Accelerated Discovery of STCH Hydrogen Production Materials via High-Throughput Computational and Experimental Methods
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Project Partners
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Project Vision
Integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH

Project Impact
Greatly increase number of viable STCH materials candidates

Compositions Studied for Nonstochiometric Redox STCH:
Today: 10’s of compositions
Project Goal: 1000’s of compositions

100x increase

Award # EE-0008087
Start/End Date 10/01/2017 – 09/31/2021
Project Funding* $767,253

* this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)
Approach – Summary

**Project Motivation**
Builds on prior Sandia/CSM STCH collaboration, which has produced two novel perovskite-based STCH candidates.

**Barriers**
Computational screening has not been attempted for compositions with greater than two cations.

Thin-film and optical screening requires films to have behaviors analogous to bulk with no substrate interactions.

**Key Impact**

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction Temperature</td>
<td>1550°C</td>
<td>1350°C</td>
</tr>
<tr>
<td>Hydrogen Production</td>
<td>150 µmol H₂/g sample (@T_{RED}=1550°C)</td>
<td>&gt;= (T_{RED}=1350°C)</td>
</tr>
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</table>

**Ultimate goal:**

- 200 °C lower $T_R$ with equal capacity to CeO₂
- Comparable Steam-to-Hydrogen Performance

**Partnerships**

- NREL (Lany): High-throughput DFT calculations
- NREL (Zakutayev): Combinatorial thin-film deposition and characterization
- Sandia (McDaniel): Stagnation Flow Reactor (SFR) for STCH materials validation
Approach – Innovation: DFT Screening

• A two-part screening method to leverage both high-throughput and detailed defect calculations focused on two main search directions:

  - **Known Perovskites**
  - **New Structure**

• Compositions

  - Ternary
  - Quaternary

Initial compositional space:

  - Low cost, earth abundant
  - Non-toxic
  - Ce and Mn present in most good STCH materials
  - Multiple oxidation state accessible to B-sites

Criterion 1

- High-throughput DFT
- $\Delta H_f$
- $\Delta \mu_O$

Criterion 2

- Defect Formation
- $\Delta H^{\text{q}}_{d}$
- $q = 0, +1, +2$

$\Delta H_f$ = Oxide Enthalpy of Formation
$\Delta \mu_O$ = Oxygen Chemical Potential
$\Delta H^{\text{q}}_{d}$ = Charged Defect Formation Enthalpy
Approach – Innovation: Thermodynamic Modeling

Develop a computational model for prediction of reduction/oxidation behavior and deeper understanding that helps to guide design of better STCH materials

- Deep-dive study of reduction in STCH materials $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ (SCM) and $\text{Sr}_{2-x}\text{Ce}_x\text{MnO}_4$ (CSM) via O vacancy
- Lower $\Delta H(V_0)$ yields higher capacity ($\Delta \delta$)
- Trade-off between $\text{H}_2$ production and $\text{H}_2\text{O}/\text{H}_2$ ratio
- Charged vacancy increases $p\text{H}_2$ for higher capacity ($\Delta \delta$) and $\text{H}_2$ production

$T_{\text{red}} = 1400 \, ^\circ\text{C}$, $p\text{O}_2 = 10^{-4} \, \text{atm}$ — $T_{\text{ox}} = 850 \, ^\circ\text{C}$, $p\text{H}_2\text{O} = 1 \, \text{atm}$
The combinatorial PLD technique allows for the simultaneous formation of many chemical compositions. These libraries can then be rapidly evaluated for structural and thermochemical behavior.
Approach – Innovation: Experimental Screening

• The combinatorial PLD technique makes many chemical compositions at once
• These “libraries” are screened with XRF and XRD for temperature dependent stability and structural behavior

The ability to investigate composition/structure relationships across such a large compositional range is nearly impossible with bulk synthesis techniques.
• The computational developments are important, and the insights and techniques can relate to many other material development efforts

• While previous efforts to develop a rapid optical thermochemical activity screening method were unsuccessful, the necessary combinatorial PLD methods, especially for oxides, were greatly refined

• Consortium resources and expertise have proven critical
  – Close relationship with computational team has provided not only access to valuable resources but allowed CSM’s materials insights to inform NREL node’s other computational work and visa-versa.
  – NREL’s Combinatorial PLD system and Sandia’s SFR are capabilities that cannot be easily duplicated in-house.
STCH cost targets require:
• Large improvements in hydrogen production capacity (mmol H₂/g oxide-cycle)
• Lower reduction temperatures
• High conversion capability
• Fast redox reaction kinetics

Achieving these goals requires new materials, as all current STCH candidates fail on at least one criteria.
Relevance and Impact: Fitting in with HydroGEN

- This project was developed to explicitly leverage the EMN model of merging high-throughput computational and experimental techniques to accelerate new materials discovery.

- Promising new STCH materials candidates as well as the broader structure-property-performance relationships discovered in this project are being shared. These discoveries are already assisting other water-splitting efforts within the HydroGEN consortium (e.g. BCM “super-node” work).

The calculation and screening techniques developed in this project could have an impact well beyond HydroGEN, with relevance to other broad materials discovery efforts.
Accomplishments: Milestone Overview

Year 2 Go/No Go Milestone

<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Type</th>
<th>Milestone Description</th>
<th>Milestone Verification Process</th>
</tr>
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<tbody>
<tr>
<td>M3.5</td>
<td>Bulk materials testing</td>
<td>Bulk testing demonstrates that at least one material composition splits water under steam-to-hydrogen ratios lower than 10:1 and with a hydrogen capacity under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C at least equal to that of ceria under the reduction conditions of 1450°C and oxidation temperatures of 850°C-1000°C.</td>
<td>Production of at least 150 µmol H₂/g sample at the conditions listed. Results of testing performed at CSM must be repeatable and duplicated by experiments using Sandia’s SFR.</td>
</tr>
</tbody>
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- Meeting the Y2 Go/No Go criteria required the discovery of a game-changing material
  - While this breakthrough material was not found, several interesting findings were uncovered, and important developments made. These are being wrapped up into at least three journal submissions.
Accomplishments: Key Results

Task 1: Computational Stability Screening

- “Random Smart” predicts suitable candidates in structure search at much lower computational cost
  - Uses unsupervised ML algorithm
  - Shown to work for simple and complex oxide compositions, from binary to quinary, with large simulation cells. Also captures outlier behavior where actual lowest energy is not near main distribution of possible energies, like in SiC.

This approach can be adapted across disciplines for high-throughput structure stability searches. We are working on a publication to disseminate this novel approach to the community.
Task 1: Computational Defect-Formation Modeling

Develop a computational model for quantitative prediction of reduction and oxidation behavior of STCH materials using detailed defect calculations

- Mn charge state plays a significant role on O vacancy formation energy

\[ \Delta H(V_O) \text{ is sensitive to the choice of DFT functional (GGA, SCAN)} \]

\[ \Delta H(V_O) \text{ depends on Mn}^{3+}/\text{Mn}^{4+} \text{ ratio, increases with increasing off-stoichiometry (}} \delta \text{)} \]

Correct prediction of STCH redox behavior requires models that incorporate “non-dilute” effects such as defect-defect interactions

\[ \text{In Collaboration w/ First Principles Theory Node (NREL)} \]

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Accomplishments: Key Results

Task 2: Combinatorial

- Double-site Ce-substituted (Ba,Sr)MnO₃ oxide perovskites are screened for exploring the potential STCH materials
- We used combi PLD to understand composition-structure-processing-performance trends in the (Ba,Sr,Ce)(Mn,Ce)O₃ material system, and demonstrates an efficient way to uncover new STCH-active compounds.

The compositional stability range of the 4P-polymorph is enhanced by substitution of Ba on (Sr,Ce)MnO₃ with wide range of Ce compositions at higher temperatures. This may offer a “sweet spot” for optimal STCH performance within the BSCM system.

Accomplishments: Key Results

Task 3: Bulk Testing

- Thermodynamic analysis of experimental oxygen reduction experiments with two families of cerium-doped strontium manganate, $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ (SCMX) and $\text{Ce}_x\text{Sr}_{2-x}\text{MnO}_4$ (CSMX)
  - Cerium content appears to impact defect enthalpy, but leaves entropy largely unaffected
  - The structure differences between SCM and CSM have a much larger affect on thermodynamics

The structural differences between perovskites and layered RP phases, when mixed with dopant levels, creates a level of tunability that likely affects far more than just non-stoichiometry. Layered RP phases (e.g. CSM), may offer a pathway to higher defect partial-molar entropy (good for STCH) vs. simple perovskites (e.g SCM)

For submission to Energy Technology
## Collaboration: Effectiveness

### Task 1: Computational

**Stephan Lany**
First Principles Materials Theory for Advanced Water Splitting Pathways
- Leads work on improving the computational accuracy of defect calculations
- Continued assistance to CSM computational team
- All new results being introduced to NREL MatDB

### Task 2: Combinatorial

**Andriy Zakutayev**
High-Throughput Experimental Thin Film Combinatorial Capabilities
- Technical guidance on film deposition strategies
- Input on improvements to Y2 strategies to maximize the benefits of their capabilities and expertise
- Spearheaded the investigation into increasing Ce content in BCM/CSM/SCM

### Task 3: Bulk Testing

**Anthony McDaniel**
Virtually Accessible Laser Heated Stagnation Flow Reactor
- Assisted in SFR operation for testing of SCM and CSM
- All experimental raw data uploaded to HydroGEN Data Hub, analyzed data follows as it is produced
- Main interface between group and pathway-specific Working Group

### “2B” Project Contributions

- Continued participation in Benchmarking/Protocols Workshops
- Producing protocol on rapid thermochemical potential screening method for inclusion in “2B” special publication
- Assisting on additional protocol and workgroup assignments
Proposed Future Work

Year Three Scope ($252k)

• Complete computational work on validating “Random Smart” protocols and improvements to predictive quality of oxygen non-stoichiometry

• Continue reporting out results of project with a series of papers across all three tasks; computation, combinatorial, and bulk

• Complete dissemination of data on HydroGEN Data Hub and other public repositories
Project Summary

• Great strides have been made in computational fast screening methods over the course of the project
  – The further development of the Random Smart method has led to a rapid winnowing of the number of expensive stability calculations, especially in the area of materials with a large number of cations (quaternary and higher). This benefit extends far beyond the arena of STCH and even HydroGEN in general.

• Improvements in both the calculations for oxygen vacancy formation energy and how those values propagate mathematically into the determination of oxygen non-stoichiometry with temperature

• Successful collaboration with three EMN nodes

• Positive reviews from 2020 HPTT & AMR

Since 2020 AMR, >8000 quinary and higher compositions computationally screened, and stability calculations performed for >30 compositions. Novel potential compositions/structures within the BSM-CSM quaternary phase space were investigated, consisting of 100s more compositions.
Publications and Presentations

• Su Jeong Heo, Michael Sanders, Ryan O’Hayre, and Andriy Zakutayev, Double-site Ce Substitution of (Ba,Sr)MnO$_3$ Perovskites for Solar Thermochemical Hydrogen Production. *ACS Energy Letters*, In Review


— Previous Performance Period —

Traditionally, DFT calculations of all structures are performed to determine lowest energy configurations.

Random Smart performs *informed* selection on a subset of structures for DFT calculation with the objective to capture low energy configurations.

The lowest energy is found with far less computation for a complex quinary compound.

**Objective**: Find lowest energy structure
Thermodynamic Modeling Workflow

- To model $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ (SCM), start with detailed defect calculations in $\text{SrMnO}_3$
- Calculate defect formation energy within the dilute limit (single defect in the supercell) for a given level of theory

Relax atomic structure ➔ Calculate defect formation energy ➔ Model thermodynamic properties

Defect diagram at $\Delta \mu_{O} = -1.61$ eV, and $\text{Sr}_2\text{Mn}_2\text{O}_5$, $\text{Sr}_2\text{CeO}_4$ as competing phases

$p_{O_2} = 10^{-4}$ atm

Neutral O vacancy
Charged (2+) O vacancy

Reduction Temp. (°C)
SrMnO$_{3-\delta}$ — Going beyond the dilute limit

Task 2: Computational Defect-Formation Modeling

- More than one O vacancy in the supercell (incorporating defect-defect interactions)
- $\Delta H(V_O)$ increases from the dilute limit value with increasing off-stoichiometry ($\delta$)
- Statistically estimating number of sites with effective $\Delta H(V_O)$ for a given $\delta$
- Currently on-going: $\Delta H(V_O)$ dependence on Ce concentration