
HydroGEN Seedling: Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

Chris Wolverton (Primary Contact), Sossina Haile
Northwestern University
Dept. of Materials Science and Engineering
2220 Campus Dr.
Evanston, IL 60208
Phone: 847-467-0593
Email: c-wolverton@northwestern.edu

DOE Manager: Katie Randolph
Phone: (720) 356-1759
Email: Katie.Randolph@ee.doe.gov

Contract Number: DE-EE0008089

Project Start Date: October 1, 2017
Project End Date: September 30, 2020

Overall Objectives

- Develop a combined high-throughput computation + experimental approach to greatly accelerate materials discovery efforts for solar thermochemical hydrogen production (STCH) materials.
- Identify promising compounds that show (a) ground state stability/synthesizeability of compound, (b) thermodynamics favorable for <1,400°C reduction, and (c) thermodynamics favorable for facile water splitting. State-of-the-art currently is CeO₂ and SLMA perovskite.
- Discovery of new, higher-efficiency materials is critical toward the practical use of STCH for hydrogen production (and solar fuels, more generally).

Fiscal Year (FY) 2018 Objectives

- Experimentally measure redox thermodynamics of computationally predicted perovskites by thermal gravimetric analysis (TGA) to validate enthalpy calculations as well as obtain high-quality entropy data.
- Experimentally measure the reduction enthalpy and entropy of nine predicted perovskites.

- Validate computational predictions of oxygen vacancy formation energy by comparing with measured reduction enthalpy for perovskite materials.
- Validate high-throughput methodology for measuring thermodynamic property using thin film through electrochemical impedance.
- Initiate high-throughput computational search for promising double-perovskite compounds.

Technical Barriers

This project addresses the following technical barriers associated with solar thermochemical production of hydrogen from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- High-Temperature Robust Materials
- Materials and Catalyst Development.

Specifically, this project is focused on the identification of promising compounds that show (a) ground state stability/synthesizeability of compound, (b) thermodynamics favorable for <1,400°C reduction, and (c) thermodynamics favorable for facile water splitting. State-of-the-art currently is CeO₂ and SLMA perovskite.

Technical Targets

In Year 1 of this project, we successfully validated our combined experimental/computational strategy for accelerated discovery of novel STCH materials. This methodology will be exploited in a high-throughput fashion in the future period of the project to address the technical barriers above.

Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE hydrogen production targets:

- Solar-to-hydrogen conversion efficiency

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Reaction material cost.

FY 2018 Accomplishments

- Synthesized >10 ABO_3 compounds and characterized structural information using X-ray diffraction.
- Characterized materials using mass loss in TGA studies to obtain enthalpies and entropies of reduction of materials.
- Determined that density functional theory (DFT) calculations of oxygen vacancy formation energy accurately predict measured enthalpies, provided the correct, experimentally observed structure is used in computation. Previous high-throughput computational surveys typically performed calculations for a single structure type and hence are not sufficiently accurate for screening purposes.
- Successfully validated the computational approach for predicting enthalpies of reduction by comparison with TGA measurements. Good agreement between computation and experiment allows us to use high-throughput approaches in future project periods to accelerate discovery of STCH materials.

INTRODUCTION

Metal-oxide-based two-step solar thermochemical (STC) H₂O- and CO₂-splitting cycles are a promising route to convert solar thermal energy into fuels. The metal-oxide materials are reduced at high temperatures (Step 1), and then at low (but still elevated) temperatures, the reduced oxide is used to split H₂O or CO₂ (Step 2). However, current applications of these cycles are limited by the efficiency of the metal-oxide materials. A lower temperature for reduction is desirable, but that brings a concomitant reduction in the driving force for gas splitting. So, designing novel, high-efficiency materials is challenging. Here, we propose a joint computational-experimental project, combined with materials design strategies and high-throughput approaches, with the goal to quickly discover and demonstrate novel thermochemical materials with superior properties.

APPROACH

Background: In the first year of this project, we will use our previously developed materials design map, combined with results from (already existing) high-throughput first-principles computation to experimentally study the properties of novel, predicted materials. In particular, we will experimentally explore a set of recently predicted high-throughput perovskites. Study of these compositionally simple materials (which encompass only single elements on the A and B sites) will focus on obtaining high-quality thermodynamic properties for validation of computational prediction of enthalpy and entropy of reduction. These thermodynamic quantities play a major role in designing materials with reduced temperatures of reduction but sufficient gas-splitting rates.

The most promising of the ABO₃ materials will be modified by A and B site substitutions, both computationally and experimentally, opening an enormous combinatorial space of materials, with the promise of being able to chemically “tune in” desired STC properties. This vast composition space can only be reasonably explored using the high-throughput approaches, both computational and experimental, of this proposal. Computational screening will narrow the list of promising compounds, and experimental synthesis, stability, and redox measurements will further refine the set of materials with optimal STC properties.

RESULTS

In Year 1, we performed experimental measurements of redox thermodynamics of computationally predicted ABO₃ compounds by TGA. The aims of the experimental studies were to validate the computational determination of reduction enthalpies and to obtain high-quality entropy data. We have experimentally synthesized >10 ABO₃ compounds and determined crystal structure information by characterization via X-ray diffraction. These materials were further characterized using mass loss in TGA studies to obtain enthalpies and entropies of reduction of materials. The complete list of materials considered in Year 1 is given in Figure 1.

In parallel, DFT calculations of oxygen vacancy formation energy were performed and compared with experimental enthalpies. We determined that DFT is able to accurately predict measured enthalpies, *provided the correct, experimentally observed structure is used in computation*. The caveat is significant because previous high-throughput studies have typically assumed a single, undistorted cubic perovskite for all ABO₃ structures in calculations of oxygen vacancy formation. We find that this assumption is not accurate enough for precise materials screening, but when the experimentally observed structure type is used, the oxygen vacancy formation energies agree well with experimental measurements. Also, we have found that DFT calculations of the ground-state stability agree with the experimentally observed structure type in most cases, and the DFT ground-state structure provides a good estimate of oxygen vacancy formation energies. Thus, the prediction of these enthalpies of reduction from DFT is suitable for materials screening in high-throughput surveys, provided care is taken to determine the correct ground-state structure (or structural distortion, in the case of perovskites). The overall comparison between DFT-calculated and experimentally measured enthalpies of reduction is shown in Figure 2.

Material	Structure Type	Crystal System	Space Group
LuFeO_3	Perovskite	Orthorhombic	Pbnm
HoFeO_3	Perovskite	Orthorhombic	Pbnm
YFeO_3	Perovskite	Orthorhombic	Pnma
LuCrO_3	Perovskite	Orthorhombic	Pbnm
ErCrO_3	Perovskite	Orthorhombic	Pbnm
HoCrO_3	Perovskite	Orthorhombic	Pbnm
PrCoO_3	Perovskite	Orthorhombic	Pbnm
SmCoO_3	Perovskite	Orthorhombic	Pbnm
LaCoO_3	Perovskite	Rhombohedral	R-3c
LaNiO_3	Perovskite	Rhombohedral	R-3c
YMnO_3	" LuMnO_3 "	Hexagonal	$\text{P6}_3\text{mc}$
LuMnO_3	" LuMnO_3 "	Hexagonal	$\text{P6}_3\text{mc}$
HoMnO_3	" LuMnO_3 "	Hexagonal	$\text{P6}_3\text{mc}$
SrMnO_3	" BaMnO_3 "	Hexagonal	$\text{P6}_3/\text{mmc}$
BaMnO_3	" BaNiO_3 "	Hexagonal	$\text{P6}_3/\text{mmc}$
CaMnO_3	Perovskite	Cubic/Ortho	$\text{Pm}3\text{m}/\text{Pnma}$
LaMnO_3	Perovskite	Orthorhombic	Pnma

Figure 1. ABO_3 compounds considered in Year 1 of this project

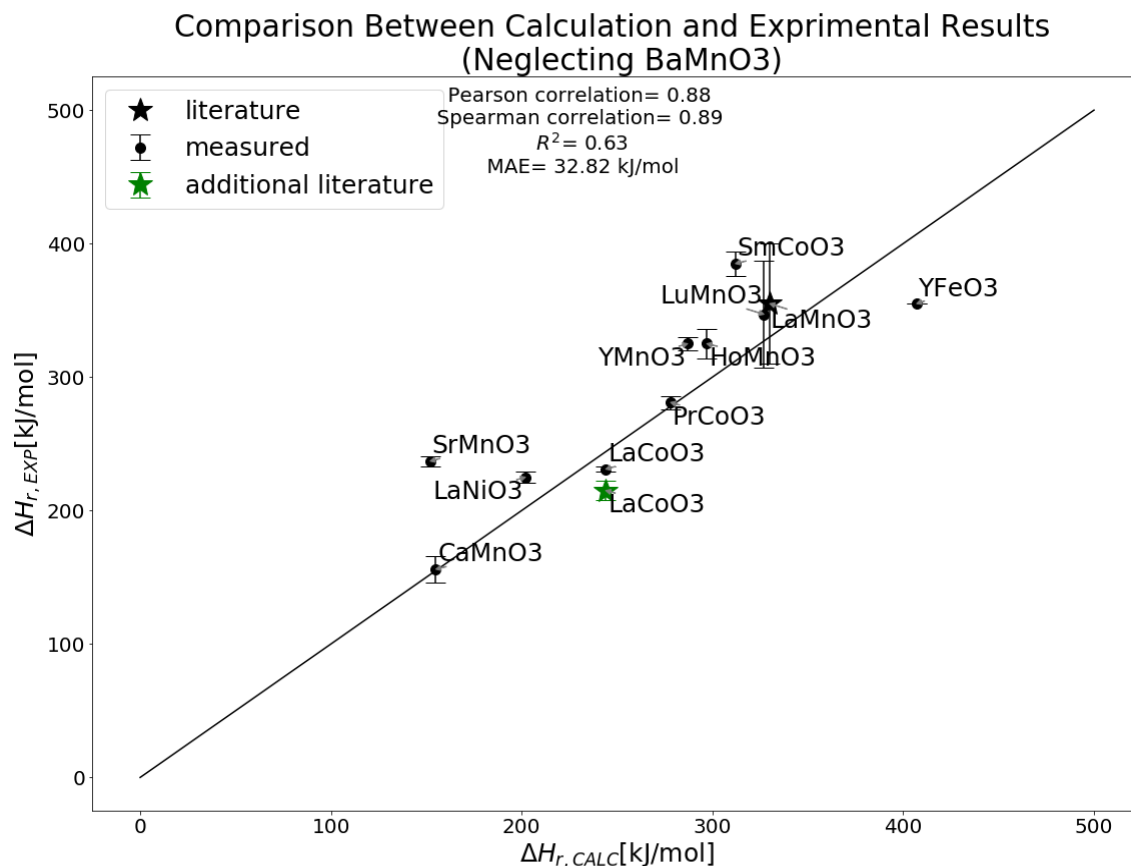


Figure 2. Comparison between calculated and experimentally measured results for reduction enthalpy of ABO₃ compounds considered. Good correlation between computation and experiment validates methodology for further high-throughput exploration to be considered in future plans.

In addition, we have begun high-throughput computational investigation of mixed A₂BB'O₆ double perovskite materials, and we have predicted several materials that satisfy screens for phase stability as well as reduction enthalpy suitable for STCH production of hydrogen. These promising materials will form the basis of some of the future experimental work in the next project period.

CONCLUSIONS AND UPCOMING ACTIVITIES

Experimental synthesis and TGA measurement of ~12 perovskite or other ABO₃ materials has been performed in Year 1. Computational prediction of these materials shows good agreement with experimental results, validating the computational strategy, provided that the correct (experimentally observed) structure is used in the calculations. Based on this successful validation, we propose the following future plans.

Experimental:

- Test site-substituted versions of the most promising materials found in Year 1
- Synthesize and test double-perovskite compounds predicted by computation in Year 1.
- Synthesize combinatorial samples for electrochemical testing.
- Continue testing of electrochemical method and comparison to TGA (e.g., thicker samples).

Computational:

- Significantly expand range of chemistries consider for potential double perovskites and use experimental data from Year 1 to validate more refined thermodynamic models.
- Begin computational search for phase-transformation reactions involving non-stoichiometry for both phases. Start with double perovskites predicted, and examine possible reduced phases involved in reactions.
- Refine models (e.g., examining outlier case of BaMnO_3 more closely):
 - Polymorphs—vacancy formation energies
 - More accurate DFT calculations.
- Obtain entropy calculations (vibrational, configurational, electronic) of reduction entropy—to compare with TGA experiments.
- Conduct high-throughput DFT screening of oxygen vacancy formation energy of double perovskites.
- Tailor oxygen vacancy formation energy by A- and B-site doping: alloying B-site metals with different reduction energies (e.g., $\text{BaMn}_x\text{Ce}_{1-x}\text{O}_3$); alloying A-site metals to control octahedral rotation, which also has large influence on oxygen vacancy formation energy.
- Expand beyond perovskites (e.g., brownmillerite $\text{A}_2\text{B}_2\text{O}_5$, Pyrochlore $\text{A}_2\text{B}_2\text{O}_7$).