Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

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PD165

NREL | Berkeley Lab | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

Project Partners

Ryan O'Hayre and Michael Sanders
Colorado School of Mines

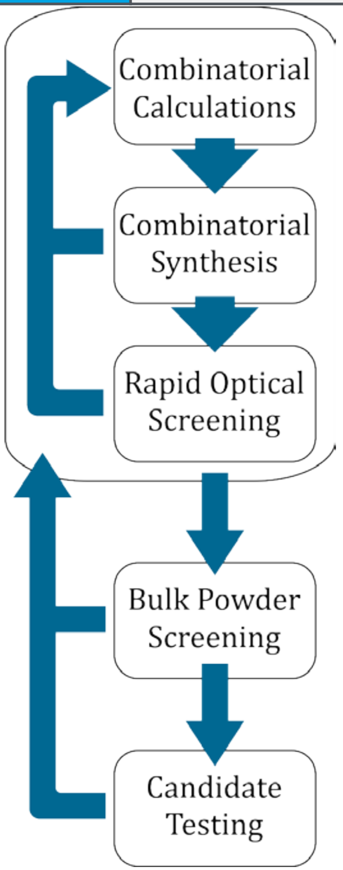
Award #	EE000808
Start Date Yr 1 End Date Project End Date	10/01/2017 09/30/2018 TBD
Total DOE Share Total Cost Share Year 1 DOE Funding*	$755,253 $83,893 $249,990

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

Current SOA STCH efficiency (CeO_2): ~2%
Efficiency for optimal STCH material: >60%

Huge opportunity for transformative improvement



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

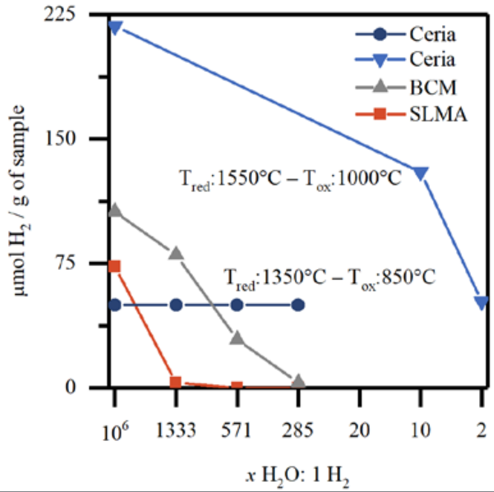
100x increase

* this amount does not cover 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



Key Impact

Metric	State of the Art	Proposed
Reduction Temperature	*1550°C*	*1350°C*
Hydrogen Production	*59 µmol H_2/g sample (@T_{RED}=1350°C)*	*≥ 59 µmol H_2/g*

Ultimate goal:
200 °C lower T_R than CeO_2
2X greater capacity than CeO_2

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

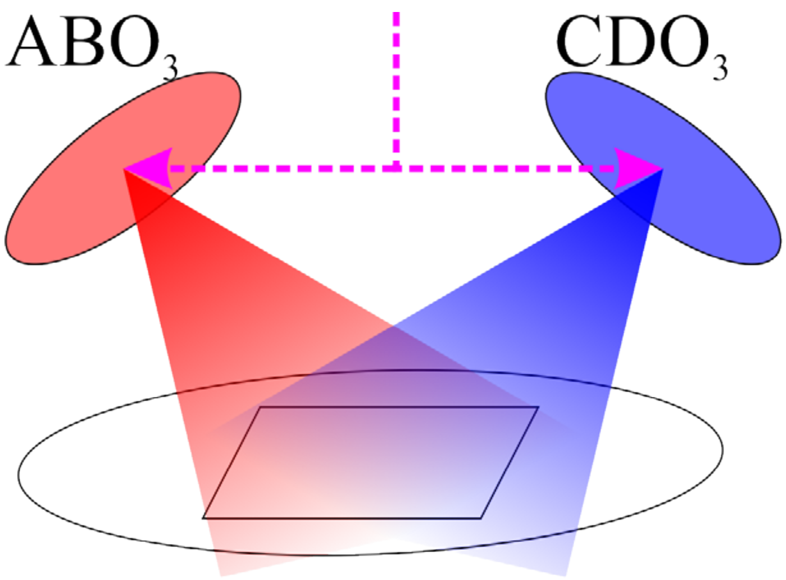
Approach- Innovation: DFT Screening

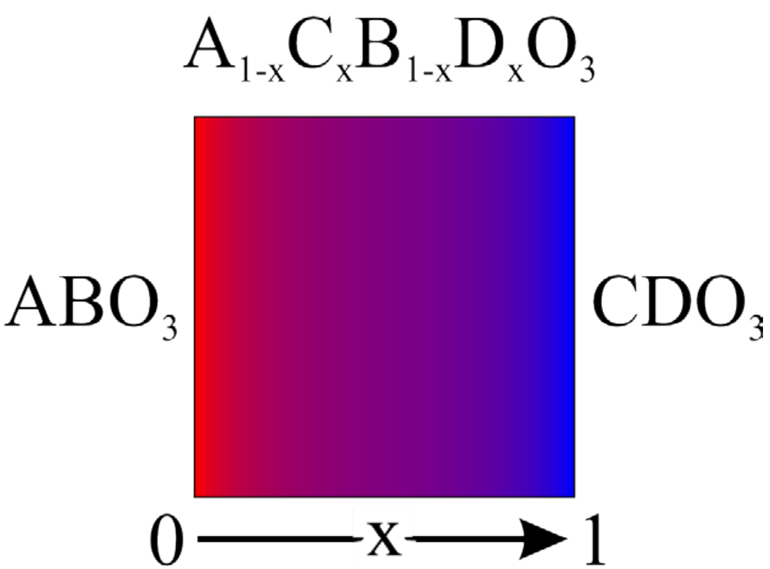
After discussions with NREL computational node on feasibility of original proposal, modifications have been made to the DFT plan

- 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

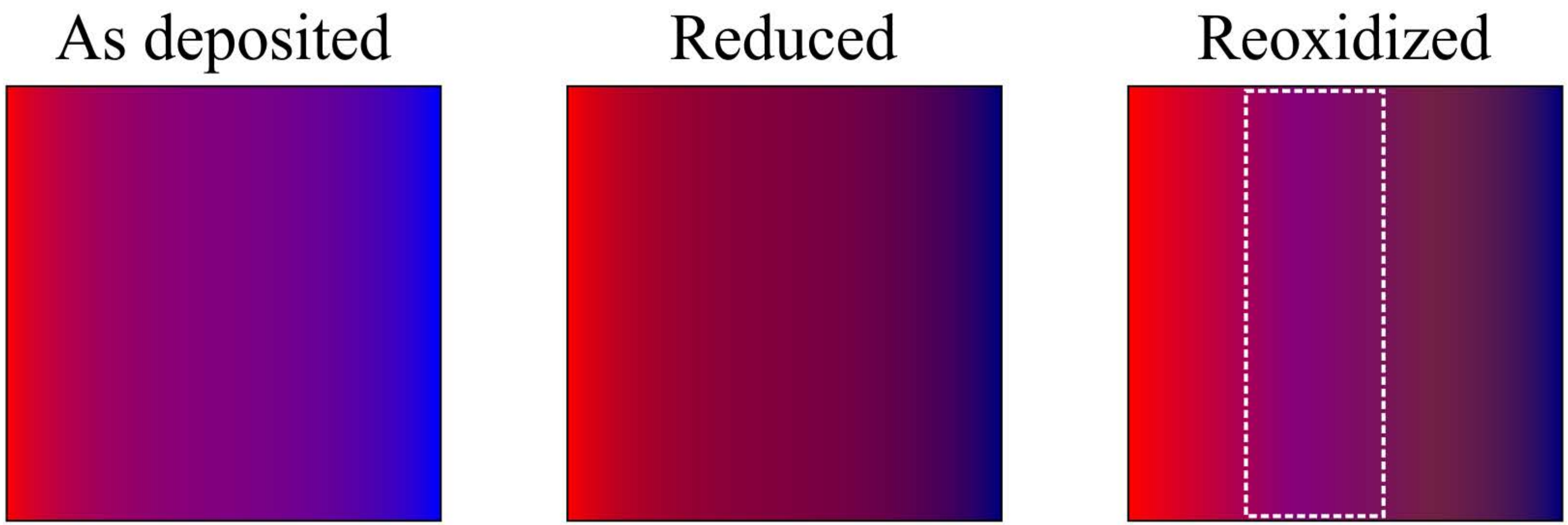
- Combinatorial thin-film deposition allows for the synthesis of compositional libraries (up to four targets)
- Enables screening of large compositional spaces and also provides validation data to inform the next round of computations





Approach- Innovation: Experimental Screening

- Many transition metal containing oxides change color depending on oxygen content
- A single screening experiment can potentially evaluate tens of different compositions simultaneously



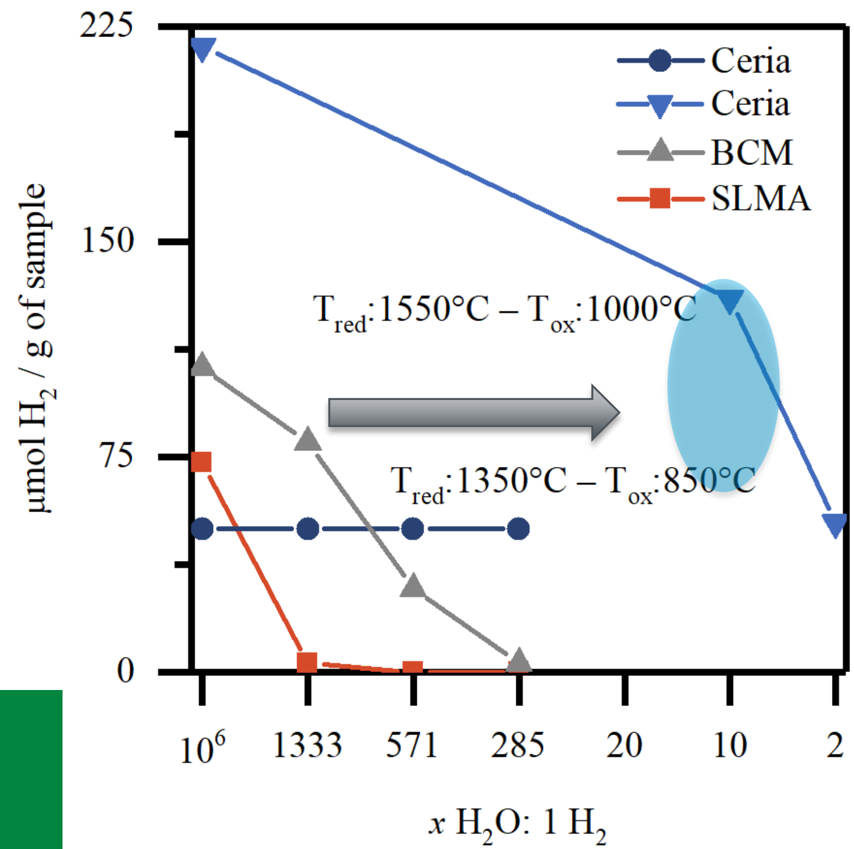
Approach- Innovation: Summary

- 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

Relevance & Impact: Support for H2<$2/kg

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

Relevance & 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 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 *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

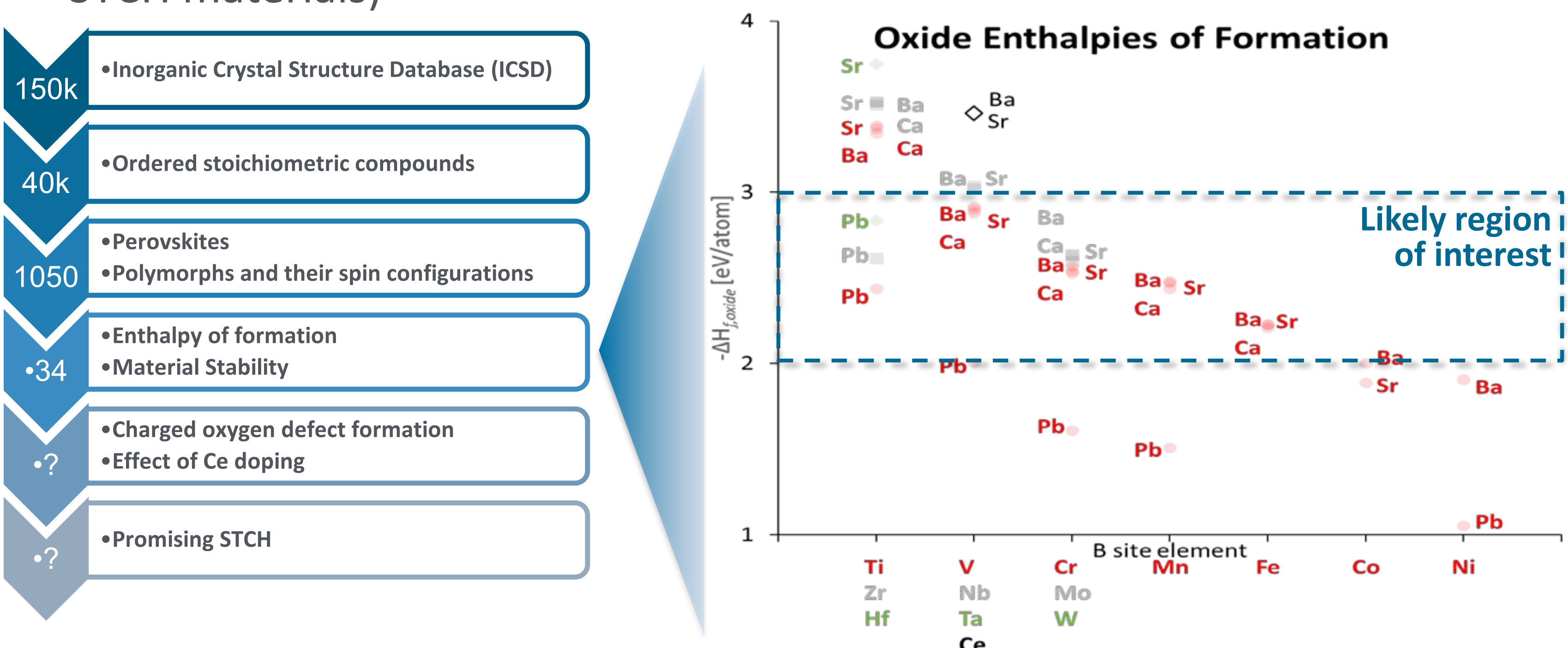
Year 1 Go/No Go Milestones

Milestone Number	Milestone Type	Milestone Description	Milestone Verification Process
M1.3	Evaluation of results to inform next iteration	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.	Extent of reduction measurements on five compositions from different oxide families and more than three across a single family
M3.2	Bulk materials testing	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.	Production of at least 59 μmol H_2/g sample at the conditions listed. Results of testing performed at CSM must be repeatable and duplicated by experiments using Sandia's SFR.

Accomplishments: Key Results

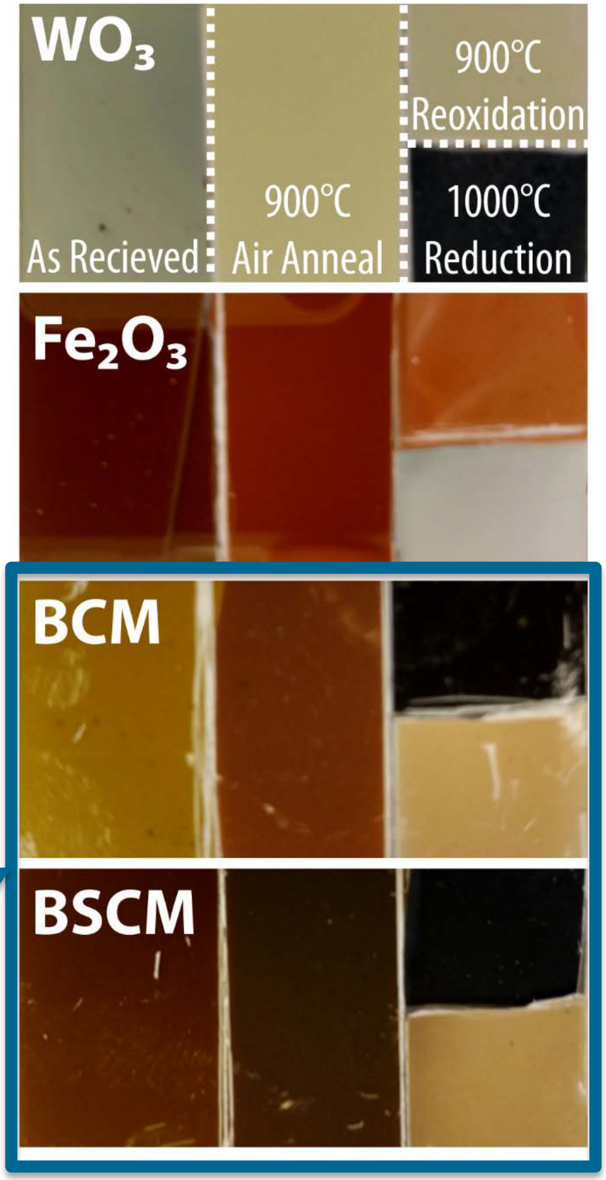
In Collaboration w/First Principles Theory Node (NREL)

- 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)



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



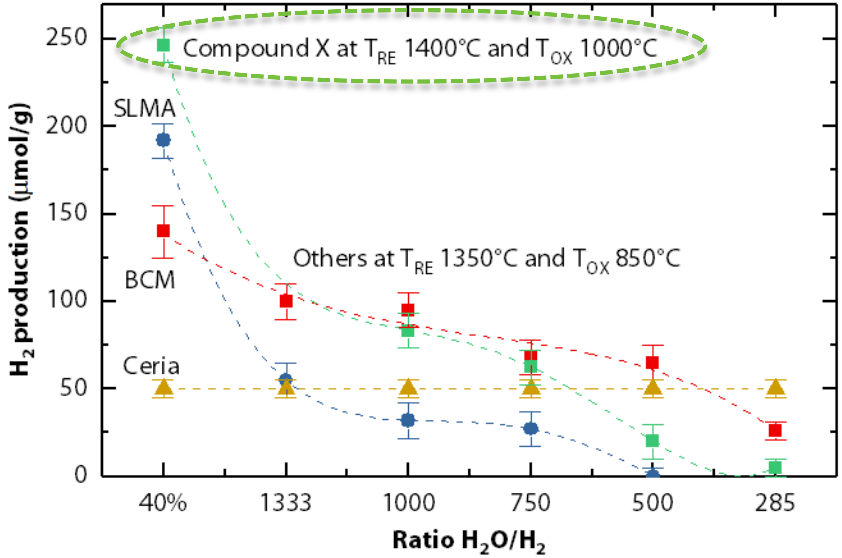
In Collaboration w/High Throughput Experiment Node (NREL)

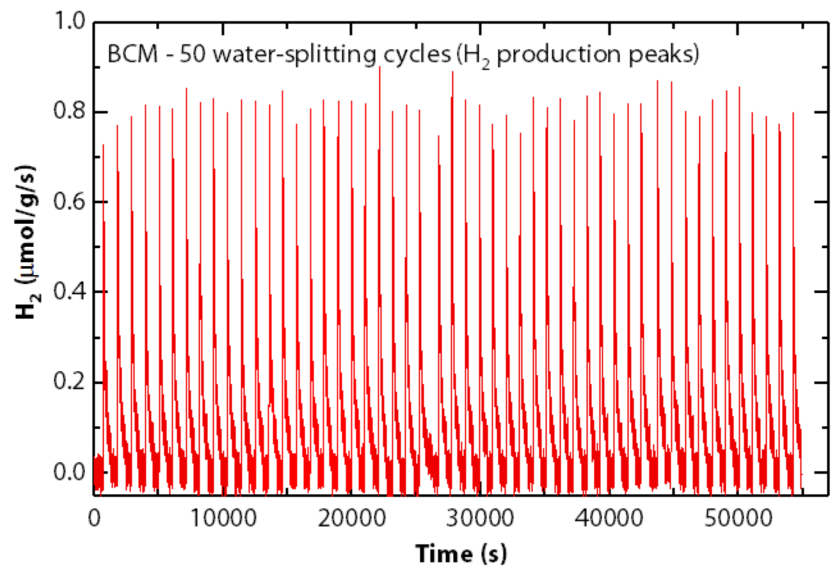
Promising STCH compounds

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