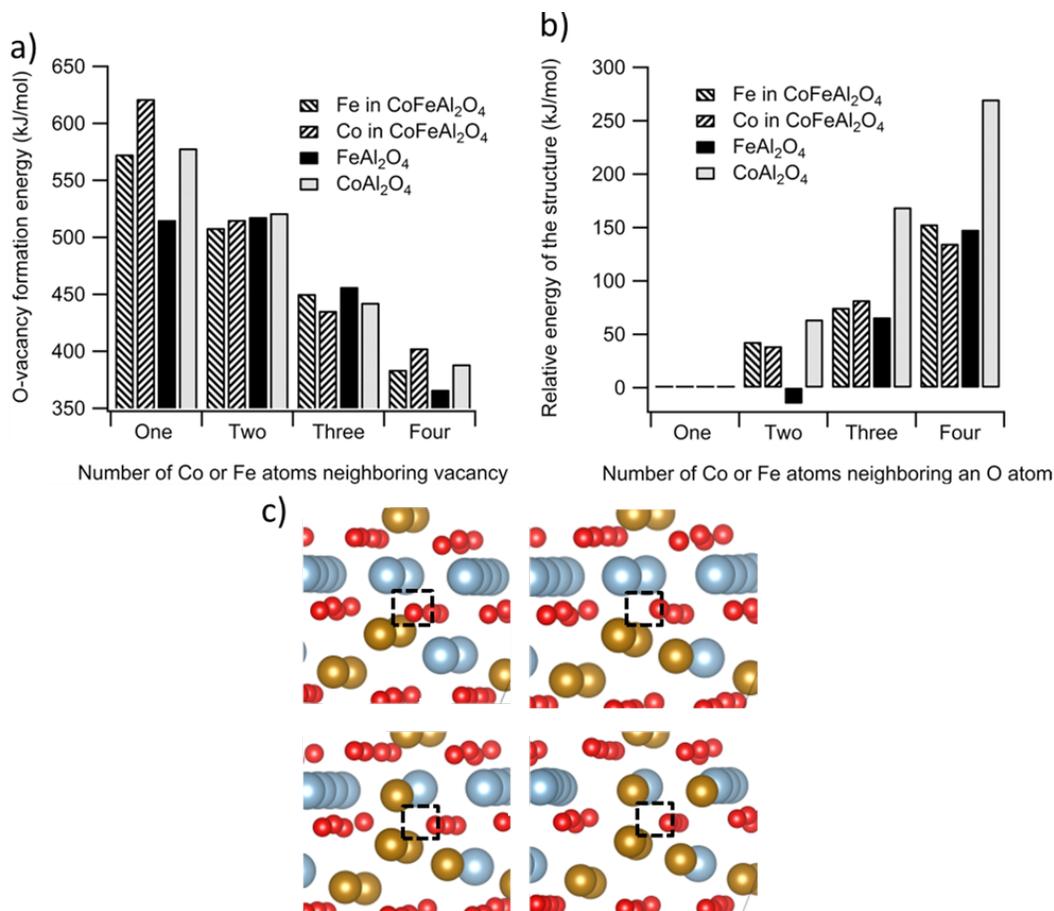
FIGURE 1. (a) Calculated O-vacancy formation energies at sites with varying numbers of Co or Fe nearest neighbors, and (b) the relative energies of exchanging cations to produce O sites with multiple Co or Fe nearest-neighbors. (c) The configurations of the ions in the $FeAl_2O_4$ spinel for an O-vacancy with one (top left), two (top right), three (bottom left), and four Fe neighbors (bottom right). The large blue, medium gold and small red spheres represent Al, Fe and O atoms, respectively and the black square indicates the location of an O-vacancy.

For this case, we have identified two kinetic pathways, which can be seen in Figure 4. In each of these pathways water dissociates into a hydroxide which occupies the oxygen vacancy. The destination of the remaining hydrogen atom differentiates these two kinetic pathways. Dissociation onto a nearby oxygen occurs in the "hydroxide pathway." This produces an intermediate with two protic hydrogens adsorbed to a defect free surface. These protic hydrogens then must pull electron density from the surface to produce H_2. For the hydroxide pathway the dissociation occurs with a lower barrier than the hydrogen formation. Along the "hydride pathway" the dissociated hydrogen adsorbs onto a nearby iron atom. When coordinated to the surface iron the hydrogen is hydridic, and the ensuing reaction between the oppositely charged hydrogens occurs with a lower activation barrier than in the hydroxide pathway.

For the defect free surface activation barriers were not considered. Without an oxygen vacancy to fill dissociation of water leaves an adsorbed oxygen on the surface. This final state lies higher in energy than the activation barriers for the oxygen vacancy case and thus its activation barrier must lie even higher and is thus unlikely to significantly contribute to the overall reaction. The O-Al3 case is currently neglected for a variety reasons. Primarily, it lies much higher in energy and, assuming a surface at equilibrium at a typical STWS temperature of 1,500°C, the O-FeAl2 vacancy would be more than 200 times more likely. Furthermore, because the vacancy lies far from the surface iron atoms, it can only react analogously to the previously discussed hydroxide pathway. After dissociation, no difference exists between these pathways and we have already determined that dissociation is not rate-limiting. As oxygen vacancy migration is studied it may become necessary to revisit this assumption.

CONCLUSIONS AND FUTURE DIRECTION

- Hercynite and doped hercynite redox reactions operate via an O-vacancy mechanism.
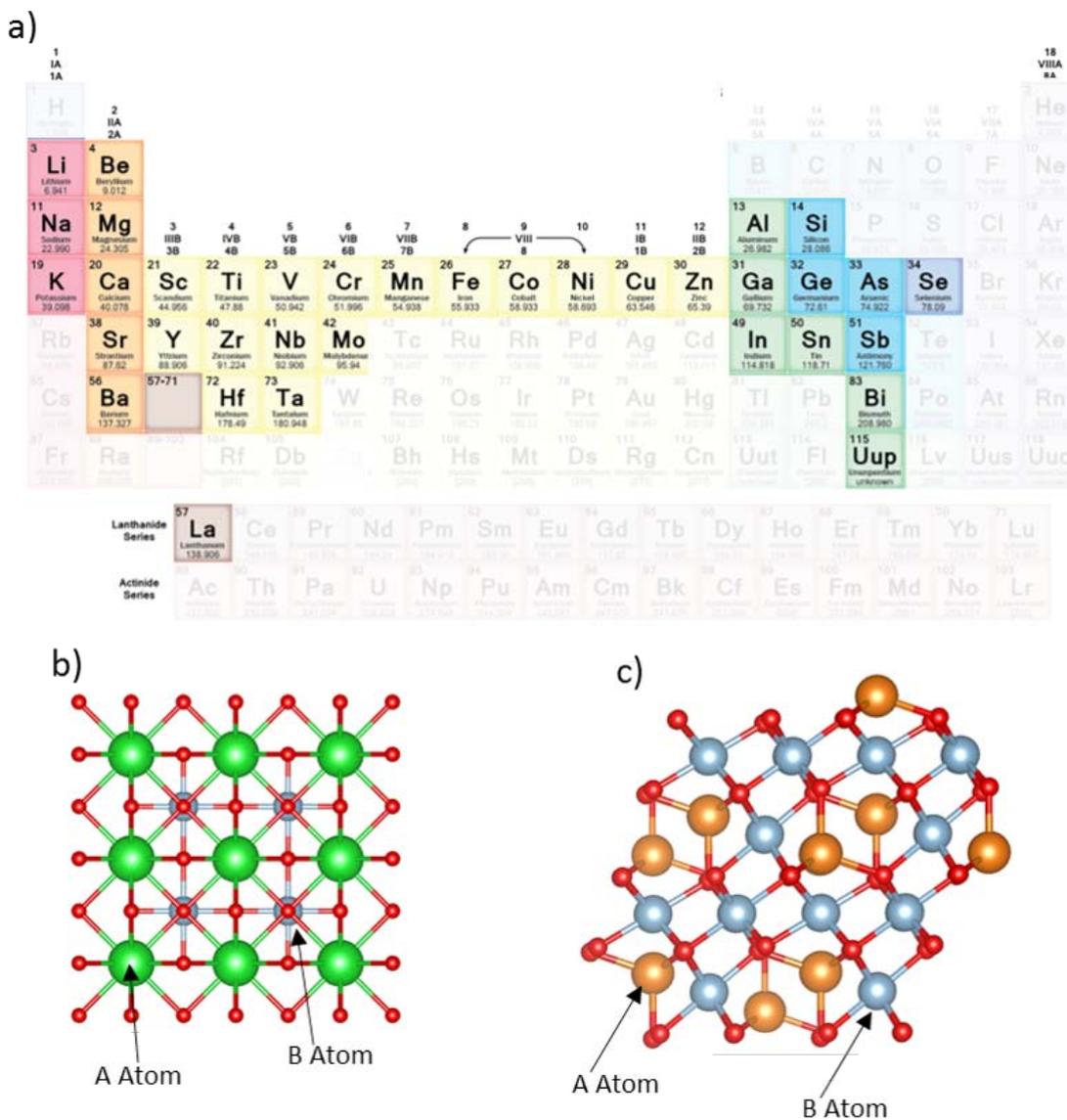
FIGURE 2. All earth abundant, non-radioactive, and non-toxic elements under consideration for forming perovskite and spinel materials.

- The two-step thermodynamic screening method can be used to accurately assess H_2 production capacities of new materials.

- An oxygen vacancy formation descriptor model was used to screen 1,078 binary perovskites and 590 binary spinels for STWS capabilities.

- Hydridic pathway for hydrogen production on a hercynite surface has a lower activation barrier than the hydroxide pathway.

- We will apply a computational approach for predicting water splitting abilities to doped perovskites and additional binary spinels.

- We will validate an oxygen vacancy formation energy model specifically for compounds of interest: perovskites and spinels.

- The project will extend the descriptor model of oxygen vacancy formation energy to systems with various spin and oxygen vacancy configurations, including "smart" scripts for automated searches.

- Important kinetic properties will be identified by substitution and removal of cations at and around the active site of reactive hercynite surface.

- We will extend results from hercynite studies to other potential STWS materials.

- We will characterize other reactions important to STWS, including oxygen vacancy formation and migration.
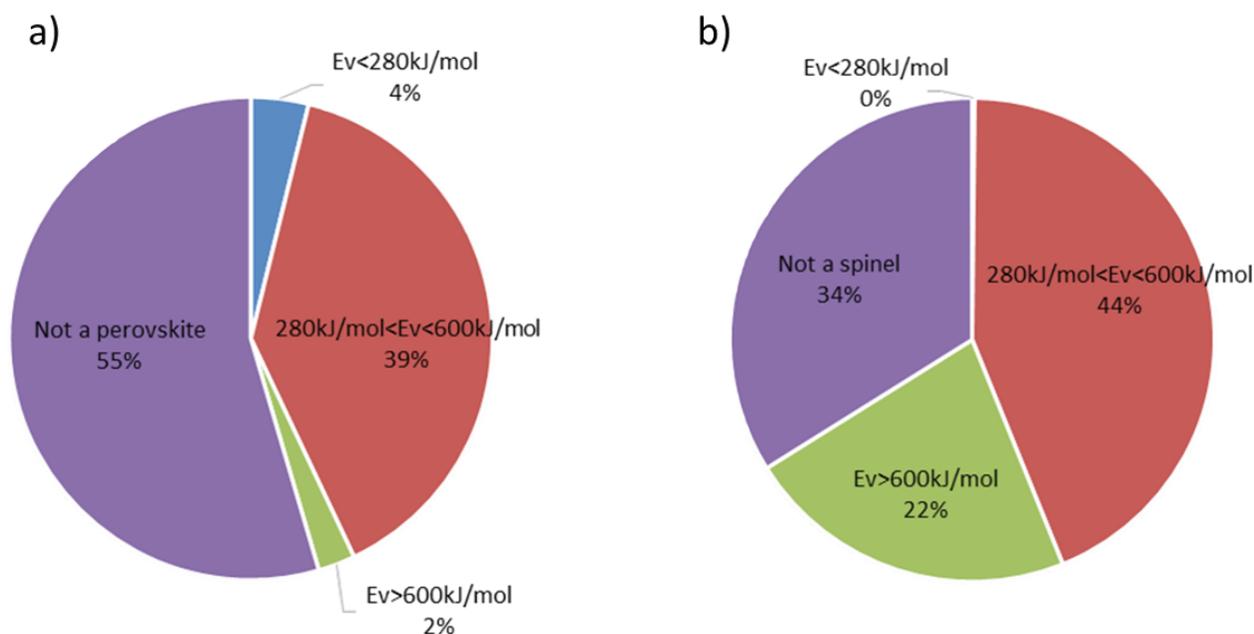
FIGURE 3. (a) Results from oxygen vacancy formation energy screening of 1078 binary perovskites. (b) Results from oxygen vacancy formation energy screening of 590 binary spinels.
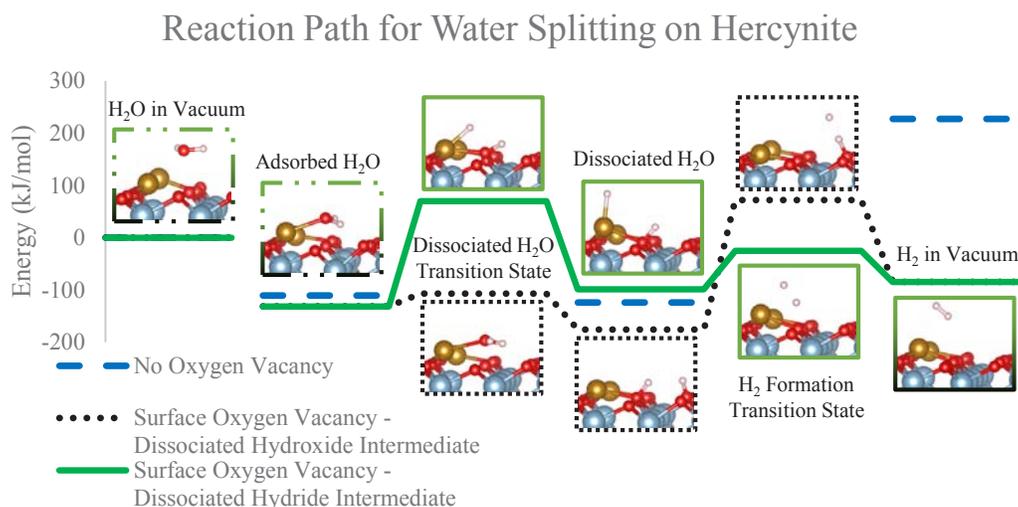
FIGURE 4. Kinetic pathways for hydrogen formation on hercynite. The surface without oxygen vacancies is show with a dashed blue, while the hydroxide and hydroxyl oxygen vacancy pathways are depicted as a dotted black line and green solid line respectively. States for which the transition state has not been identified have been left unconnected. Geometries for the oxygen vacancy pathways are depicted and formatted with borders matching the pathways as described above. Note that the first two states, H_2O in vacuum and adsorbed H_2O are identical and only shown once.

FY 2015 PUBLICATIONS/PRESENTATIONS

Publications

1. Muhich, C.L., B.D. Erhardt, I. Al Shakeri, B.J. Ward, C.B. Musgrave and A.W. Weimer, "A Review and Perspective of Efficient Hydrogen Generation via Solar Thermal Water Splitting," *WIREs Energy and Environment*, In Press, DOI: 10.1002/wene.174.

2. Muhich, C.L., K.C. Weston, D. Arifin, A.H. McDaniel, C.B. Musgrave, A.W. Weimer, "Extracting Kinetic Information from Complex Gas-solid Reaction Data," *Industrial and Engineering Chemistry Research*, 54 (16) 4113-4122 (2015). DOI: 10.1021/ie503894f.

Presentations

1. C. Muhich, B. Ehrhart, V. Witte, K. Weston, D. Arifin, A. McDaniel, E. Coker, C. Musgrave, and A. Weimer, "The Mechanism of Transition Metal Aluminates in Solar Thermal Water Splitting Reactions," presented at *The American Society of Mechanical Engineers Power and Energy Conference*, June 2015 (San Diego, CA).

2. C. Muhich, B. Ehrhart, I. Alshankiti, B. Ward, C. Musgrave, A. Weimer, "Near-Isothermal Doped-Hercynite Redox Cycle for Solar-Thermal Water Splitting," presented at *The 227th Electrochemical Society Meeting*, May 2015 (Chicago, IL).

3. C. Muhich, B. Ehrhardt, I. Al Shankiti, B. Ward, C. Musgrave, and A. Weimer, "Needed Research Focus for Achieving Cost-Effective and Reliable Solar-Thermal Water Splitting," presented at *The 227th Electrochemical Society Meeting*, May 2015 (Chicago, IL).

4. C. Muhich, K. Weston, D. Arifin, A. McDaniel, E. Coker, B. Ehrhart, V. Witte, C. Musgrave, A. Weimer, "The Mechanism of the Doped-Hercynite Cycle for Solar-thermal Water Splitting," presented at the *American Chemical Society Spring National Meeting*, March 2015 (Denver, CO).

5. A. Deml, R. O'Hayre, V. Stevanovic, A.M. Holder, C.B. Musgrave, "Material Descriptor of Oxygen Vacancy Formation Energies in Wide Band Gap Oxides," presented at the *American Chemical Society Spring National Meeting*, March 2015 (Denver, CO).

6. C. Muhich, A.W. Weimer, and C.B. Musgrave, "Rapid Computational Screening and Prototyping of Solar Thermal Water Splitting Materials," presented at *Department of Energy Fuel Cells Technology Office Webinar*, December 2014.

7. C. Muhich, K. Weston, B. Ehrhart, V. Witte, D. Arifin, A. McDaniel, E. Coker, C. Musgrave, A. Weimer, "The Chemistry and Thermodynamics of the Hercynite Cycle Solar-thermal Water Splitting Reaction," presented at *AIChE Annual Meeting*, November 2014 (Atlanta, GA).

8. C. Muhich, B. Ehrhart, K. Weston, I. Al-Shankiti, D. Arifin, A. McDaniel, C. Musgrave, A. Weimer, "Extracting Kinetic Information from Complex Gas-solid Reaction Data: the Kinetics of Hercynite Materials for Solar Thermal CO_2 Splitting," presented at *AIChE Annual Meeting*, November 2014 (Atlanta, GA).

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1. Deml, A.M., Holder, A.M., O'Hayre, R.P., Musgrave, C.B., Stevanovic, V., "Intrinsic Material Properties Dictating Oxygen Vacancy Formation Energetics in Metal Oxides," *The Journal of Physical Chemistry Letters*, 6 (2015): 1948-1953.