SAND2024-03881C

Solar Thermochemical Water Splitting (STCH): Tony McDaniel (lead)

Participating Labs: SNL, NREL, LLNL, INL

Project ID # P148D

HydroGEN STCH Seedling Projects & Lab Collaboration

Barriers
- Cost
- Efficiency
- Durability

STCH Node Labs

Sandia National Laboratories

INL Idaho National Laboratory

Lawrence Livermore National Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Support through:

Personnel
Equipment
Expertise
Capability
Materials
Data

Interactive STCH Projects

ASU Arizona State University

University of Colorado Boulder

MIT Massachusetts Institute of Technology

Washington University in St. Louis

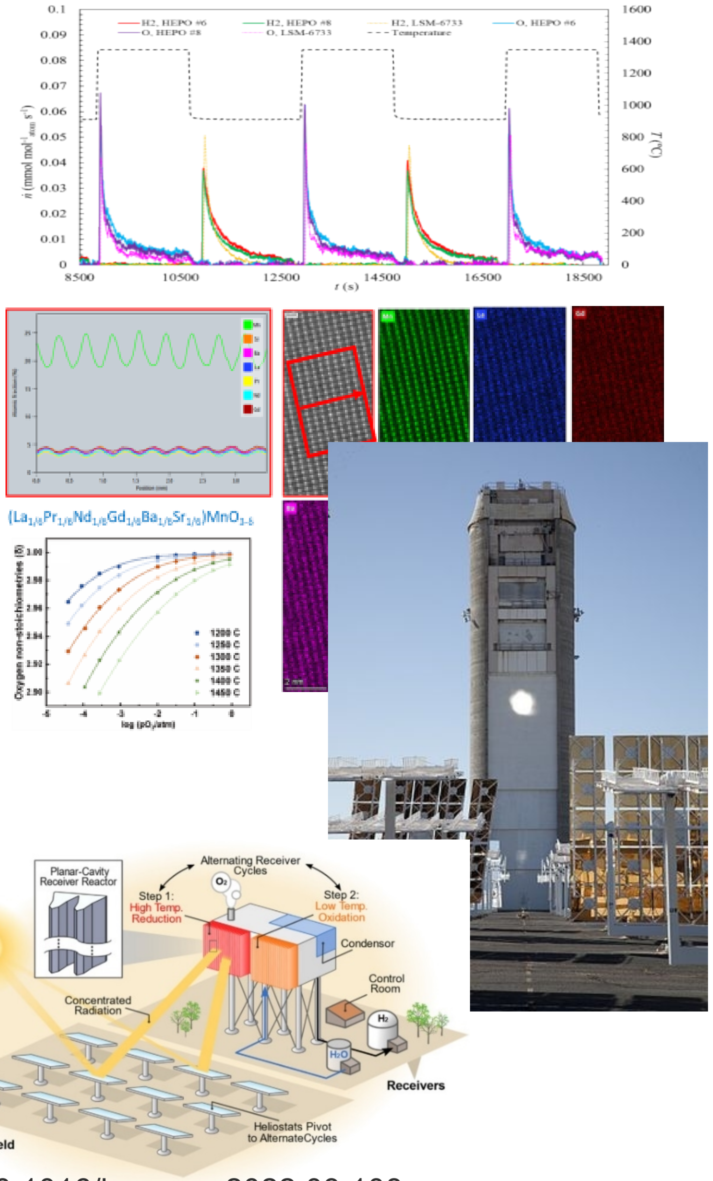
SAINT-GOBAIN

HydroGEN STCH Seedling Projects with Lab Capability Support

Technical Accomplishment Highlights

10 Lab capabilities support 5 new FOA-awarded projects:

- **(P211, ASU, SNL, INL and NREL) Design of Perovskite Materials for Solar Thermochemical Hydrogen Production:** Initial multiscale modeling of STCH redox reactors with comprehensive thermal-chemical models predicting component design and performance
- **(P208, CU, NREL) Non-Intermittent, Solar-Thermal Processing to Split Water Continuously via a Near-Isothermal, Pressure-Swing Redox Cycle:** Preliminary multiscale modeling evaluating STCH materials for commercial scale-up with TEA assessment
- **(P210, CU, SNL and NREL) Accelerated Discovery and Development of Perovskites for Solar Thermochemical Hydrogen Production:** Identified path forward to on-sun testing using prior reactor development.
- **(P217, St. Gobain, SNL, LLNL, and NREL) Scalable Solar Fuels Production in A Reactor Train System by Thermochemical Redox Cycling of Novel Nonstoichiometric Perovskites:** Computed energy barriers for water splitting process on STM and performed preliminary analysis of on-sun reactor testing
- **(P212, WASHU, SNL and NREL) Ca-Ce-Ti-Mn-O-Based Perovskites for Two-Step Solar Thermochemical Hydrogen Production Cycles:** Performed initial evaluation of balance of plant needs for on-sun testing.



10.1016/j.renene.2022.03.108

Assess Technology Viability, Enable DFT-ML Material Discovery

STCH Lab R&D Goals and Approach

6 Nodes

Goals: Comprehensively validate known STCH material properties and demonstrate theory-guided design of materials approach that optimizes the capacity/yield tradeoff.

- Develop computational toolset to define and establish material performance targets.
- Rigorously assess selected material formulations.
- Develop a materials search strategy for optimizing the capacity/yield tradeoff using DFT + Machine Learning (ML).
- Discover new materials using the ML model and characterize by detailed calculations, synthesis, and experimental validation.

STCH R&D:Q4 Annual Milestone	STCH Material Down-Select. Criteria: Use the technology assessment methodology derived from FY23 work to critically assess new ML-based solid solution STCH materials. The metric accounts for material-specific cycle dynamics and plant operational modality. (~10 new solid solution materials).

DFT = density functional theory
T_{RED} = reduction temperature

Exemplar Material Commercial Viability Study

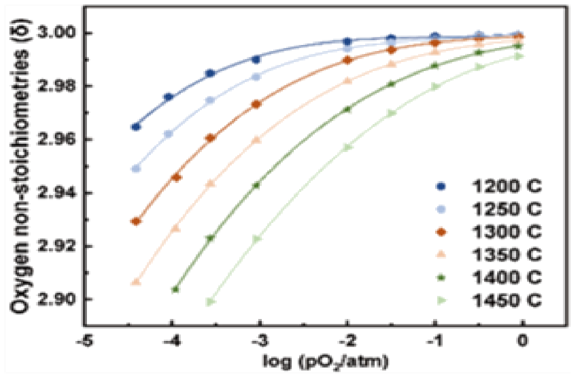
STCH Lab R&D Accomplishments

- Exemplar materials, methods and metrics determined by community consensus (via Benchmarking).
- Software platform developed for "end to end" processing of experimental data.
  - Will be made available to public

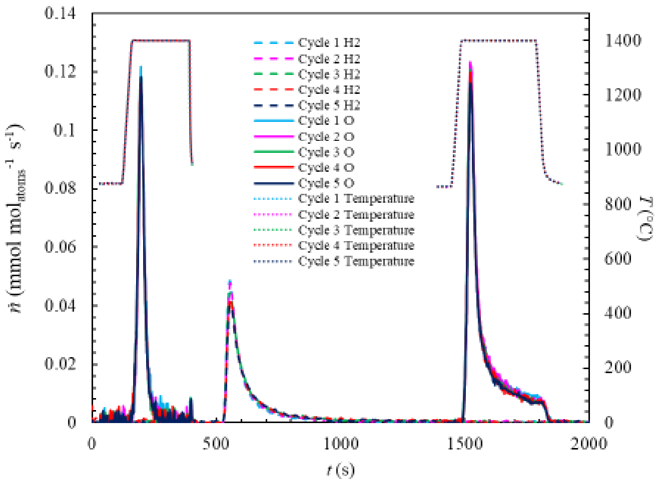
Key accomplishment: Measured and analyzed thermodynamics and H_2 production of five exemplar materials

Next step: Complete exemplar evaluation of cycle efficiency with estimator tool and publicize results

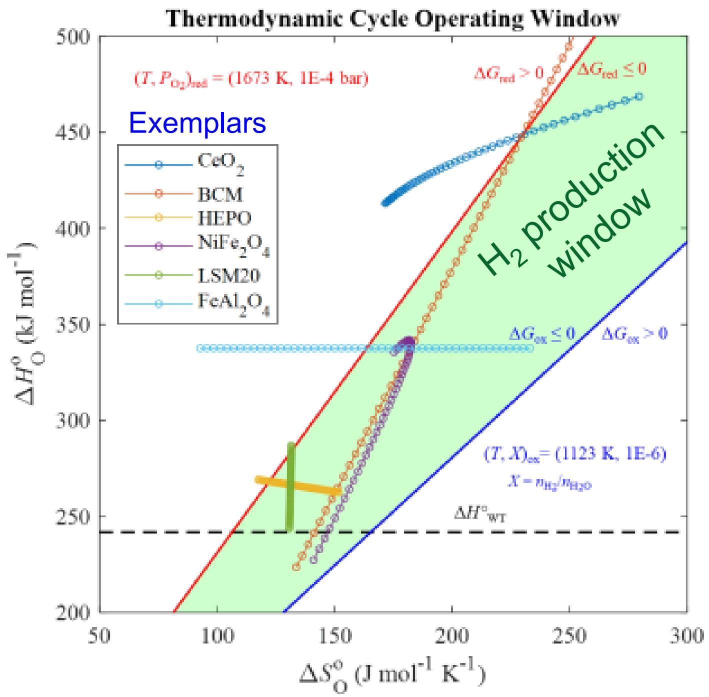
Thermodynamic parameters (from thermo-gravimetric analysis)

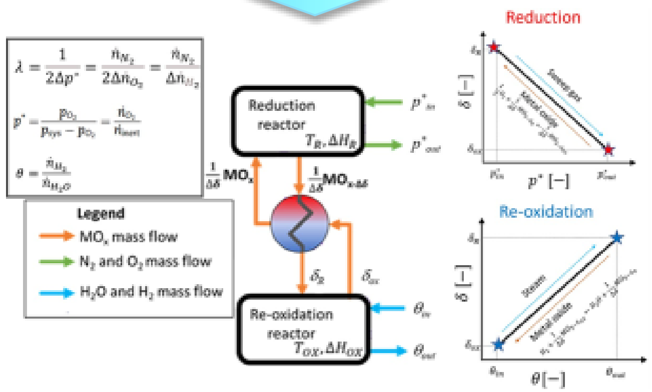


Hydrogen production and kinetic parameter (from flow reactor)



BCM: $BaCe_{0.25}Mn_{0.75}O_3$
HEPO: $La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Ba_{1/6}Sr_{1/6})MnO_3$
LSM20: $La_{0.8}Sr_{0.2}MnO_3$



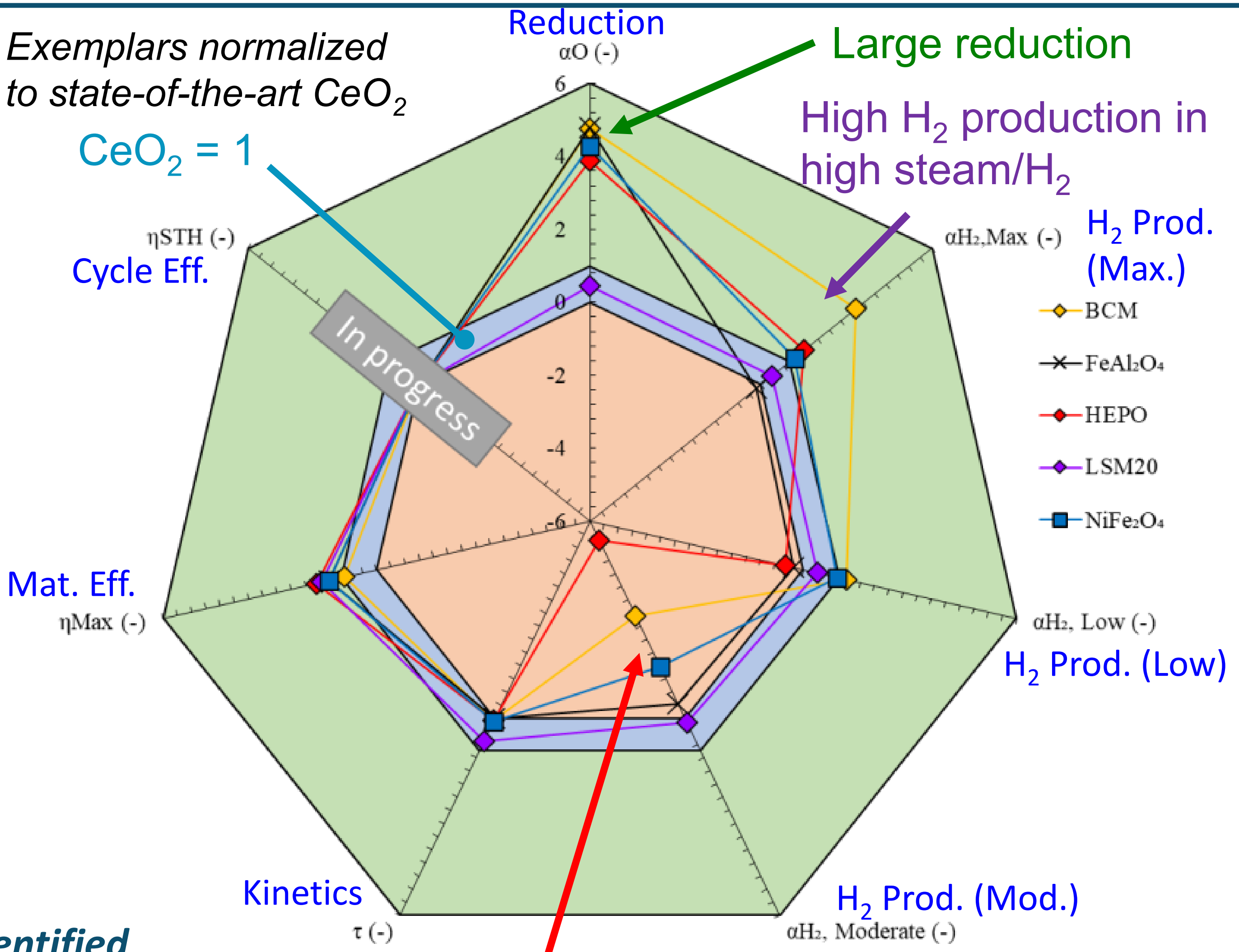


Cycle efficiency estimation

Exemplar Material Commercial Viability Study

STCH Lab R&D Accomplishments

Metrics	Descriptor	Target Values
Cycle Efficiency (STH)	Solar-to-hydrogen conversion efficiency derived from detailed cycle analysis using a thermodynamic model based on specific plant operational assumptions	$\eta_{STH} > 26\%$
Material Efficiency	$\frac{\Delta G^o_{WS}}{\Delta H^o_O}$ is the maximum possible thermal efficiency of the two-step process. (ΔG^o_{WS} evaluated at 25 °C)	$\eta_{Max} > 50\%$
Reduction Capacity	mmol O / mol atom in solid reduced @ neutral low condition	$\alpha_O > 5$
STCH Capacity (Maximum Yield)	mmol H_2 / mol atom in solid reduced @ neutral low condition, oxidized in pure H_2O @ optimal T_{OX} for material	$\alpha_{H2,Max} > 5$
STCH Capacity (Low Yield)	mmol H_2 / mol atom in solid reduced @ neutral low condition, oxidized in steam-to-fuel ratio H_2O/H_2 = 1000 @ optimal T_{OX} for material	$\alpha_{H2,Low} > 2.5$
STCH Capacity (Moderate Yield)	mmol H_2 / mol atom in solid reduced @ neutral low condition, oxidized in steam-to-fuel ratio H_2O/H_2 = 100 @ optimal T_{OX} for material	$\alpha_{H2,Mod} > 1$
Kinetic Performance	Time to 90% of $\alpha_{H2,Max}$ in pure H_2O at optimal T_{OX} for specific material in a dispersed powder configuration	$\tau > 0.20$



...but H_2 “consumption” in low steam/H_2 → only LSM20 competitive with CeO_2

Key accomplishment:

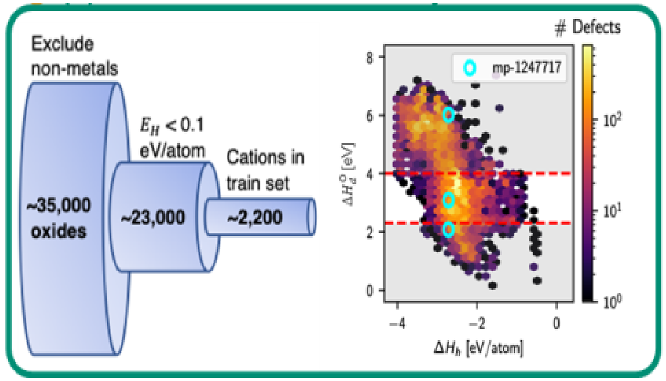
- ***Evaluation framework created and metrics identified***
- ***Weakness of exemplars in low steam/H_2 ratio → critical need for new materials***

High Throughput Screening of Materials Project: Version 2

STCH Lab R&D Accomplishments

ML screens 10,000’s of MP structures in minutes that would take 1,000’s of DFT months

Metric	Requirement
Frac. of defects w/ $\Delta H_d^O > 2.3$ eV	$x_{min} = 1$
Frac. of defects w/ $\Delta H_d^O \in [2.3, 4.0]$ eV	$x_{rng} > 0$
STCH operating range conditions (P_{O_2})	$\Delta\mu'_{O_2}$
Compound stability range	$\Delta\mu_{O_2}^{\phi_H < \{0, 0.1, ...\}}$
Stable in the target range	$\Delta\mu_{O_2}^{\phi_H < X} \cap \Delta\mu'_{O_2}$

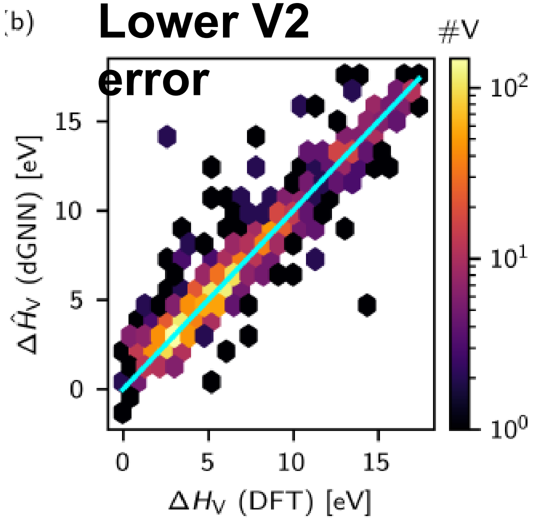


- **V2 training data** = V1 + V1 validation + lit. + new cations

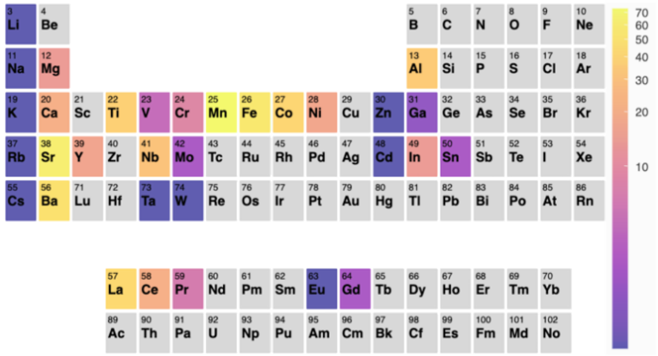
Data Source	#Hosts	#V_O	#V_M
V1	199	795	686
{Ga,Cr,Pr,Sn}-containing	23	75	57
(SrLa)(AlCoFeMn)O_3 alloys	12	12	0
SCM	2	86	0
BXM	4	18	9
Quat.+ Perovskites	4	8	13
ABO_3	29	43	0
V2 Totals	273	1037	765

Key accomplishments:

- Version 2 (V2): More compounds for training and more elements included
- Improved ΔH_V MAE for unseen compounds from ~0.5 eV to ~0.4 eV.
- New approach → target “unexpected” STCH compounds for experimental validation



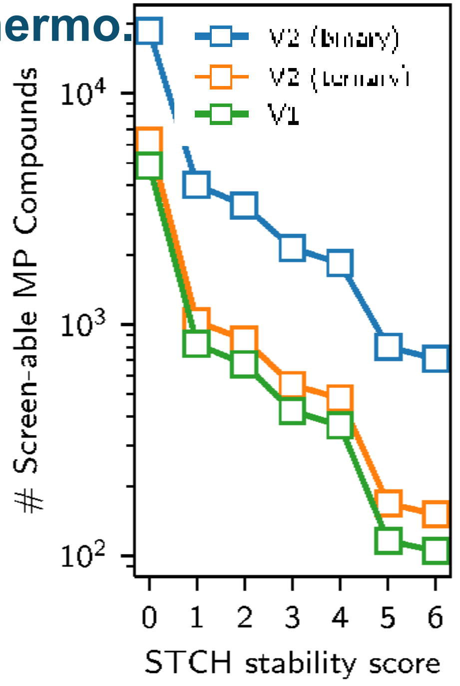
- New cations in V2: V, Pr, Sn, Cr, Ga, Gd, Cs, Rb, Eu, Li, Na, K, Zn, Cd, Mo, W, and Ta
- Prevalence of training compounds containing a given cation



MAE = mean absolute error
MP = Materials Project (https://materialsproject.org/)

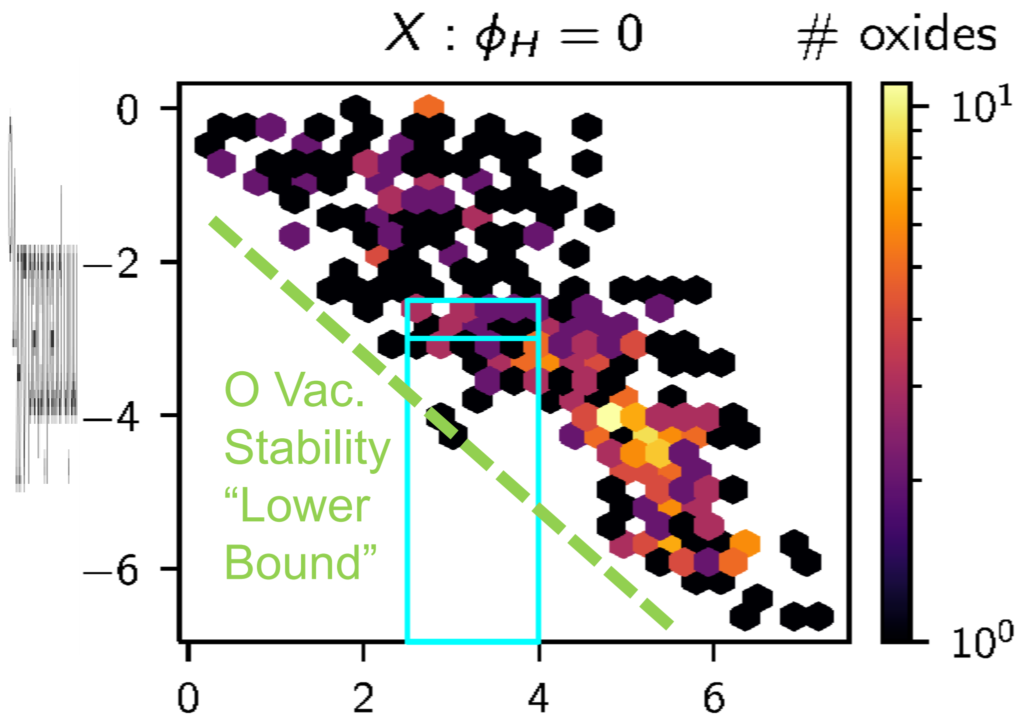
High Throughput Screening of Materials Project: Version 2
STCH Lab R&D Accomplishments

V2: 10x increase in high stability oxides with desired thermo.



- **~30x reduction** in # of oxides with STCH Stability Score = 6 vs. 0
- BUT… V2 screening will **~10x increase** # of oxides from V1 screening with STCH Stability Score = 6

Identify candidates for experiment in STCH "Golidilocks zone"



Computationally validate with high-throughput DFT

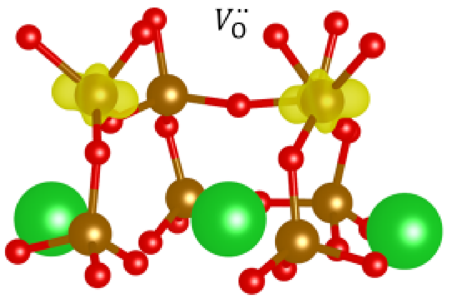
- Between ~50-400 new oxides targeted for DFT calc. of ΔH_{V_O}

10x more predicted oxides → next step of model validation with computation and experiment

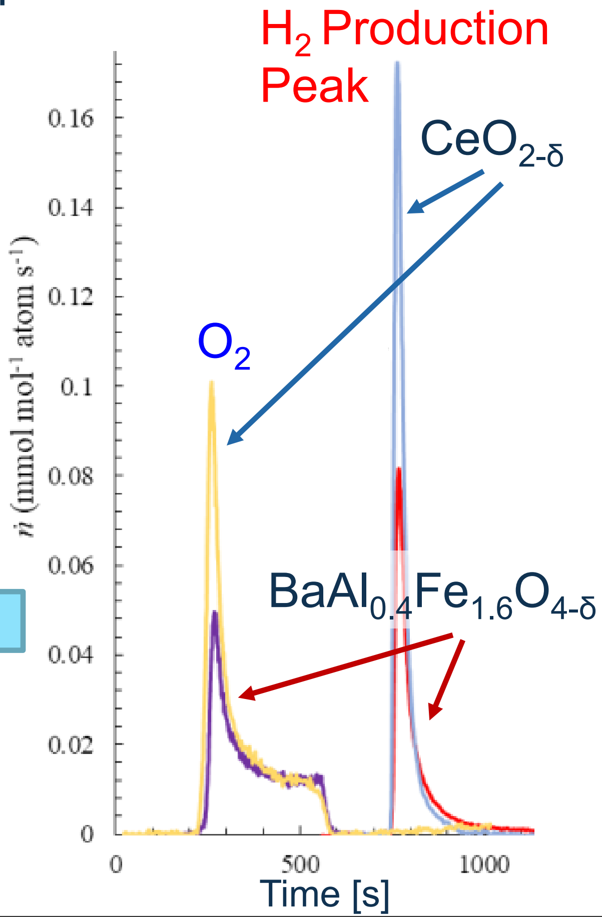
High Throughput Screening of MP Identified New STCH Materials
STCH Lab R&D Accomplishments

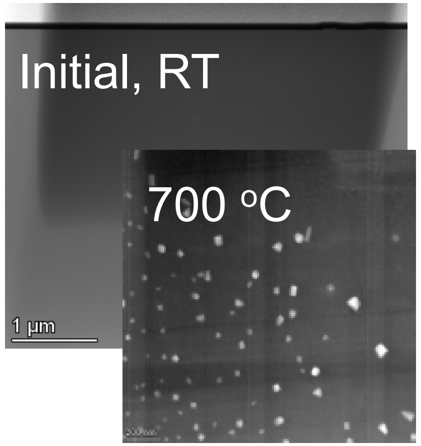
Predicted V1 STCH Compounds → Water-splitters!

$BaFe_2O_4$ – predicted water splitter (*Al → increased hi-T stability*)



DFT → oxygen vacancy preferred vs. cation defects

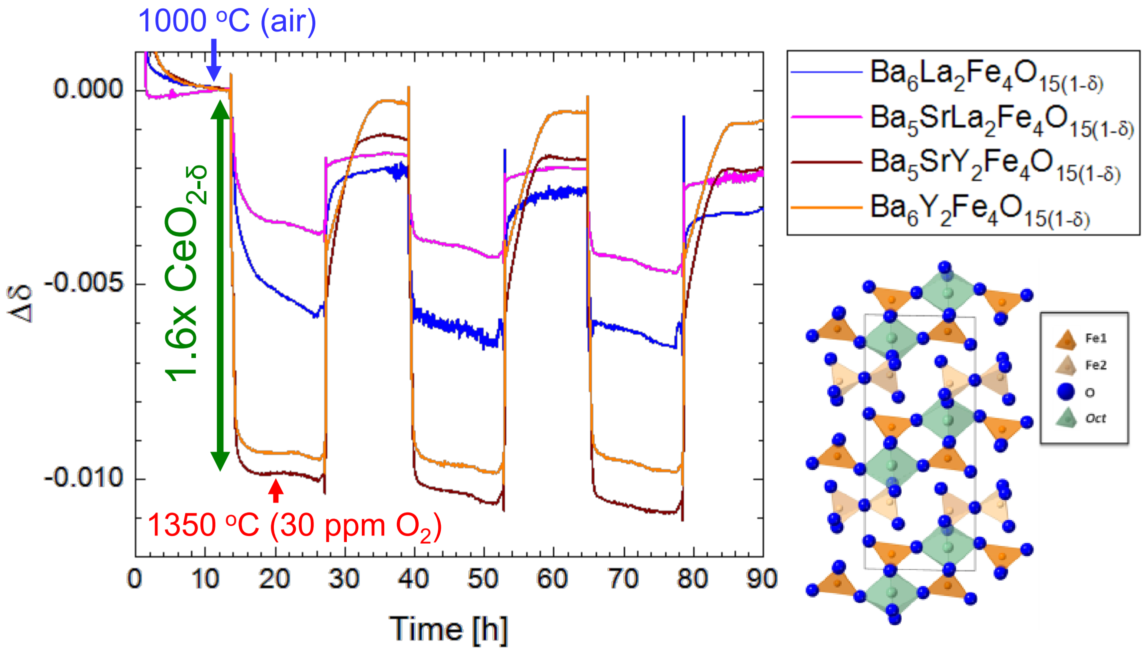




Fe-rich particles formed *in situ* TEM

Identified fabrication and stability challenges in other predicted V1 compounds

$(Ba,Sr)_6Oct_2Fe_4O_{15}$ family → $\Delta\delta$ > CeO_2



STCH screening protocol[1] → $Ba_6Y_2Fe_4O_{15}$ is best (flow reactor testing next)

[1] *Sanders et al., Front. Energy Res. 10:856943 (2022)*

Milestone accomplishment: >10 new compositions identified from V2 for STCH validation

- Selected by "ease" of fabrication, melting point, ΔH_V, and stability
- Examining unexpected STCH compounds

STCH Summary and Proposed Future Work

Summary:

- Evaluated exemplar materials' potential to meet DOE STCH technology performance targets using a technology assessment methodology developed in this project. Exemplars have attractive H_2 production in dilute H_2/steam, but in concentrated conditions, only one is competitive with state of the art ceria. → Need for new materials
- Successfully demonstrated a water splitting material predicted from theory-guided design of materials using a Machine Learning algorithm developed in this project.

Proposed Future Work:

- STCH Lab R&D
  - Apply technology assessment methodology derived in this project to evaluate viability of the >10 predicted V2 STCH materials to meet DOE STCH technology performance targets.
  - Complete technology assessment framework by evaluating exemplars using cycle efficiency model and publicize
  - Continue validation and development of machine learning model for theory-guided design of materials
- Leverage HydroGEN nodes to enable successful completion of new seedling projects.

(future work subject to available funding)

Content incorporated in other parts of the main presentation

Responses to Reviewers

Degradation mechanisms studies should be planned. Most durability data was short, which limits the significance of project progress.

- Per the DOE requirement for seedlings, long-term (multi-week) testing of materials on-sun is planned for STCH.

In the future, the consortium can provide a year-to-year progress (since 2016) that would provide an overall outlook of the accomplishments.

- Metrics have now been established in STCH to which new materials will be benchmarked against

Responses to Previous Year Reviewers' Comments

- It is hard to really get a feel for how HydroGEN, as a project, functions at the overall coordination level, as much of the discussion (with the exception of the cross-cutting work) was about the seedlings. It would be good to understand **how TEA is informing the choice of performance metrics so that there is a clearer focus on the critical ones**. The impression is that there is a certain inflexibility, or at least inertia, in the work program; so it would be interesting to better understand **how agility could be brought to the portfolio and whether there should be an element of tactical, as opposed to strategic, work**. The **PFAS bans** will need to be addressed, for instance, and the consortium could look for ways to support industry and/or use operational data to inform the work program.

  – All five STCH seedling projects have requested TEA support from the NREL node

Acknowledgements

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15