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HydroGEN
Advanced Water Splitting Materials

HydroGEN: Solar Thermochemical Hydrogen (STCH) Water Splitting

#P148D

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Assess Technology & Enable Material Discovery

DOE Energy Materials Network to Accelerate STCH Materials R&D

HydroGEN is a U.S. Department of Energy EMN consortium aiming to accelerate the research, development, and deployment of advanced water splitting technologies for clean, sustainable hydrogen production, with a specific focus on materials innovations that lower cost and increase durability.

HydroGEN has a world-class materials science network comprising more than 80 unique capabilities/expertise in synthesis, advanced characterization and computation, fundamental theory, and systems analysis and integration. ***10 capability nodes from 4 National Laboratories support 5 seedling projects comprised of 4 university and 1 company leads conducting collaborative R&D on STCH materials.***

Approach: Summary

Project Motivation

- Use a technology assessment methodology to evaluate exemplar materials' potential to meet DOE STCH technology performance targets.
- Demonstrate high-throughput theory-guided discovery of materials using Machine Learning (ML).

Key Impact

- Develop framework to define and establish material performance targets.
- Rigorously assess exemplar materials.
- Develop a materials search strategy using DFT + ML.
- Discover new materials using DFT + ML model.

Barriers

- Evaluation protocols and rigorous assessment absent for evaluating materials to meet DOE technology performance targets.
- High efficiency and low cost materials for STCH remain elusive because high capacity ($\Delta\delta$ at lower T_{RED}) ***and*** reaction yield in non-stoichiometric oxides has not been adequately demonstrated.

• Cost
• Efficiency
• Durability

Partnerships

STCH Node Labs

Sandia National Laboratories · Idaho National Laboratory · Lawrence Livermore National Laboratory · NREL National Renewable Energy Laboratory

Support through:

Personnel
Equipment
Expertise
Capability
Materials
Data

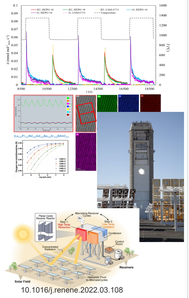
Interactive STCH Projects

ASU Arizona State University · University of Colorado Boulder · Massachusetts Institute of Technology · Washington University in St. Louis · SAINT-GOBAIN

Lab Supported STCH Seedlings

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

Relevance & Impact

- Setting standards for STCH material performance
- Benchmarking most well-known exemplar materials
- Discovering new materials with accelerated computation
- Enabling Seedling Project successes through advanced research

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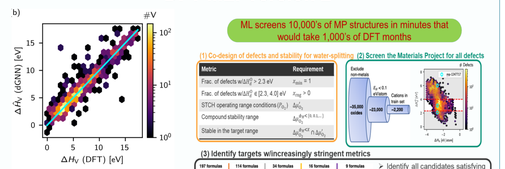
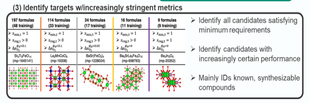
Accomplishments & Progress

High Throughput Screening of Materials Project Using DFT-ML: Version 2



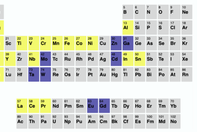
ML screens 10,000's of MP structures in minutes that would take 1,000's of DFT months

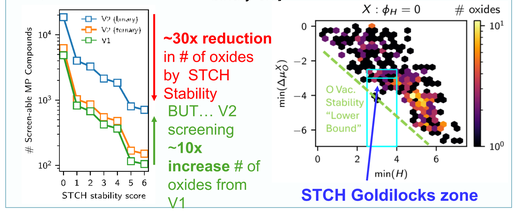


- More compounds for training and more elements included
- Improved ΔH_V MAE for unseen compounds from ~0.5 eV to ~0.4 eV.
- New approach → target "unexpected" STCH compounds for experimental validation

➢ **Yellow** = covered by *ternary+* oxides

➢ **Purple** = covered by *binary only*





Technology Viability & DFT-ML Material Discovery

- Complete framework to define and establish material performance targets.
- Rigorously assess exemplar material formulations.
- Develop a materials search strategy using DFT + Machine Learning.
- Find new STCH materials using ML model and characterize by detailed calculations, synthesis, and experimental validation.

FY24 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).

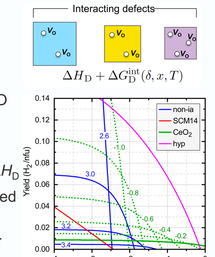
Thermochemical Equilibria with Interacting Defects

New approach for interacting defects: $Sr_{1-x}Ce_xMnO_{3-\delta}$ (SCMx)

- **Blue**: non-interacting (ΔH_D in eV)
- **Red**: Interacting defects (SCM14)
- Defect interactions limit yield and H_2:H_2O

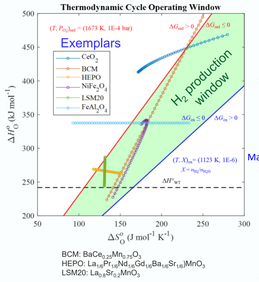
Charged defect model for CeO_2 and hypothetical materials

- **Green**: CeO_2-like oxides with reduced ΔH_D
- **Magenta**: Hypothetical oxide with reduced ε_{ion} and stronger CBM *T*-dependence
- High yield at high H_2:H_2O requires lower defect ionization energies than CeO_2

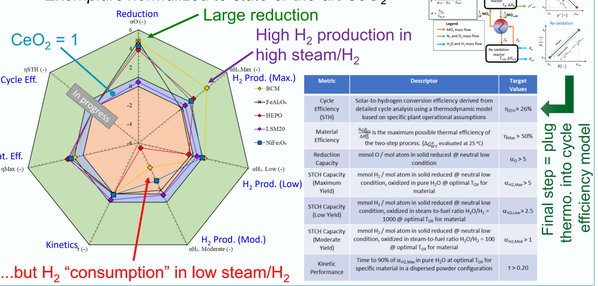


Exemplar Material Commercial Viability Study

- Material exemplars, methods and metrics determined by community consensus.
- Software platform developed for "end to end" processing of experimental data.
- Developed robust TGA and flow reactor experimental protocols → thermodynamic feed into models



Exemplars normalized to state-of-the-art CeO_2

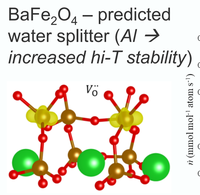


Metric	Descriptor	Target Values
Cycle Efficiency (STH)	Solar-to-hydrogen conversion efficiency derived from detailed cycle analysis using a thermodynamic model based on specific plant operational assumptions	η_{STH} > 26%
Material Efficiency	$\frac{\Delta H_O}{\Delta H_{RED}}$ is the maximum possible thermal efficiency of the two-step process, ΔH_{RED} evaluated at 25 °C)	η_{Max} > 50%
Reduction Capacity	mmol O_2 / mol atom in solid reduced @ neutral low condition	α_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	τ > 0.20

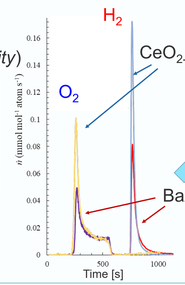
Final step = plug thermo. into cycle efficiency model

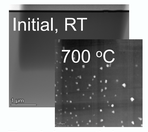
Predicted ML-V1 STCH Compounds → Water-splitters!

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



DFT → oxygen vacancy preferred vs. cation defects



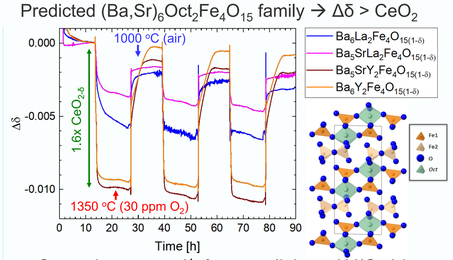


Fe-rich particles formed *in situ* TEM

$BaAl_{0.4}Fe_{1.6}O_{4-\delta}$

Predicted base compound shows water splitting!

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



Screening protocol[1] → monoclinic and Y(Oct) best

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

FY23/24 Joint Publications Document Collaboration Effectiveness

- M. Witman, A. Goyal, T. Ogitsu, A. McDaniel, and S. Lany. "Defect graph neural networks for materials discovery in high-temperature clean-energy applications," *Nature Comp. Sci.* **2023**, (3) 8. DOI: 10.1038/s43588-023-00495-2
- A. Goyal, M.D. Sanders, R.P. O'Hayre, S. Lany, "Predicting Thermochemical Equilibria with Interacting Defects: $Sr_{1-x}Ce_xMnO_{3-\delta}$ Alloys for Water Splitting," PRX Energy 3, 013008 (2024). DOI: 10.1103/PRXEnergy.3.013008
- C. Liu et al., "Manganese-based A-site high-entropy perovskite oxide for solar thermochemical hydrogen production," *J. Mater. Chem. A*, 2024, 12, 3910. DOI: 10.1039/d3ta03554a
- A. Fernandes Cauduro, E. Gager, K. King, D. McCord, A. McDaniel, J. Scheffe, J. Nino, and F. El Gabaly, "Stabilization of Catalytically Active Surface Defects on Ga-doped La-Sr-Mn Perovskites for Improved Solar Thermochemical Generation of Hydrogen," Topics on Catalysis, Accepted

Project Summary

Assess Technology & Discover New Materials

- 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.
- Successfully demonstrated a water splitting material predicted from theory-guided design of materials using a Machine Learning algorithm developed in this project. New materials are needed as existing exemplars have shown limited performance.

Collaboration: Effectiveness

Enable Seedling Projects to achieve project Go/No-Go Milestones by providing experimental and theoretical data sourced from world class National Laboratory facilities. Effectiveness documented by joint peer-reviewed publications and presentations.

HydroGEN's inter-Laboratory collaboration has produced tools and methods that have lead to the discovery of new STCH materials.

Proposed Future Work

Use technology assessment methodology derived in this project to evaluate viability of newly discovered materials to meet DOE STCH technology performance targets.

Continue theory-guided design of materials using machine learning to identify more redox active materials that optimize the capacity/yield tradeoff.

Leverage HydroGEN nodes to enable successful completion of seedling projects.

(subject to available funding)

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