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

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Overall Objectives

- Develop a combined high-throughput computation and experimental approach to greatly accelerate materials discovery efforts for solar thermochemical (STCH) materials.

- Identify promising compounds which show (1) ground state stability/synthesizeability of compound, (2) thermodynamics favorable for <1,400°C reduction, and (3) thermodynamics favorable for facile water splitting. State-of-the-art is currently CeO_2 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) 2019 Objectives

- Prepare and evaluate a site-substituted perovskites system using an electrochemical approach in the thin film form.

- Evaluate optimal material in bulk form, establish chemical stability limits, and validate thermodynamic properties.

- Prepare and evaluate predicted double-perovskite oxides undergoing one- or two-phase, off-stoichiometric reactions.

- Expand computational double perovskite survey to 10,000s of compounds.

- Develop validation of computational entropies for screening promising compounds.

Technical Barriers

This project addresses the following technical barriers associated with solar thermochemical production of hydrogen from the Hydrogen Production Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- High-Temperature Robust Materials

- Materials and Catalyst Development.

Specifically, this project is focused on the identification of promising compounds that show (1) ground state stability/synthesizeability of compound (2) thermodynamics favorable for <1,400°C reduction, and (3) thermodynamics favorable for facile water splitting. State-of-the-art is currently CeO_2 and SLMA perovskite.

Technical Targets

In Year 2 of this project, we synthesized and tested several double perovskites as suggested by density functional theory (DFT) calculations based on the computation model built in Year 1. Among them, two doped perovskites (B-site disordered double perovskite) show characteristics of high-efficiency STCH: (1) suitable oxygen vacancy formation enthalpies, (2) large reduction entropies, and (3) high thermal stabilities at high temperature. 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

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

storage materials that meet the following DOE hydrogen production targets:

- Solar-to-hydrogen conversion efficiency

- Reaction material cost.

FY 2019 Accomplishments

- Synthesized the targeted compounds and characterized their crystal structures using x-ray diffraction (XRD).

- Evaluated the thermal stability of these materials using ex-situ and in-situ approaches.

- Measured redox thermodynamics of these materials through thermogravimetry analysis (TGA) in the temperature range of 300–1,500°C and pO_2 range of 10^{-6}–1 atm.

- Discovered two materials with excellent thermal stability and moderate enthalpy of reduction in the range of 200–300 kJ/mol-O.

- Predict hydrogen production of 21.5 mL/g in a thermochemical cycle with reduction at 1,400°C under 10^{-5} atm O_2 and oxidation at 800°C under 20% H_2O (experimental validation under way).

- Established electrochemical approach for characterizing thermodynamic parameters using thin films.

- High-throughput DFT screening of 10,000 compositions of double perovskites. Used four prototype structures to further determine the low-lying crystal structure of the composition that has less than 100 meV/atom convex hull distance.

- High-throughput DFT screening of oxygen vacancy formation energy of the known double perovskites.

- Computing vibrational entropy of several ABO_3 compounds.

- Oxygen vacancy formation energy calculations for oxides beyond perovskite, e.g., brownmillerite $A_2B_2O_5$, pyrochlore $A_2B_2O_7$, and spinel AB_2O_4.

- The influence of exchange-correlation functionals on oxygen vacancy formation energies of several single perovskites.

INTRODUCTION

Metal-oxide-based two-step solar thermochemical (STC) H_2O- and CO_2-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. Next, the reduced oxide is used to split H_2O or CO_2 (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

In the second year of the project, we measured the reduction enthalpy and entropy of the selected double perovskites as suggested by our DFT calculations based on our computational method and structural mode verified in the first year. We also compared our measured enthalpy with the computed ones to further test the scalability of our method/mode from single perovskite to double perovskite. Meanwhile, we computed the reduction entropy (including configuration entropy, vibrational entropy, electronic entropy, etc.) of perovskite measured in the first year and find out a correct approach to calculate it.

RESULTS

In Year 2 of this project, we started working on developing several predicted double perovskites. The thermal stability of these materials is characterized by both ex-situ and in-situ XRD under air and low oxygen partial pressure conditions The redox thermodynamics is evaluated by thermogravimetric measurements in the temperature range of 300–1,500°C and pO_2 range of 10^{-6}–1 atm.

Among the materials evaluated, Material A, which adopted a disordered (solid solution) simple perovskite structure rather than an ordered double-perovskite structure, was found to be most promising. It demonstrated thermal stability up to 1,500°C under 10 ppm O_2 and a high degree of oxygen release at high temperature. Oxygen non-stoichiometry curves obtained under a combination of continuous and stepped heating profiles are shown in Figure 1. The thermodynamic functions were obtained from these data using a van Hoff't analysis, the results of which are shown in Figure 2.
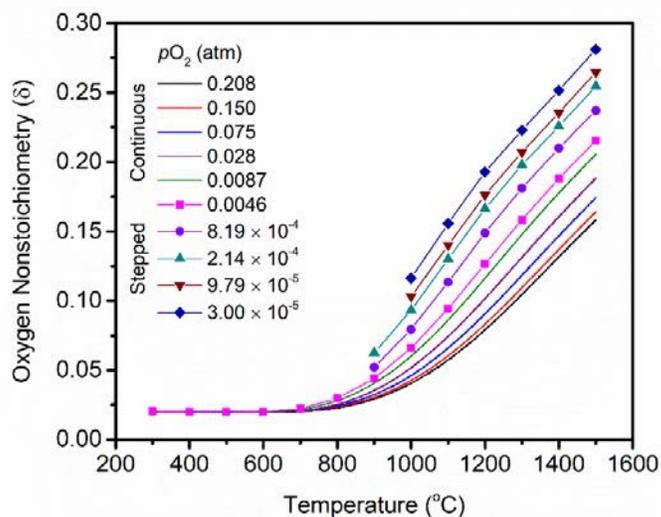

Figure 1. The oxygen non-stoichiometric curves as obtained by thermogravimetric measurements in the temperature range of 300–15,00°C and pO_2 range of 10^{-6}–1 atm.
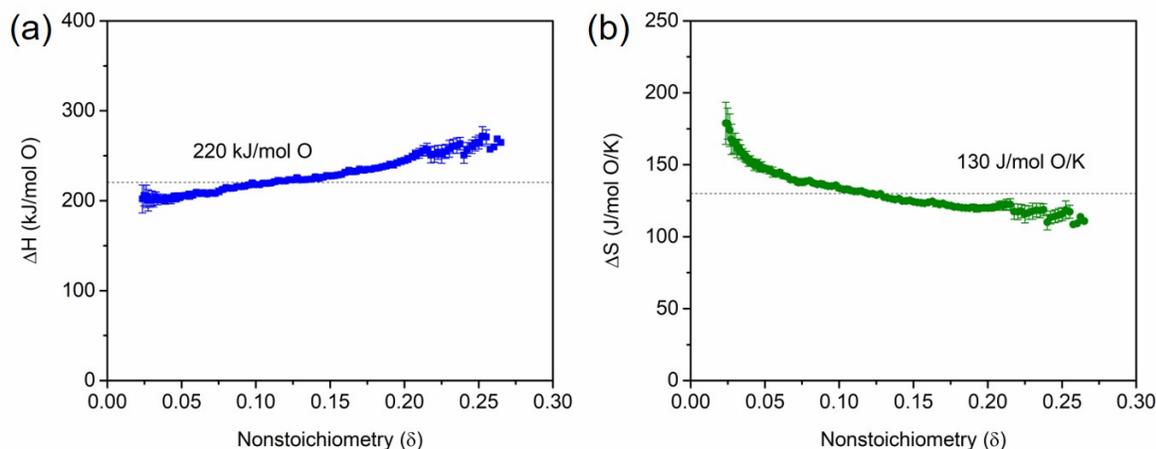

Figure 2. (a) Standard enthalpy and (b) standard entropy of reduction of Material A extracted from the TGA measurements shown in Figure 1.

The enthalpy and entropy of reduction vary with oxygen non-stoichiometry. The enthalpy increases slightly with δ, implying that the material becomes somewhat more difficult to reduce as the reduction reaction proceeds. The average value is 220 kJ/mol-O. The entropy obeys the classic profile for a configurational entropy dominated process. The average entropy beyond the region of steep decline is 130 J/mol-O/K.

It is straightforward to use the measured thermodynamic properties to predict the equilibrium thermochemical fuel production for a given cycle. For example, for a typical equilibrium cycle with reduction carried out at

1,400°C under inert gas (10 ppm O_2) and oxidation carried out at 800°C with $pH_2O = 0.2$ atm, oxygen non-stoichiometry is predicted to swing between 0.27 and 0.09, respectively, and the corresponding fuel production per cycle is predicted to be 21.5 mL H_2/g oxide. This value far exceeds any result that has been reported in the open literature. The predicted equilibrium fuel production after complete re-oxidation and the fuel production under three different oxidation conditions using thermo-kinetic model [1, 2] are displayed in Table 1. These thermodynamics analysis and predictions show that this material is very promising for STC hydrogen production. The real thermochemical measurements of hydrogen production are on the way.

Table 1. Predicted equilibrium fuel production of Material A and the real fuel productivity in a given oxidation time of 160 min for the cycles indicated.

Cycle	Reduction condition ($\delta_{eq} = 0.27$)	Oxidation condition	$\Delta\delta_{eq}$	Equilibrium mL H_2 / g oxide	160 min Produced mL H_2 / g oxide
1	1,400°C, 10 ppm O_2	800°C, $pH_2O = 0.2$ atm	0.180	21.5	9.3
2	1,400°C, 10 ppm O_2	1,000°C, $pH_2O = 0.2$ atm	0.125	15.0	9.6
3	1,400°C, 10 ppm O_2	1,000°C, $pH_2O = 0.4$ atm	0.130	15.6	11.6

In parallel we have established an analytical method to retrieve thermodynamic properties from A.C. electrical impedance spectroscopy (ACIS) of thin-film ceria and Zr-doped ceria samples. Specifically, from films deposited onto the single crystal yttria stabilized zirconia, we use ACIS to measure the film capacitance. From measurements of several films of different thicknesses, we distinguish between the volumetric chemical capacitance, which carries the thermodynamic information, and the interfacial capacitances, which are not of interest for determining thermodynamic behavior. With the chemical capacitance so determined, we perform a numerical integration to obtain the nonstoichiometry, and a conventional van Hoff't analysis then yields the thermodynamic properties (Figure 3). While the method requires greater numerical analysis than thermogravimetric measurements, it is substantially more time efficient due to the smaller sample volumes, and provides far more accuracy, particularly in the low d regime. The electrochemical approach is being implemented for evaluation of perovskite materials. We are in the process of developing an analysis program to extract the thermodynamic parameters automatically with high computational efficiency.
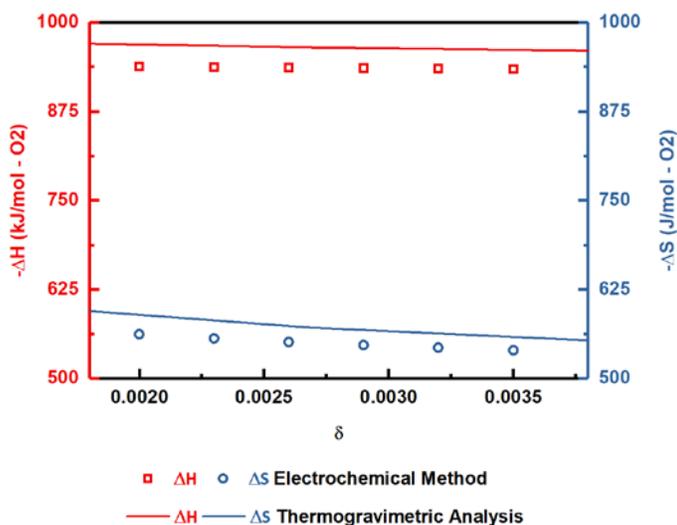

Figure 3. Reduction behavior of Ceria as measured by electrical impedance spectroscopy of thin film Ceria: enthalpy and entropy of reduction. Thin-film results are compared with the themogravimetric results from Panlener et al. *J Phys. Chem. Solids*, 1975.

In parallel with the experimental effort, high throughput DFT calculations have been performed to computationally screen for the discovery of new, stable double perovskites within the framework of the Open Quantum Materials Database (OQMD). After screening more than 10,000 compositions and 40,000 structures,

we have found 22 more potential candidates exhibiting a reduction enthalpy in the window of interest (Figure 4) and around 1,000 new synthesizable $A_2BB'O_6$ (A=Ba, Sr, Ca, Zn, Cd, Hg, and Pb). See Figure 5 for the thermal stability map of $Ba_2BB'O_6$ and $Sr_2BB'O_6$ compounds.
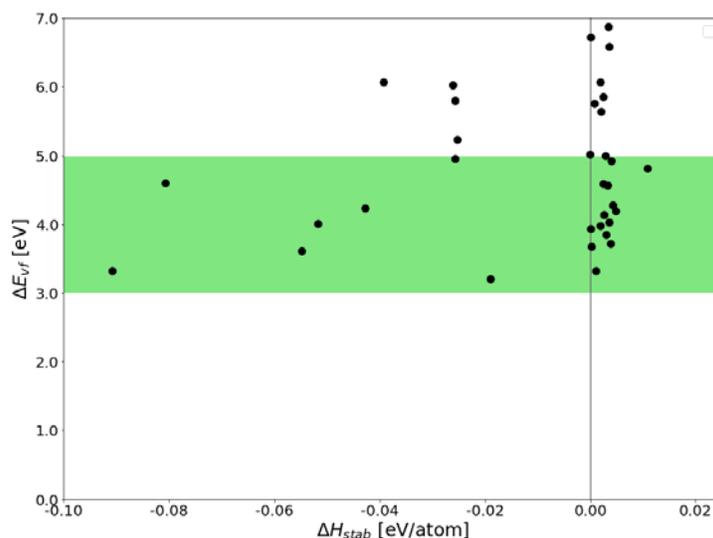

Figure 4. Calculated oxygen vacancy formation energy as a function of stability for a group of experimentally synthesizable double perovskites.
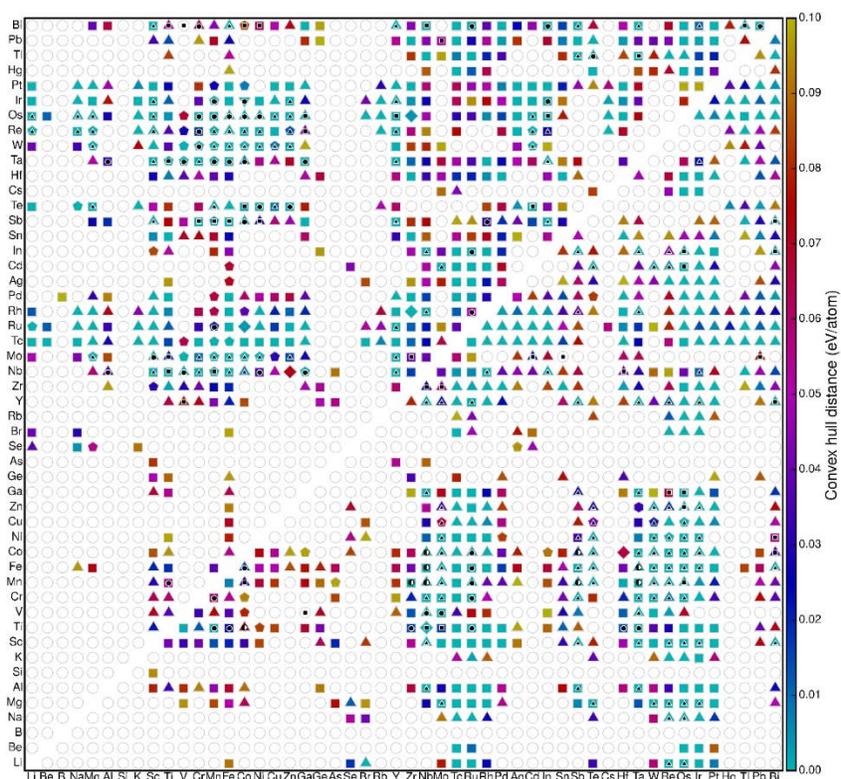

Figure 5. Thermal stabilities of $Ba_2BB'O_6$ (upper left from diagonal) and $Sr_2BB'O_6$ (lower right from diagonal) double perovskites screened by high-throughput DFT calculations. Nearly all of the experimentally reported compounds (labeled by small symbols. Filled circle: triangle: B/B' rock-salt ordered; B/B' disordered; filled square: unknow structure; half-filled circle: B/B' rock-salt ordered and disordered coexist; filled hexagonal: non-perovskite) are "re-predicted" by our DFT calculations with convex hull distance less than 100 meV/atom. Good correlation between computation and experiment validates methodology for further new compound exploration to be considered in future plans.

In the first year of the project, an extensive comparison between experimental and calculated vacancy formation energies was performed, demonstrating the accuracy of both approaches to characterize the reduction thermodynamics of STCH materials. This finding also provides confidence in the utility of our computational approach to predict thermodynamic properties of new materials, and hence screen new materials for STCH applications. In the second year, we have begun to explore the entropic contributions to the reduction reaction. The configurational entropy contributions to these reactions is well known. Hence, we focus mainly on the vibration entropy contribution to reduction, which is a largely unexplored contribution. We computed the oxygen vacancy formation entropy of several perovskites, whose thermodynamics were measured in the first year. Although the phonon calculations of the defective structure (one oxygen vacancy in an 80-atom cell) required for formation of vibrational entropy is very expensive, we have finished three compounds with at least two Hubbard U values.

The influence of exchange-correction functional within DFT calculations on the oxygen vacancy formation energy has been investigated with three functionals, PBE, PBEsol, and SCAN for six ABO_3 compounds studied in the first year. We found PBE functional performs well if a suitable Hubbard U is adopted. The newly developed functional SCAN always tends to overestimate the oxygen vacancy formation energy due to its over-localized behavior for the d orbitals transition metal, which is consistent with literature [3].

We have explored the influence of chemical environment on oxygen vacancy formation energy by comparing a series of oxides with different crystal structures, including brownmillerite $A_2B_2O_5$, pyrochlore $A_2B_2O_7$, and spinel AB_2O_4. We found the coordination number of the cation and connecting way of polyhedral (corner-sharing, edge-sharing, face-sharing) have large effects on oxygen vacancy formation energy, and we will further explore these discovered trends in the future to help us discovery new compounds with tailored values of the oxygen vacancy formation energy.

CONCLUSIONS AND UPCOMING ACTIVITIES

Experimental synthesis and evaluation of predicted quaternary perovskites (with mixing/ordering on the B sites) help identify two doped perovskites with excellent stability and large oxygen non-stoichiometry under an oxidizing atmosphere, thermodynamics analysis shows that an extraordinary amount of hydrogen can be produced in a thermochemical cycle by using these materials. Based on the material discovery, we propose the following future plans:

Experimental:

- Evaluation of fuel production under realistic thermochemical cycling conditions on the most promising materials.

- Based on computational input from Year 2, the most promising double perovskite oxides for two-phase, off-stoichiometric reactions will be prepared and evaluated in bulk form.

- Electrochemical method using chemical capacitance is an alternative approach for obtaining thermodynamic parameters. This approach will be applied to new perovskite materials for high-throughput study.

Computational:

- Validate DFT vibrational entropy calculations of reduction entropy – to compare with TGA experiments.

- High-throughput DFT screening of oxygen vacancy formation energy of the predicted stable double perovskites.

- Computing oxygen vacancy formation energies of disordered double perovskites with special quasi-random structures.

- Tailoring oxygen vacancy formation energy by A- and B-site doping: alloying B-site metals with different reduction energies, e.g., $AB_xB'_{1-x}O_3$; alloying A-site metals to control octahedral rotation, which also has a large influence on oxygen vacancy formation energy.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. R. Barcellos, F. G. Coury, A. Emery, M. Sanders, J. Tong, A. McDaniel, C. Wolverton, M. Kaufman, R. O'Hayre, "Phase Identification of the Layered Perovskite CexSr2–xMnO4 and Application for Solar Thermochemical Water Splitting", *Inorg. Chem.* 58, 12, (2019): 7705-7714

2. X. Qian, J. He, B. Baldassarri, R. Huang, C. Wolverton, S.M. Haile, (Invited) "Thermochemical Properties of Non-Stoichiometric Oxides for Solar Fuel Generation," Meeting Abstracts, MA2019-02 (2019) 2008. 236th ECS Meeting, October 13–17, 2019, Atlanta, Georgia, US.

3. S.M. Haile, X. Qian, "Thermochemical Trends in ABO_3-Type Compounds for Solar Fuel Generation, Meeting Abstracts." MRS Spring Meeting and Exhibit, April 22–26, 2019, Phoenix, Arizona, US.

4. R. Bell, X. Qian, E. Coker, M. Rodriguez, P. Parilla, S.M. Haile, D. Ginley, "In-Situ Defect Mapping of High Temperature STCH Materials in Oxidizing and Reducing Environments, Meeting Abstracts." MRS Spring Meeting and Exhibit, April 22–26, 2019, Phoenix, Arizona, US.

5. C. Wolverton (Invited) "Oxygen Off-Stoichiometry and Defect Entropies in Solar Thermochemical Water Splitting Materials." MRS Spring Meeting and Exhibit, April 22–26, 2019, Phoenix, Arizona, US.

6. C. Wolverton (Invited) "Oxygen Off-Stoichiometry and Defect Entropies in Solar Thermochemical Water Splitting Materials." Chinese Academy of Sciences, Institute of Engineering Thermophysics, Beijing, China, Apr. 2019.

7. C. Wolverton (Invited) "Oxygen Off-Stoichiometry and Defect Entropies in Solar Thermochemical Water Splitting Materials." 2019 Spring ACS Meeting, Orlando, FL, Apr. 2019.

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1. Davenport, T. C., et al. (2016). "Implications of Exceptional Material Kinetics on Thermochemical Fuel Production Rates." Energy Technology 4(6): 764-770.

2. Davenport, T. C., et al. (2017). "Interplay of material thermodynamics and surface reaction rate on the kinetics of thermochemical hydrogen production." International Journal of Hydrogen Energy 42(27): 16932-16945.

3. Yuhao Fu and David J. Singh, Applicability of the Strongly Constrained and Appropriately Normed Density Functional to Transition-Metal Magnetism, Phys. Rev. Lett. 121, 207201 (2018)