II.C.4 NSF/DOE Solar Hydrogen Fuel: 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 the two overall objectives above.

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

## Fiscal Year (FY) 2016 Objectives

- Apply a descriptor model [1] to predict the oxygen vacancy formation energy of binary spinels.

- Investigate spinel inversion as a method for identifying new materials.

- Validate computational methods for predicting hydrogen production capacities in binary perovskites.

- Determine reaction barriers on hercynite and doped hercynite surfaces.

- Determine transport barriers for hercynite and doped hercynite materials.

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.

(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 hydrogen 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 ultimate hydrogen production targets:

- Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost: $2.00/kg

- Annual Reaction Material Cost: $11,000/yr.-TPD H_2

- Solar to Hydrogen Energy Conversion Ratio: 26%

FY 2016 Accomplishments

- Developed a robust approach for predicting STWS ability of materials.

- Screened 1,041 binary normal spinels for thermodynamic viability. 52% of materials were found to have an O-vacancy formation energy potentially capable of driving STWS.

- Incorporated inversion into screening of spinels to identify additional promising materials.

- Evaluated the effect of structure and spin on the predicted STWS behavior for 1,343 perovskites.

- Determined the bulk transport barriers in hercynite and doped hercynite.

- Worked to identify descriptors for reaction kinetics in spinels.
- Determined reaction barriers for water dissociation reactions on hercynite and doped hercynite.

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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. Materials which operate via an oxygen vacancy based mechanism, as shown in Equations 1 and 2, are of particular interest due to their thermal stability owing to the formation of oxygen vacancies within the lattice rather than complete phase change of the material.

Equation 1. MO_x à $MO_{x-\delta} + \delta/2\ O_2$

Equation 2. $MO_{x-\delta} + \delta\ H_2O$ à $MO_x + \delta\ H_2$
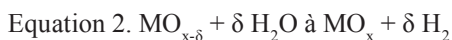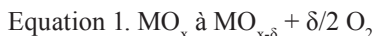
The ideal material for efficiently driving STWS has not yet been identified, although a large number of materials have been examined. To be a STWS material, a candidate material must undergo both reduction and water oxidation; to be a practical STWS material, it must reduce at temperatures which are 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 or (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 hydrogen production process involves (1) using computational materials modeling based primarily on density functional theory quantum mechanical simulations to (2) 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 (3)

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 density functional theory 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 density functional theory 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 is being increased, and materials not meeting material performance criteria, i.e., possessing a high likelihood of poor STWS performance, are eliminated. Throughout this process, experiments are being carried out in conjunction with our DOE sister project led by Prof. 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, chosen to be high enough to enable fast kinetics and high extents of reduction, but still significantly below the 1,700°C temperature at which the reactor materials degrade), 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 understanding computationally complex factors impacting predicted thermodynamic behavior of spinels (AB_2O_4) and perovskites (ABO_3), and performing kinetic studies of surface and bulk processes in spinels.

We previously established that the viability of candidate STWS materials can be assessed using the criteria that

the reduction enthalpy of a material must be greater than 286 kJ/mol to drive water splitting [1]. However, if this reduction enthalpy is too high, the material will have sufficient energy to split water, but the extent of reduction, and thus the associated H_2 production capacity, will likely be too low to meet the $2/kg H_2 production target. 500 kJ/mol has been initially chosen as the threshold to develop this screening approach. Using this screening criteria in conjunction with a predictive O-vacancy formation energy (E_v) model [2], we screened 1,041 out of a possible 1,089 binary normal spinel materials for STWS thermodynamic capability. As shown in Figure 1, we found that 52% of the materials screened have an E_v potentially capable of driving STWS.

In normal spinels, like those used for the high-throughput screening, each oxygen atom is bound to three B cation and one A cation; however, these structures may have cation disorder leading to oxygen atoms having different local cation environments in the lattice. To study the effect of this on our calculations, for six spinel materials, we calculated the E_v for oxygen vacancies in four different cation environments, ranging from 1 A to 4 A cation nearest neighbor. Each of the materials shows decreasing E_v with increasing number of A cation nearest neighbors, as shown in Figure 2a. Two materials, shown in light blue and dark blue, are found to have lower oxygen formation energies at 4 A-atom nearest neighbors than the experimentally tested material, shown in green, while maintaining the minimum required enthalpy. This indicates that they are predicted to have a higher extent of reduction at a given temperature. In
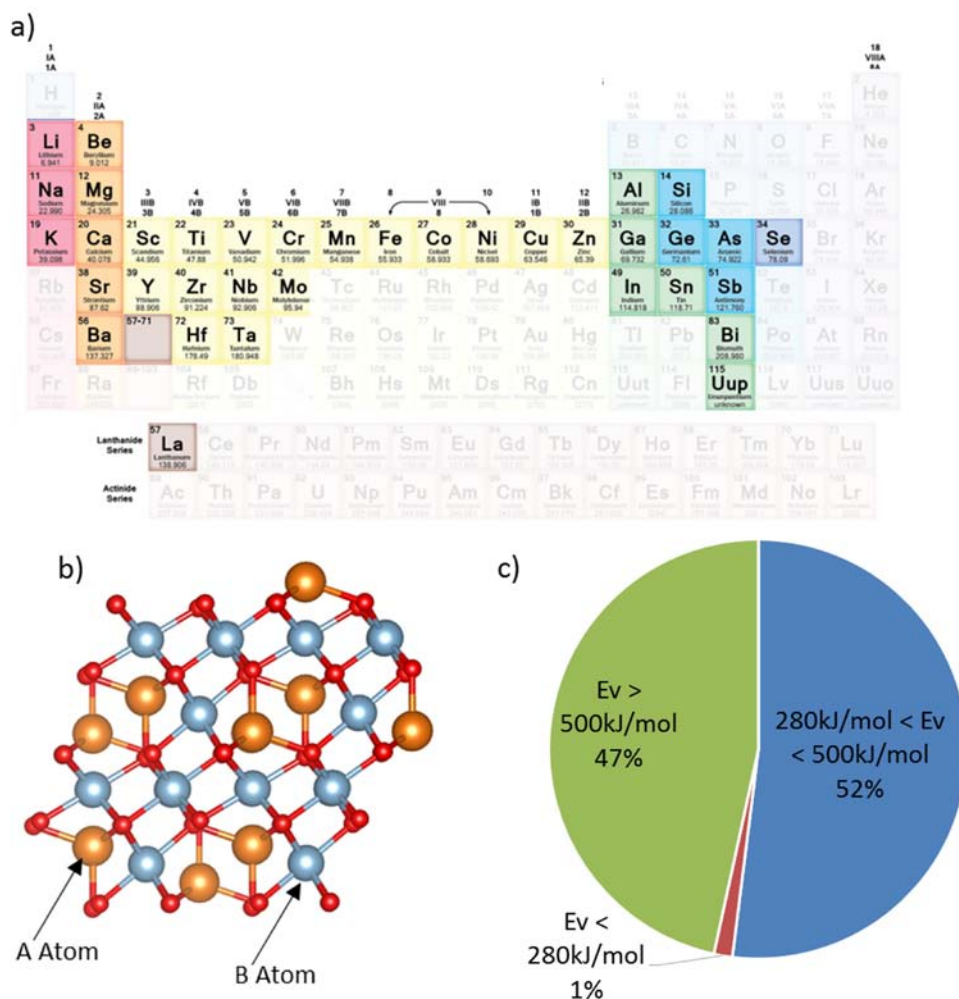

FIGURE 1. (a) All earth abundant, non-radioactive, and non-toxic elements under consideration for spinel computational screening. (b) Representative spinel structure used for high-throughput computational screening. The normal spinel structure consists of A cations which are octahedrally coordinated (orange spheres), B cations which are tetrahedrally coordinated (blue spheres), and oxygen anions (red spheres) which are bound to three A atoms and one B atom. (c) Screening results of 1,041 binary spinels.
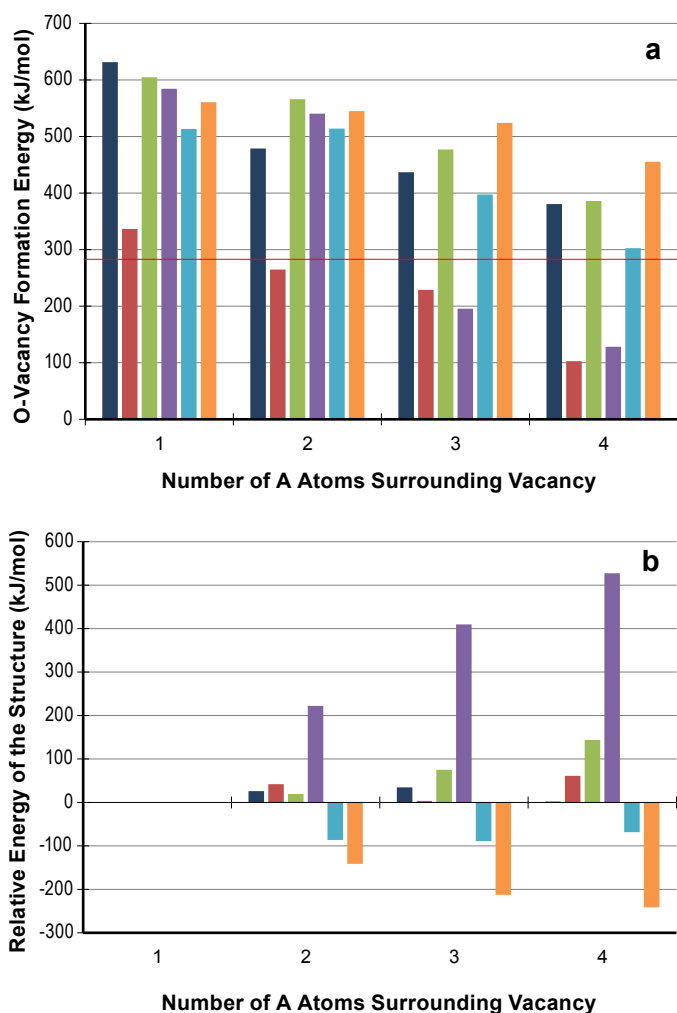
FIGURE 2. (a) Calculated O-vacancy formation energies at sites with varying numbers of A cation nearest neighbors for six spinel materials. The red line indicates the minimum required reduction enthalpy to split water. (b) The relative energies of exchanging cations to produce O sites with multiple A cation nearest-neighbors. A negative value indicates that the inverse structure is more favorable than the normal structure.

addition, as shown in Figure 2b, those two materials have negative or near zero relative structure energy at 4 A-atom nearest neighbors which indicates that these structures are more favorable than the inverse structure of the experimental material, and thus will have more active sites present. Since these materials have both a lower reduction enthalpy and more favorable inverse structures than the experimental material, they are promising materials for STWS as either dopants in the known water splitting material or as binary spinels.

For our study of perovskites, we focused on understanding the effect of structure and magnetic order on the computed STWS capability of the materials. Of particular interest, is understanding how elevated temperatures impact

these factors. This work is ongoing, but completion of this study will allow us to correctly model new perovskite materials for STWS.

To examine the kinetic properties of these materials for STWS we have been studying dopants that can be substituted into hercynite in order to improve the reaction rate. Our previous work showed that the lowest barrier to reaction occurs with what we will refer to as a hydride intermediate, a negatively charged hydrogen atom (H^-) adsorbed atop a surface metal. This can be seen in Figure 3. Our work this year has focused on the effects of doping the hercynite lattice on the sites specified in Figure 3. The most important steps for this pathway are the initial dissociation of water, and the formation of hydrogen. On undoped hercynite, dissociation is rate limiting: occurring with a significantly higher barrier (50 kcal/mol) than hydrogen formation (20 kcal/mol). Doping on nearest neighbor, and subsurface sites does not qualitatively change this picture, regardless of the dopant. The small quantitative effects can be seen for the dissociation reaction in Figure 4. Only active site doping has an appreciable effect on the reaction barrier. This year we have focused on the rate limiting step on undoped hercynite, water dissociation. A strong trend for this reaction can be seen just by visual inspection of Figure 4. Earlier transition elements have high barriers, and later transition elements have lower barriers. A simple linear fit of the periodic column to activation barrier has an r^2 value of 0.821. A few other
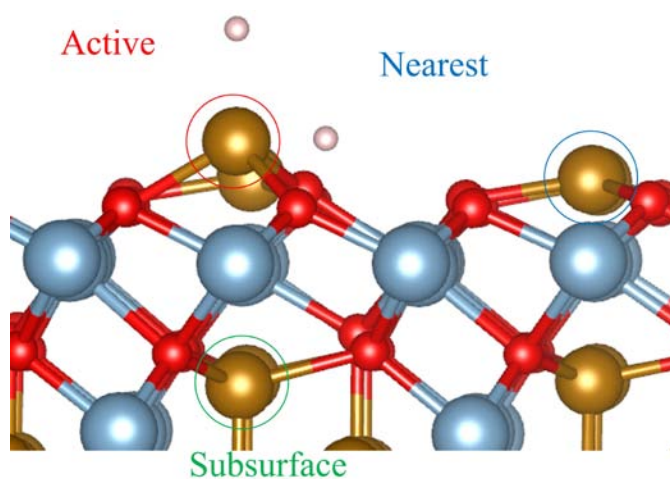

FIGURE 3. Products of water dissociation along the most active pathway, forming a surface hydride adsorbed to Fe, and a proton adsorbed to O. Also marked are the various dopant sites considered, and how they are labeled. The active site, denoted in red, participates in bonding during the reaction. The nearest site, blue, does not participate directly in reaction but neighbors the active site on the surface. The subsurface site, green, also does not participate directly in the reaction. It is the nearest Fe-dopant site to the active site
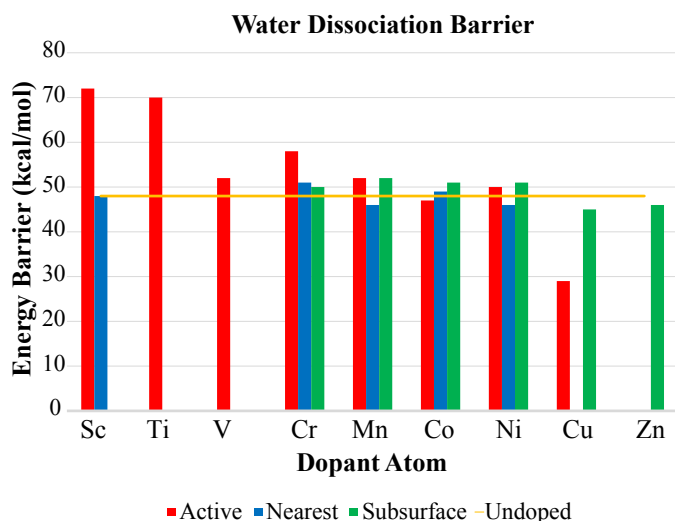
Water Dissociation Barrier

Chart: Energy Barrier (kcal/mol) vs Dopant Atom (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn)

Legend: ■ Active ■ Nearest ■ Subsurface — Undoped

FIGURE 4. Kinetic pathways for hydrogen formation on hercynite. The surface without oxygen vacancies is show in blue, while the hydroxide and hydroxyl oxygen vacancy pathways are in black and green respectively. Dashed lines connect stable states for which the transition state has not been identified. Geometries for the oxygen vacancy pathways are depicted, and color coded to match the lines. Note that the first two states, H_2O in Vacuum and Adsorbed H_2O are identical and only shown once.

descriptors, d-band center, reaction energy, and adsorption energy, were tried but did not have as strong a fit.

The limitation of our current focus, is that we are assuming identical rate limiting steps, regardless of the dopant introduced. This coming year we will need to address this assumption because we have already encountered evidence to the contrary. Earlier transition metals appear to favor a different pathway entirely. Many of the attempted transition state calculations favored relaxing towards a new pathway, which is unstable for pure hercynite. Preliminary calculations also show that later transition metals have a significant increase in the hydrogen formation reaction, causing it to be rate limiting. However, the barrier for hydrogen formation appears to be closely tied to the reverse reaction of the process. Time permitting, we would like to test this hypothesis, but it has provided an initial justification for focusing on the hydrogen dissociation reaction.

We have also begun work characterizing the relevant bulk reactions in hercynite, notably oxygen vacancy migration. So far, only a limited number of calculations have been done, but we have a found a few important trends. Due to the symmetry of the spinel lattice of hercynite there are only three possible oxygen vacancy migration pathways. Of these three, one has a significantly lower barrier than the other two. This holds even when Cu, Co, or Mn are added into the lattice. This barrier is of similar order to the surface reaction, and which reaction is most important for describing

hydrogen production would be dependent on the pre-exponential factors, and the size of the reactant particle.

CONCLUSIONS AND FUTURE DIRECTION

- Used O-vacancy formation descriptor model to screen 1,041 binary spinels for STWS capabilities.

- Identified two potential water splitting spinel materials based on screening of inverse structures.

- Evaluated the effect of structure and magnetic ordering on STWS capability of perovskites.

- Water dissociation on hercynite shows a strong periodic trend.

- Determined nearest neighbor dopants do not have a strong influence on transition state properties of reactions.

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

- Will utilize knowledge gained in study of perovskites to accurately screen new materials.

- Will modify screening methods to compute the O-vacancy formation energy of inverse spinels in a high-throughput manner.

- Will begin screening doped perovskite and spinel metal oxides for STWS capability.

- Will continue to model bulk reactions for all first row transition elements.

- Will look at other potential rate limiting steps for the surface hydrogen evolution reaction.

- Will study kinetics of promising thermodynamic candidates.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Muhich, C.L. et al., "Predicting the solar thermochemical water splitting ability and reaction mechanism of metal oxides: a case study of the hercynite family of water splitting cycles." *Energy Environ. Sci.* **8**, 3687–3699, doi:10.1039/c5ee01979f (2015).

2. Muhich, C.L., V. Poole-Aston, R.M. Trottier, A.W. Weimer and C.B. Musgrave, "A First Principles Analysis of Cation Diffusion in Mixed Metal Ferrite Spinels," *Chemistry of Materials*, **28** (1), 214–226, (2016). DOI: 10.1021/acs.chemmater.5b03911

3. Muhich, C.L., Erhardt, I. Al Shankiti, 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*, **5** (3), 261–287 (2016). DOI: 10.1002/wene.174.

4. S. Miller, C. Muhich, R. Trottier, B. Ehrhart, C. Musgrave, and A. Weimer, "Screening of Metal Oxide Materials for Solar

Thermochemical Water Splitting." Presented at the annual meeting for the American Institute of Chemical Engineers, November 2015 (Salt Lake City, UT).

5. S. Miller, R. Trottier, K. Sun, A. Weimer, and C. Musgrave, "Evaluating the Effect of Modeling Variables and Experimental Conditions on Material Development for Solar Thermochemical Water Splitting." To be presented at the annual meeting for the American Institute of Chemical Engineers, November 2016 (San Francisco, CA).

6. R. Trottier, S. Miller, and C. Musgrave. "Kinetic Evaluation of Doped Hercynite for Two Step Solar Thermochemcial Water-Splitting," To be presented at the 2016 Theory and Applications of Computational Chemistry Conference, August 2016 (Seattle, WA).

REFERENCES

1. Muhich, C.L. et al., "Predicting the solar thermochemical water splitting ability and reaction mechanism of metal oxides: a case study of the hercynite family of water splitting cycles." *Energy Environ. Sci.* **8**, 3687–3699, doi:10.1039/c5ee01979f (2015).

2. 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." *J Phys Chem Lett* **6**, 1948–1953, doi:10.1021/acs.jpclett.5b00710 (2015).