Accelerated Discovery of STCH Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

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Project Overview

Project Partners
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Integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH

Current SOA STCH efficiency (CeO$_2$): $\sim$2%
Efficiency for optimal STCH material: $>$60%

Project Impact
Greatly increase number of viable STCH materials candidates

Compositions Studied for Nonstoichiometric Redox STCH:
Today: 10’s of compositions
Project Goal: 1000’s of compositions 100x increase
Approach- Summary

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

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>59 µmol H₂/g sample ((T_{RED}=1350°C))</td>
<td>≥ 59 µmol H₂/g</td>
</tr>
</tbody>
</table>

Ultimate goal:
- 200 °C lower \(T_R\) than CeO₂
- 2X greater capacity than CeO₂

Barriers
- Quick calculations could have trouble being accurate enough to be useful
- Optical evaluation may be insufficient
- Screening of thin films may not fully correlate to bulk properties

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

Metric State of the Art Proposed

Temperature
- \(T_{ref}=1550°C\) – \(T_{ex}=1000°C\)
- \(T_{ref}=1350°C\) – \(T_{ex}=850°C\)

Hydrogen Production
\[ \mu\text{mol H}_2/\text{g sample} \]

Ultimate goal:
- 200 °C lower \(T_R\) than CeO₂
- 2X greater capacity than CeO₂
After discussions with NREL computational node on feasibility of original proposal, modifications have been made to the DFT plan

• **Scope:**
  – Based on recent success of new class of ceria-doped perovskite compounds, can we find other potential cation combinations that yield similar behavior?

• **Strategy:**
  – Screen >1000 perovskites for suitability and stability under two-step STCH cycling conditions
  – Directly calculate the effect on vacancy formation energy by adding cerium to the perovskite families that meet the stability screening
  – Expand search to look at more complex multi-cation permutations to identify potential underlying trends
Approach- Innovation: Experimental Screening

- Combinatorial thin-film deposition allows for the synthesis of compositional libraries (up to four targets)
- Enables screening of large compositional spaces and also provides validation data to inform the next round of computations
Many transition metal containing oxides change color depending on oxygen content.
A single screening experiment can potentially evaluate tens of different compositions simultaneously.
Approach- Innovation: Summary

• Budget Period One acts as a proof-of-concept and development cycle to determine feasibility of combining high-throughput DFT screening with combinatorial and high-throughput STCH materials production and screening
  – The discovery of even one new compound family within a year represents a significant acceleration

• Consortium resources and expertise have proven critical
  – Weekly interactions with node experts have accelerated progress with valuable modifications to our project plan
STCH cost targets require:

- Large improvements in hydrogen production capacity (mmol H$_2$/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.
• 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 will be shared. These discoveries may assist other water-splitting efforts within the HydroGEN consortium.

The calculation and screening techniques developed in this project could have an impact well beyond HydroGEN, with relevance to other broad materials discovery efforts.
Relevance & Impact: Leveraging Nodes

- Current roles and utilization of EMN Nodes
  - First Principles Materials Theory for Advanced Water Splitting Pathways
    - Computational resources (Peregrine)
    - Expertise and guidance on research plan development and execution
  - High-Throughput Experimental (HTE) Thin Film Combinatorial Capabilities
    - Deposition of proof-of-concept and combinatorial library PLD films
    - Characterization of both as deposited and post-processed films
    - Expertise and guidance on deposition effort
  - Virtually Accessible Laser Heated Stagnation Flow Reactor for Characterizing Redox Chemistry of Materials Under Extreme Conditions
    - Bulk testing for initial performance quantification and cycling durability

- Currently unavailable resources of possible future value
  - High-resolution multi-spectral optical capabilities for \textit{in-situ} measurement of gas production

The capabilities afforded by access to the EMN nodes are invaluable to this project. Such tools would be prohibitively expensive to develop internally and cumbersome to utilize through normal user agreements.
Accomplishments: Milestone Overview

• Should both Go/No Go criteria be met, it sets the stage for the discovery of many more STCH compounds and a broader understanding of the property and behavior relationships for redox oxide-cycle water splitting

<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Type</th>
<th>Milestone Description</th>
<th>Milestone Verification Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1.3</td>
<td>Evaluation of results to inform next iteration</td>
<td>Experimentally validate method to qualitatively predict thermodynamic trends in oxide reduction (and hence potential STCH suitability) as a function of oxide composition by DFT across five different families and within at least one compositional family.</td>
<td>Extent of reduction measurements on five compositions from different oxide families and more than three across a single family</td>
</tr>
<tr>
<td>M3.2</td>
<td>Bulk materials testing</td>
<td>Bulk testing demonstrates that at least one material composition splits water with a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C, under any steam-to-hydrogen ratio.</td>
<td>Production of at least 59 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>
</table>
Accomplishments: Key Results

- Task 1: Computational
  - Recommended computational workflow implemented
  - Perovskite stability calculated (using NREL resources) or located from existing DB for all A-B element pairs of interest (Q2 Milestone met)
  - Selection criteria being adjusted (first criteria screened out known STCH materials)

In Collaboration w/First Principles Theory Node (NREL)

- Inorganic Crystal Structure Database (ICSD)
- Ordered stoichiometric compounds
- Perovskites
- Polymorphs and their spin configurations
- Enthalpy of formation
- Material Stability
- Charged oxygen defect formation
- Effect of Ce doping
- Promising STCH

Oxide Enthalpies of Formation

Likely region of interest
Accomplishments: Key Results

• Task 2: Combinatorial
  – Seven proof-of-concept films have been produced and characterized at NREL, and tested in simulated redox cycles at CSM (using low concentration hydrogen during reduction and air for oxidation)
  – Color changes due to redox cycling have been observed for a number of transition metal oxides, additional quantification and characterization is ongoing at NREL
  – Q1 Milestone (M2.1) is late, but nearing completion

In Collaboration w/High Throughput Experiment Node (NREL)

Promising STCH compounds
Accomplishments: Key Results

- **Task 3: Bulk Testing**
  - **Go/No Go Milestone (M3.2)** has been completed early, based on newly identified composition (Compound X), tested using SFR
  - Cycling durability testing of previously discovered material BCM has been performed, using SFR, in order to understand the impact of potential phase changes during redox cycle
  - Six additional compounds related to Compound X family have been synthesized and are ready for initial testing in Q3 at CSM

**In Collaboration w/Stagnation Flow Reactor Node (SNL)**
Accomplishments: Outlook

• With M3.2 already met for one composition, current project focus is on the M1.3 milestone
  – Single compositional family TPR experiments are scheduled to begin early Q3
  – Depending on modeling results recently completed, additional candidate families for experimental screening should be identified in early Q3 with synthesis and testing scheduled for late Q3 and early Q4

We are confident that both Go/No Go criteria will be met by the end of Budget Period One, allowing for the leveraging of those results into a strong position for Budget Periods Two and Three
# Collaboration: Effectiveness

## Task 1: Computational

**Stephan Lany**  
First Principles Materials Theory for Advanced Water Splitting Pathways  
- Bi-monthly meetings on results and strategy  
- Reviewed computational plan and directed alterations  
- Shared recent paper on charged vacancies  
- 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  
- Brought post-doc (Yun Xu) onboard to alleviate deposition bottleneck, greatly increasing the number of films available for early testing

## Task 3: Bulk Testing

**Anthony McDaniel**  
Virtually Accessible Laser Heated Stagnation Flow Reactor  
- Discussions on durability testing of BCM and assisted with execution  
- Assisted in SFR operation for testing of Compound X  
- Main interface between group and pathway-specific Working Group

## Data Hub

All data produced using nodes is being stored on Data Hub for internal work and eventual public release  
- SFR data for all runs  
- High-Temp XRD for BCM  
- Characterization data for proof-of-concept films
Proposed Future Work

- **Year Two Scope ($250k)**
  - Expand computational and combinatorial search to more complex compositions (quaternary perovskites, single-dopant layered perovskites)
  - Discover at least two more quality candidates that split water
  - Discover at least one excellent candidate that produces hydrogen at steam-to-hydrogen ratios lower than 10:1 and, under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C, has a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1450°C and oxidation temperatures of 850°C-1000°C

- **Year Three Scope ($250k)**
  - Full characterization and advanced study of excellent candidate, including H2A analysis

The identification of an excellent STCH material candidate greatly increases the likelihood that the production of industrial scale quantities of hydrogen using solar thermal energy at <$2/kg becomes technically feasible

Any proposed future work is subject to change based on funding levels
Project Summary

• Project is on pace to meet GNG milestones
• Nodes are an integral part of the project and its success
  – Project was specifically designed to leverage node capabilities. Geographic proximity has enabled regular face-to-face meetings and sharing of staffing resources.
• Proof-of-concept work demonstrates potential of the optical screening process