
HydroGEN Seedling: Mixed Ionic Electronic Conducting Quaternary Perovskites: Materials by Design for Solar Thermochemical Hydrogen

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Overall Objectives

- Adapt and apply computational materials design capability, developed in the Carter group and newly developed capability (a DFT+U sublattice formulation), to calculate and validate chemical potentials for complex off-stoichiometric redox-active mixed ionic electronic conducting (MIEC) perovskite metal oxides with open metal d- and f-shells and with disorder: $A_yA'_{1-y}B_zB'_{1-z}O_{3-x-\delta}$, otherwise expressed as $(A,A')(B,B')O_{3-x-\delta}$.
- Relate the calculated solid-state chemical potentials to materials thermodynamics, enthalpy and entropy of reduction, and the equilibrium off-stoichiometry as a function of gas-phase operating conditions.
- Relate the thermodynamics of materials to theoretical and expected water-splitting performance, noting that performance is a function of operating variables (obtainable via an exergy analysis or constraints from

equilibrium calculations) and a key driver of cost.

- Identify promising material candidates that should perform better than the state-of-the-art criteria, meet the target efficiency (solar-to-hydrogen thermal efficiency >30%), and have the potential to meet the ultimate production cost goal of <\$2/kg H₂.

Fiscal Year (FY) 2019 Objectives

- Advance the screening for promising materials candidates and elucidate further trends and correlations while increasing materials complexity.
- Extend the chemical potential theory to include phase transitions, provided they are rapid.
- Demonstrate that the computational methodology skills proficiency to successfully port to a new platform.
- Demonstrate that we can calculate with acceptable accuracy (sufficient to extract trends) and determine reduction extent as a function of temperature and the partial pressure of oxygen, measured as chemical potential within 20% of this important class of oxides, while further increasing complexity to quaternaries.
- Validate the first principle's computational approach for determining the chemical potential, off-stoichiometry response map, and extract the thermodynamics (within 20%).

Technical Barriers

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

- (S) High-Temperature Robust Materials.

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

Technical Targets

This project is focused on developing materials for solar thermochemical hydrogen (STCH) production that result in technologies to produce hydrogen consistent with the following DOE technical targets:

- Sustainably produce hydrogen for <\$2/kg
- Achieve 2.1×10^{-6} kg/s/m² at 1 sun (252 W/m²) or equivalent to 25.2% efficiency
- Achieve \$1.1M for a 1-metric-ton-per-day plant (\$790/kW assuming 9.3%/year financial recovery rate)
- Achieve \$11,000 in materials cost for a 1-metric-ton-per-day plant. Key parameters will determine whether we can meet this goal \$/kmol of material, $\Delta\delta$ reduction capacity and the number of cycles per day. A 1-metric-ton-per-day plant is 496 kmol of hydrogen per cycle, which is 496 kmol/ $\Delta\delta$ of active material. Therefore, $\$11,000 < 496 \text{ kmol} * \$/\text{kmol}/\Delta\delta$. This shows the importance of being able to achieve many cycles in a day and to achieve relatively high reduction capacity, as well as low cost for the active materials.

FY 2019 Accomplishments

- Obtained ideal U values to treat all 3d transition metal (TM) based oxides within the SCAN+ U framework, contributing to the goal of accurate calculations of the solid-state oxygen chemical potential.
- Evaluation of oxygen vacancy formation energy in several ternary Ca-TM-O, Ce-TM-O, and quaternary Ca-Ce-TM-O systems completed, contributing to the goal of predicting candidates to meet the targets listed above.
- Rigorous thermodynamic relationships between operating conditions, enthalpy of reduction, yield, and productivity developed, again contributing to meeting the above targets.
- Previously unknown constraints on temperature swing (between reduction and re-oxidation) and enthalpy/yield elucidated, contributing to the challenge of co-optimizing a material and the operating conditions to meet targets.
- Framework for density functional theory (DFT) derived sub-lattice model for quaternary and quinary perovskites completed.

INTRODUCTION

The current project aims to contribute to materials discovery for improved STCH materials through fundamental quantum mechanics investigations into an exciting class of redox-active, mixed ionic electronic conducting metal oxides, which can stably exist over a range of oxygen stoichiometries. By characterizing key thermodynamic properties and stability, we aim to offer strategies to boost solar to hydrogen thermal efficiency, as well as to provide experimentalists with crucial input to synthesize, validate, and perform further tests on promising candidates. We choose off-stoichiometric materials over phase change materials for two principal reasons. First, materials undergoing a major reorganization of heavy atoms will challenge the durability criteria and will typically have kinetic limitations during reduction and/or reoxidation, whereas materials that only undergo minor ordering-disordering, structural rocking, or distortion transitions should have acceptable thermomechanical stresses and fast kinetics of reduction and reoxidation. Vacancies in the anion lattice contribute to oxygen transport moving oxygen to and from the bulk and the surface. Second, going off-stoichiometry and having disorder on the anion and cation lattices generates solid-state entropy of configurational disorder, typically absent in materials undergoing a phase transition to another crystallographic structure.

APPROACH

Sub-Lattice Formalism

To determine off-stoichiometry in the solid, which is a key figure of merit that determines hydrogen productivity, researchers calculated the oxygen chemical potential within the solid phase and equate it to the chemical potential of the gas phase. The latter is a unique and known function of the temperature and partial pressure of oxygen. It is, therefore, important to accurately describe the Gibbs energies of both the oxidized

and reduced solid. The sub-lattice formalism, which forms the backbone of thermodynamic assessments across chemistries (*i.e.*, CALPHAD-style calculation of phase diagrams), can be used to model the Gibbs energies.

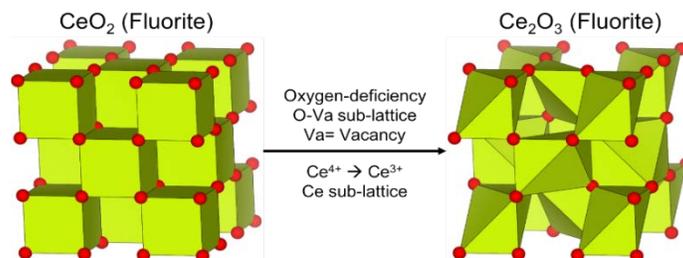


Figure 1. Illustration of the sub-lattice formalism for the fluorite phase in Ce-O binary. The structure on the left indicates stoichiometric CeO₂ while on the right refers to a fluorite structure with a Ce₂O₃ stoichiometry.

As an example of applying the sub-lattice formalism, consider the case of the fluorite phase of CeO₂, which undergoes thermal reduction leading to the formation of oxygen vacancies and Ce³⁺ ions. Zinkevich et al. [1] employed the sub-lattice formalism described here in their thermodynamic assessment of the Ce-O binary system. Nominally, the fluorite structure has two distinct sub-lattices, Ce and O, respectively. Both sub-lattices can have two species occupying those sites, namely, Ce³⁺ and Ce⁴⁺ in Ce sites, and oxygen (nominally O²⁻) and vacancies in O sites. The Gibbs energy for this fluorite phase ($G_{CeO_{2-\delta}}^F$) can be written in the following functional form:

$$G_{CeO_{2-\delta}}^F = y_{Ce^{4+}}y_O G_{Ce^{4+}:O}^0 + y_{Ce^{3+}}y_O G_{Ce^{3+}:O}^0 + y_{Ce^{4+}}y_{Va} G_{Ce^{4+}:Va}^0 + y_{Ce^{3+}}y_{Va} G_{Ce^{3+}:Va}^0 + RT (y_{Ce^{4+}} \ln y_{Ce^{4+}} + y_{Ce^{3+}} \ln y_{Ce^{3+}}) + 2RT (y_O \ln y_O + y_{Va} \ln y_{Va}) + G_{excess}^F \quad (1)$$

In Equation 1, $G_{Ce^{4+}:O}^0$, $G_{Ce^{3+}:O}^0$, $G_{Ce^{4+}:Va}^0$, and $G_{Ce^{3+}:Va}^0$ are referred to as “end member” Gibbs energies with y_X corresponding to the site fraction of species X within the relevant sub-lattice. Each end member energy corresponds to a distinct species occupancy within the fluorite structure with (i) Ce⁴⁺ and O occupying Ce and O sites (see left structure in Figure 1), (ii) Ce³⁺ and O occupancies (right panel in Figure 1), (iii) Ce⁴⁺ and oxygen vacancies within the fluorite structure and (iv) Ce³⁺ and oxygen vacancies, respectively. Note that the Gibbs energies of non-charge-neutral structures, such as (Ce⁴⁺:Va) and (Ce³⁺:Va) are typically obtained by setting a reference state and/or using reciprocal relationships. For example, the Gibbs energy of the (Ce⁴⁺:Va) end member is referenced to:

$$G_{Ce^{4+}:Va}^0 = G_{CeO_2} - G_{O_2}(g) \quad (2)$$

Typically, only ideal solution configurational entropy (and no other entropic contributions) is accounted for within the sub-lattice formalism. Indeed, Equation 1 has ideal-solution configurational entropy on both Ce and O sub-lattices. Finally, G_{excess}^F indicates any contributions to the Gibbs energy of the fluorite phase not captured by the end-member energies and entropy terms. Numerically, G_{excess}^F is significantly smaller as compared to the end-member and entropy contributions.

In thermodynamic assessments, experimental data (such as specific heat, enthalpy measurements, phase transition temperatures, etc.) are used as input parameters to obtain values for the end-member and excess Gibbs energies, while the entropy term has a simpler analytical form. Here, we are calculating the relevant end-member and excess Gibbs energies entirely through DFT-based calculations, without any experimental input, and benchmark predictions that arise from a DFT-predicted model with experimental data. The sub-lattice engineering approach is not new-what is new is the computational methodology, validating first that significant information about high-temperature processes can be extracted from zero-temperature calculations, and second our chemical potential approach for calculating off-stoichiometry as a function of gas-phase temperature and partial pressure of oxygen.

Specific interactions with the nodes include working closely with (1) Sandia National Laboratory (SNL) Uncertainty Quantification Node (Dr. Bert Deusschere and a student), (2) National Renewable Energy Laboratory (NREL) Synthesis and Characterization Node (Drs. Dave Ginley, Robert Bell, and Phil Parilla) on synthesizing candidate materials, and (3) the SNL Thermal Analysis Nodes (Dr. Eric Coker) to measure equilibrium off-stoichiometry as function of temperature and pO_2 as well as in situ XRD. Budget Period 1 for this project was primarily computational and developing capabilities. Toward the end of the Budget Period, the experimental collaboration became much more important. This project also has a close association with the 2B team. Expected benefits will derive from a closer relationship between what experimentalists can and do measure and what theorists calculate, with defined protocols. Furthermore, standardization and defined protocols will lower the barrier to entry.

RESULTS

The focus has been on comparing the accuracy of sub-lattice models based on “simple and cheap” 0 K DFT-based calculations against qualitative and quantitative experimental trends. The unanswered question is what level of accuracy is accurate enough. It is no surprise that adding complexity will increase accuracy; however, it is not evident that added expense provides for value add, in terms of materials screening and providing relevant guidance to experimentalists.

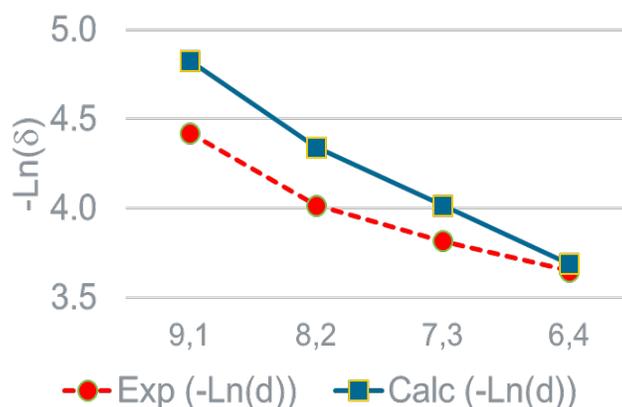


Figure 2. Measured and calculated oxygen equilibrium off-stoichiometry at a reduction temperature of 1,400 °C and a partial pressure of oxygen of 10 Pa for $La_xSr_{1-x}MnO_{3-\delta}$.

Using our zero temperature, DFT+U derived sub-lattice model for a quaternary perovskite, and we gained confidence that the model is sufficient for materials screening. Our results demonstrate that we can approximate the off-stoichiometry at high temperature and reduced partial pressure, and directly compare theory and experiment. The off-stoichiometry depends on knowing the oxygen chemical potential in the solid and equating it to the known oxygen chemical potential in the gas phase. Figure 2 shows the logarithm of the calculated and measured [2] off-stoichiometry as a function of the doping concentration of strontium in lanthanum manganese oxide. 9,1 refers to $La_{0.9}Sr_{0.1}MnO_{3-\delta}$ or 10% doping; 8,2 refers to $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ or 20% doping; etc. The error in the logarithm of the off-stoichiometry is $5.9\% \pm 3.6\%$, and all errors are under 10%. More importantly, the calculated result faithfully reproduces the trend.

We next demonstrate that by reducing conditions and choosing the desired yield, Θ (amount of steam converted to hydrogen), we can precisely target the optimum enthalpy of reduction, δH , which, from the well-known van't Hoff analysis, is the slope of constant off-stoichiometry δ (reflecting the tradeoff between temperature and partial pressure). It is nearly a straight line when plotted in $\log pO_2$ versus inverse temperature. More importantly, we find that there is virtually no solution space for ΔT (temperature swing between reduction and re-oxidation) less than 400 °C and δH less than ceria for Θ equal or greater than 10%. For a chosen thermal reduction temperature, T_{TR} and yield (here fixed at $\Theta=10\%$)—higher T_{TR} or lower pO_2 permits lower δH but only at larger ΔT . Assuming 600 °C as an arbitrary lower bound on reoxidation, then there is a unique target for δH for fixed Θ .

It is evident that lower δH will result in larger δ 's (all else equal) or equivalently more hydrogen production per unit of active oxide, assuming there is no competing phase. However, what is not immediately evident is how strong is the trend, and how much gain is feasible from lowering the reduction enthalpy. Figure 4 shows the result from artificially lowering the enthalpy in ceria, by reducing the energy difference between the two reference states in the model, CeO_2 , and $\frac{1}{2} Ce_2O_3$. The result is the red line in Figure 4, showing a near-linear relationship between the off-stoichiometry and the enthalpy and a dramatic increase with reducing enthalpy. Figure 4 also shows the gain possible from a second redox-active sublattice, which shows a substantial increase in off-stoichiometry at the same enthalpy. Hence, a strategy to achieve an optimal material is to engineer a perovskite to simultaneously redox on both the A and B cation sub-lattices and then tune the enthalpy with an appropriate doping strategy.

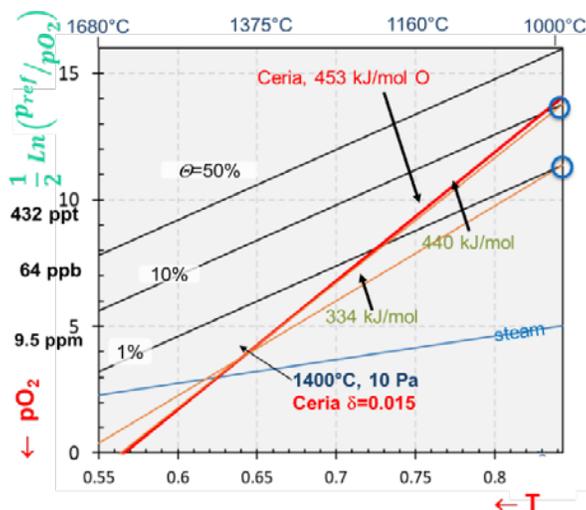


Figure 3. Segment of a two-step thermochemical cycle, with thermal reduction temperature at 1,400°C and partial pressure of oxygen reduced to 10 Pa, shown in units of T_{ref}/T ($T_{ref}=1073.15$ K) and natural log of pO_2 . Black lines correspond to several values of Θ . Orange lines correspond to hypothetical materials with varying enthalpy of reduction; the red line corresponds to ceria, and the blue line is steam. Enthalpies of reduction are per mole O.

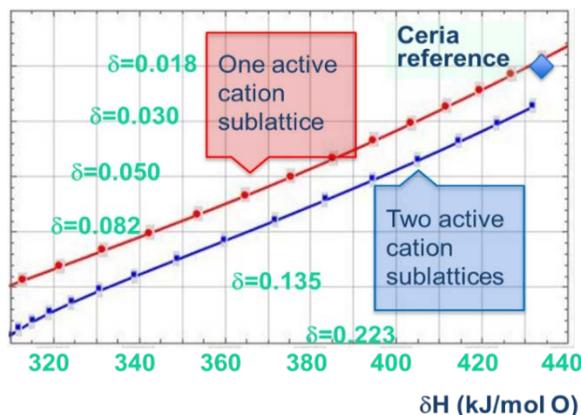


Figure 4. Calculated off-stoichiometry for reduction at 1,400°C and 10 Pa, shown on a log scale versus artificially reduced reduction enthalpy starting from a ceria reference and reducing the energy difference between the two end states CeO_2 and $\frac{1}{2} Ce_2O_3$ (see Figure 1). The red line is ceria with reduced enthalpy of reduction. The blue line is the result if there were two distinct cation sub lattices.

We also found significant constraints on ΔT for off-stoichiometric oxides. Rigorous thermodynamics suggest that below 400°C (e.g., 300°C), it is necessary to either sacrifice yield (to <10%), increase T_{TR} above 1,500°C (excessive re-radiation losses and materials volatility), decrease pO_2 below 10 Pa (technically challenging), or increase δH above that of ceria (sacrificing productivity).

CONCLUSIONS AND UPCOMING ACTIVITIES

We have found that the construction of chemical potential maps is useful to decouple the energetic contributions of the gas and solid phases in a thermochemical cycle. Equilibrium off-stoichiometry δ comes from equating solid-state and gas-phase chemical potentials. The prediction of chemical potentials in solid phases is, however, not trivial. Nevertheless, the construction of sub-lattice models, with energy values from DFT, continues to prove to be a promising approach – while it is not high-throughput, a reasonable number of zero-temperature DFT (SCAN+U is proving good accuracy) calculations – provides acceptable accuracy for non-trivial off-stoichiometry and for trends. A promising pathway to improve capacities (increase in entropy, without compromising kinetics from phase transitions) is to engineer redox (cation) couples for $(A,A')(B,B')O_3$ quaternary ($B'=B$) and quinary perovskites with A' and B simultaneously redox-active.

We have developed rigorous thermodynamic relationships and constraints as a function of reduction conditions (T_{TR} and pO_2) and re-oxidation (Θ and T_{WS}) and δH of reduction – that has strong implications for the operating cycle and efficiency.

In on-going work, we are constructing sub-lattice models for $(A,A')(B,B')O_3$ quinary perovskites, with both A' and B simultaneously redox-active. We will predict oxygen off-stoichiometries and validate with experimental data. We will identify key performance limiting factors and formulate design rules. NREL has developed synthesis routes and has synthesized newly proposed candidates. SNL node will measure off-stoichiometry, and we will infer enthalpy and entropy.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. G.S. Gautam, E.A. Carter, “Evaluating Transition Metal Oxides within DFT-SCAN and SCAN+U Frameworks for Solar Thermochemical Applications,” *Phys. Rev. Mater.* 2 (2018): 095401.
2. G.S. Gautam, “Estimating Off-Stoichiometry Using Density-Functional-Theory-Based Calculations and the Sub-Lattice Formalism,” American Chemical Society, Orlando FL March 31–April 4, 2019.
3. G.S. Gautam, “Using SCAN+U Calculations and the Sub-Lattice Formalism to Estimate Off-Stoichiometry in Oxides,” Materials Research Society, Phoenix AZ, April 22–26, 2019.
4. G.S. Gautam, E.B. Stechel, E.A. Carter, “A First-Principles-Based Sub-Lattice Formalism for Predicting Off-Stoichiometry in Materials,” *Physical Review Materials*, in review.

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1. Matvei Zinkevich, Dejan Djurovic, Fritz Aldinger, “Thermodynamic Modeling of the Cerium–Oxygen System,” *Solid State Ionics* 177, 989 (2006).
2. A. Nicholas Grundy, Bengt Hallstedt, Ludwig J. Gauckler, “Assessment of the La–Sr–Mn–O System,” *Computer Coupling of Phase Diagrams and Thermochemistry* 28 (2004): 191–201.