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Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Project ID #P148D

# HydroGEN:
# Solar Thermochemical Hydrogen Production

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**Sandia National Laboratories**

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DOE Hydrogen Program 2024 Annual Merit Review and Peer Evaluation Meeting

NREL Transforming ENERGY

BERKELEY LAB Bringing Science Solutions to the World

Sandia National Laboratories

INL Idaho National Laboratory

Lawrence Livermore National Laboratory

# Project Goal, Overview, & Approach

## 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).

### Barriers

- Cost
- Efficiency
- Durability

- 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.

### 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.

### Partnerships

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

Arizona State University

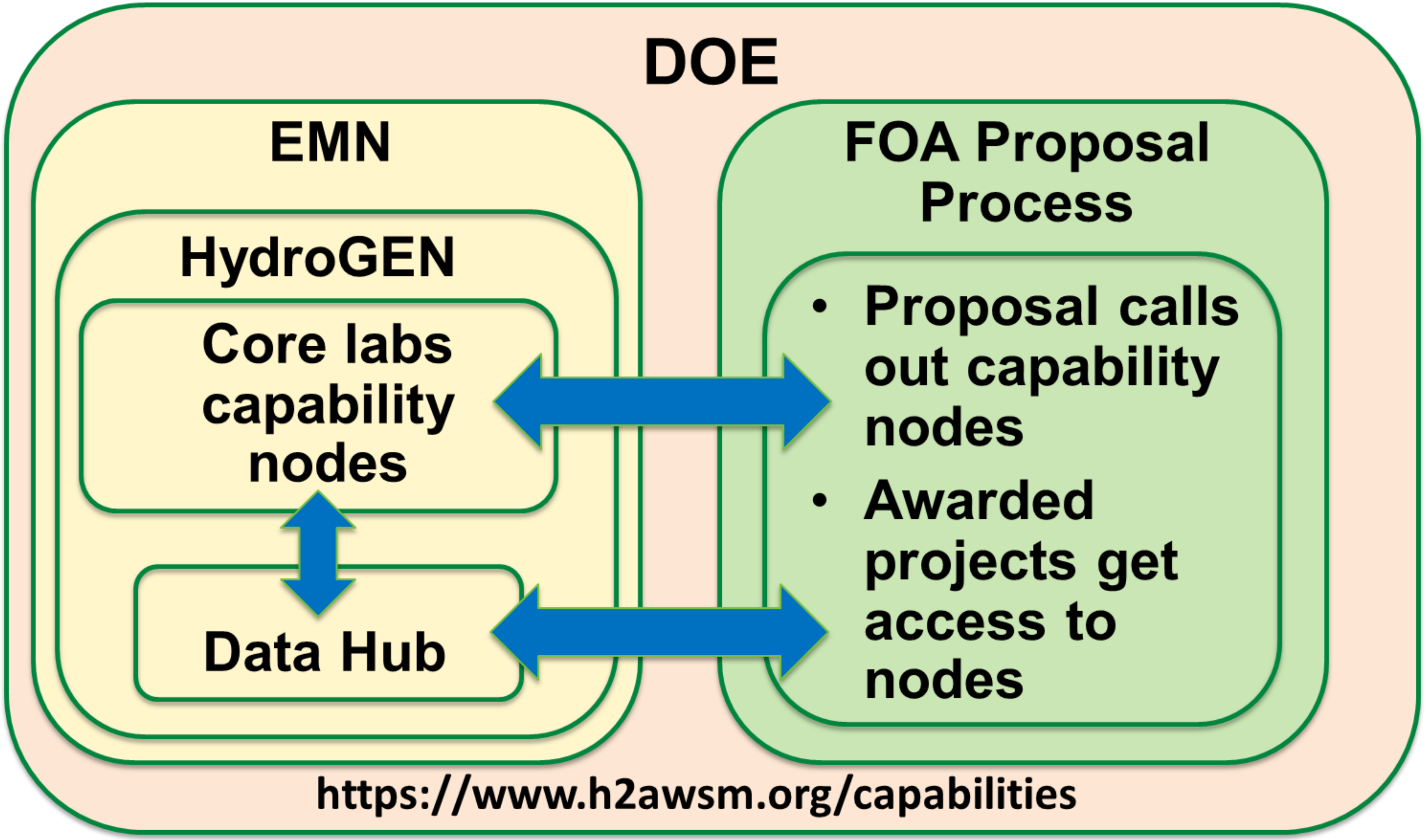
University of Colorado Boulder

Massachusetts Institute of Technology

Washington University in St.Louis

SAINT-GOBAIN

# Approach – Innovation



DOE

EMN

HydroGEN

Core labs capability nodes

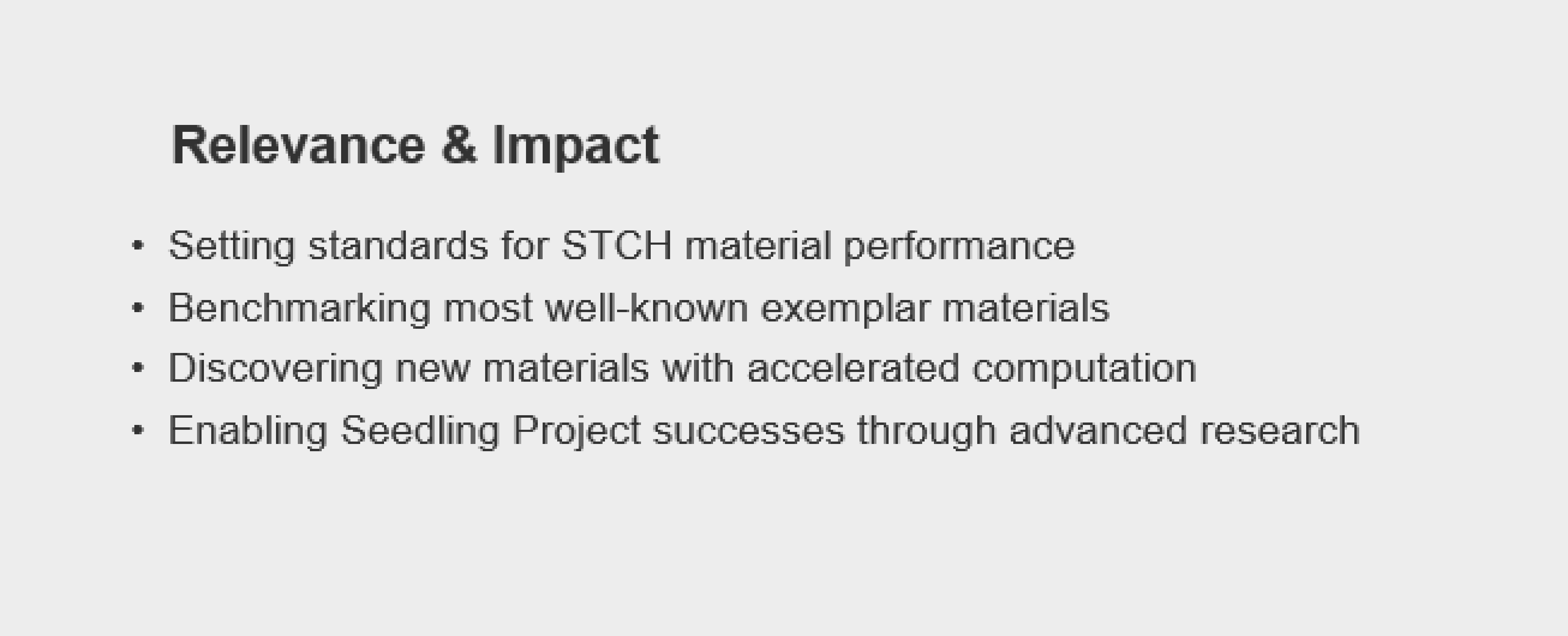
Data Hub

FOA Proposal Process

- Proposal calls out capability nodes
- Awarded projects get access to nodes

https://www.h2awsm.org/capabilities

# Potential Impact



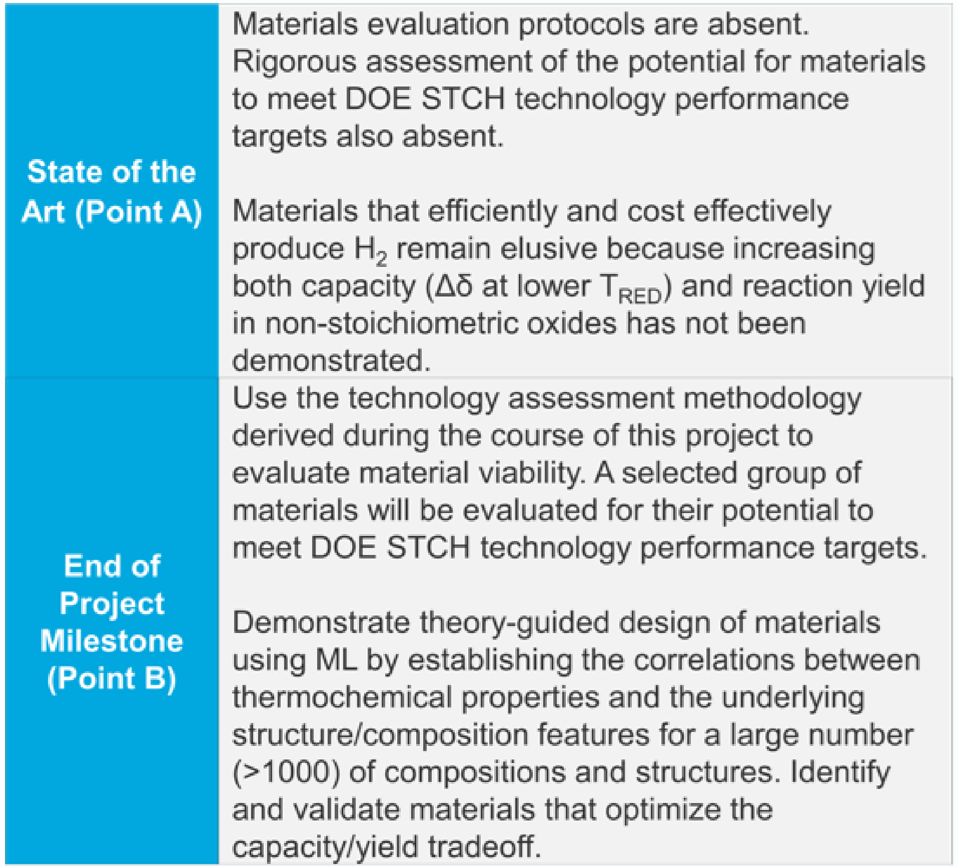
## Relevance & Impact

- 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

# Accomplishments

## Technology Viability & DFT-ML Material Discovery

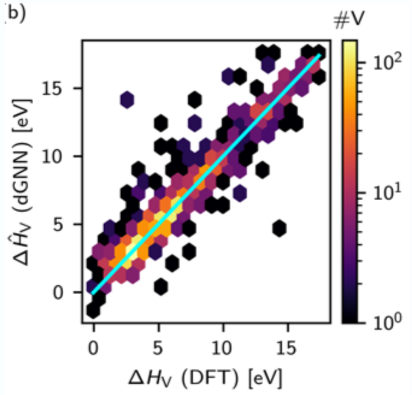
- Develop framework to define and establish material performance targets.
- Rigorously assess exemplar material formulations.
- Develop a materials search strategy using DFT + Machine Learning.
- Find new materials using the ML model and characterize by detailed calculations, synthesis, and experimental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



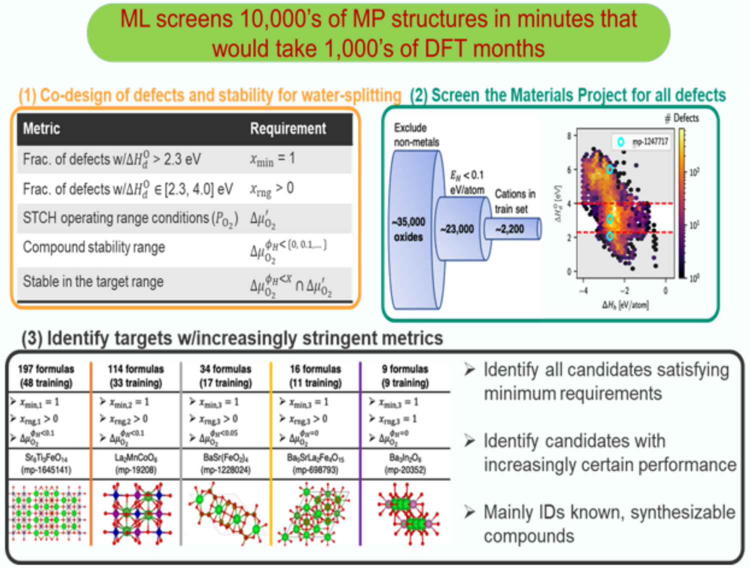
| | |
|---|---|
| **State of the Art (Point A)** | Materials evaluation protocols are absent. Rigorous assessment of the potential for materials to meet DOE STCH technology performance targets also absent.<br>Materials that efficiently and cost effectively produce $H_2$ remain elusive because increasing both capacity ($\Delta\delta$ at lower $T_{RED}$) and reaction yield in non-stoichiometric oxides has not been demonstrated. |
| **End of Project Milestone (Point B)** | Use the technology assessment methodology derived during the course of this project to evaluate material viability. A selected group of materials will be evaluated for their potential to meet DOE STCH technology performance targets.<br>Demonstrate theory-guided design of materials using ML by establishing the correlations between thermochemical properties and the underlying structure/composition features for a large number (>1000) of compositions and structures. Identify and validate materials that optimize the capacity/yield tradeoff. |

# Accomplishments

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



- More compounds for training and more elements included
- Improved $\Delta H_V$ MAE for unseen compounds from ~0.5 eV to ~0.4 eV.
- New approach → target “unexpected” STCH compounds for experimental validation


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

(1) Co-design of defects and stability for water-splitting

| 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 | $\Delta\mu_{O_2}^{\phi_H < X} \cap \Delta\mu'_{O_2}$ |

(2) Screen the Materials Project for all defects

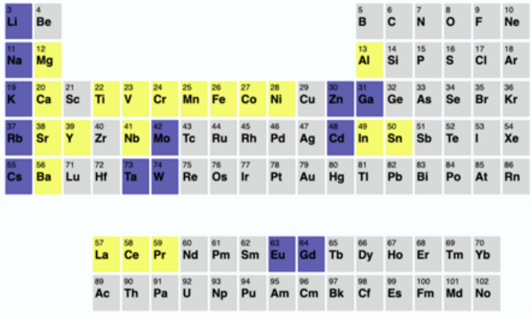
(3) Identify targets w/increasingly stringent metrics

| 197 formulas (48 training) | 114 formulas (33 training) | 34 formulas (17 training) | 16 formulas (11 training) | 9 formulas (9 training) |
|---|---|---|---|---|
| ➢ $x_{min,1} = 1$<br>➢ $x_{rng,1} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$ | ➢ $x_{min,2} = 1$<br>➢ $x_{rng,2} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$ | ➢ $x_{min,3} = 1$<br>➢ $x_{rng,3} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H<0.05}$ | ➢ $x_{min,3} = 1$<br>➢ $x_{rng,3} > 0$<br>➢ $\Delta\mu_{O_2}^{\phi_H=0}$ | ➢ $x_{min,3} = 1$<br>➢ $x_{rng,3} = 1$<br>➢ $\Delta\mu_{O_2}^{\phi_H=0}$ |
| $Sr_6Ti_3FeO_{14}$ (mp-1645141) | $La_2MnCoO_6$ (mp-19208) | $BaSr(FeO_2)_4$ (mp-1228024) | $Ba_5SrLa_2Fe_4O_{15}$ (mp-698793) | $Ba_3In_2O_6$ (mp-20352) |

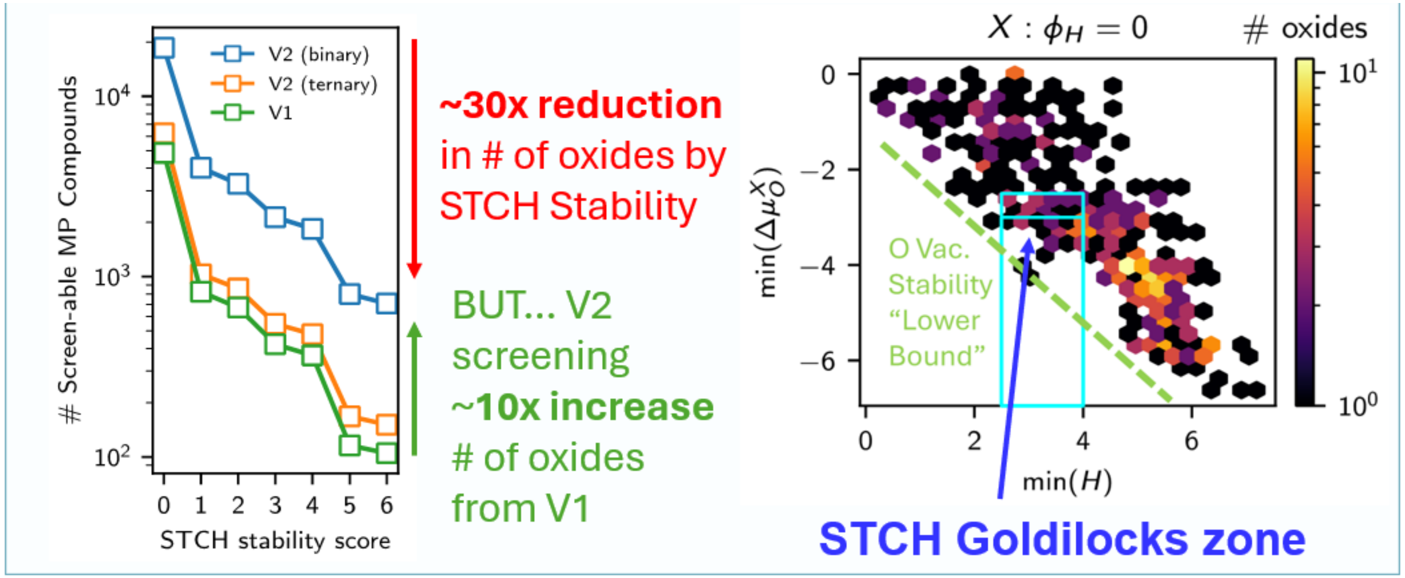
- ➢ Identify all candidates satisfying minimum requirements
- ➢ Identify candidates with increasingly certain performance
- ➢ Mainly IDs known, synthesizable compounds

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

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



# Accomplishments



**~30x reduction** in # of oxides by STCH Stability

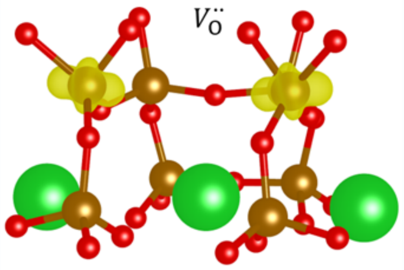
BUT… V2 screening **~10x increase** # of oxides from V1

**STCH Goldilocks zone**

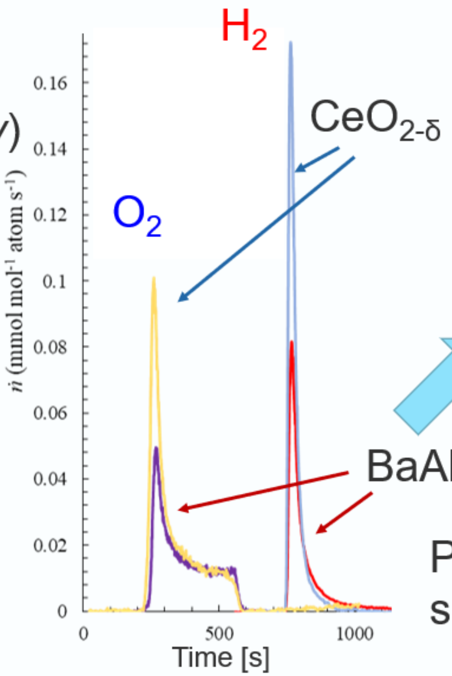
# Accomplishments

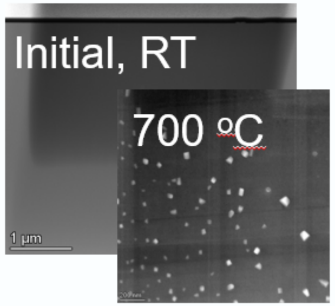
**Predicted ML-V1 STCH Compounds → Water-splitters!**

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



DFT → oxygen vacancy preferred vs. cation defects

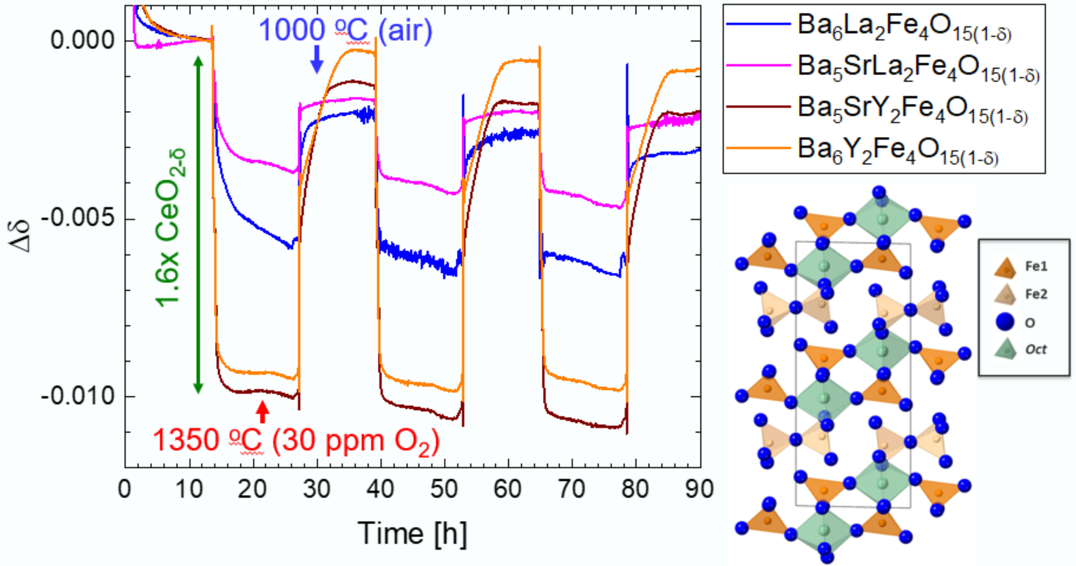




Fe-rich particles formed *in situ* TEM

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)*

# Accomplishments

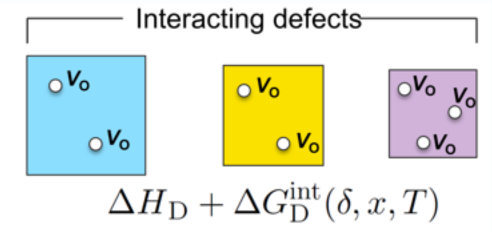
## Thermochemical Equilibria with Interacting Defects

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

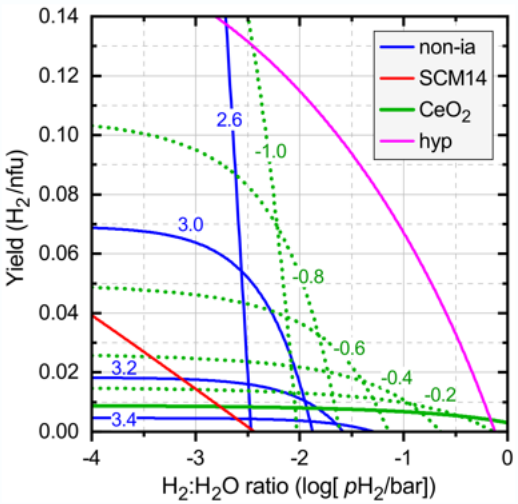
- **Blue**: non-interacting ($\Delta H_D$ in eV)
- **Red**: Interacting defects (SCM14)
- Defect interactions limit yield and $H_2$:$H_2O$

Charged defect model for $CeO_2$ and hypothetical materials

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



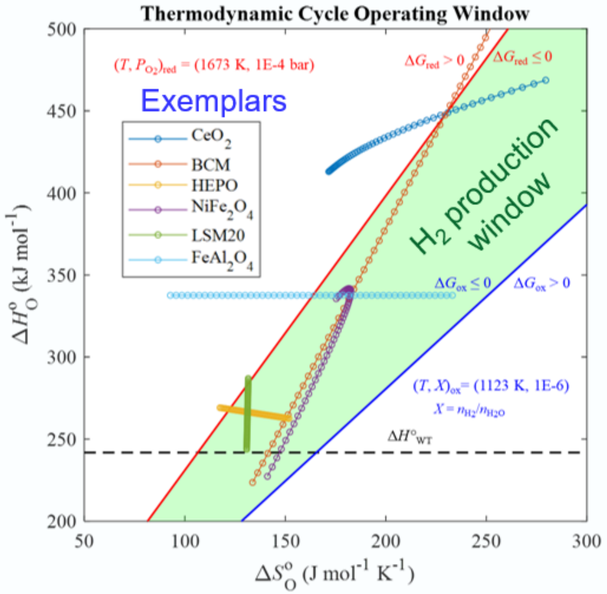
$$\Delta H_D + \Delta G_D^{int}(\delta, x, T)$$



# Accomplishments

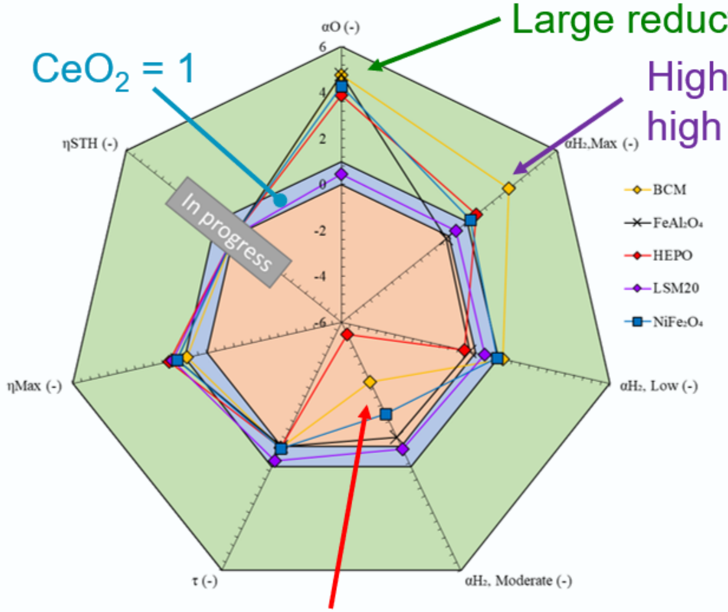
## Exemplar Material Commercial Viability Study

- 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



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: $La_{0.8}Sr_{0.2}MnO_3$

*Exemplars normalized to state-of-the-art $CeO_2$*

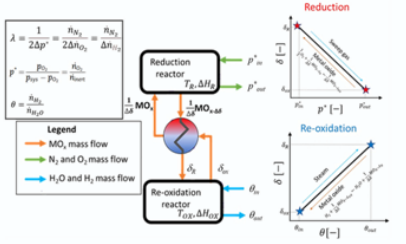


$CeO_2$ = 1

Large reduction

High $H_2$ production in high steam/$H_2$

...but $H_2$ "consumption" in low steam/$H_2$



| 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 | $\eta_{STH} > 26\%$ |
| Material Efficiency | $\frac{\Delta G^{o}_{WS}}{\Delta H^{o}_{O}}$ is the maximum possible thermal efficiency of the two-step process. ($\Delta G^{o}_{WS}$ 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 | $\tau > 0.20$ |

Final step = plug thermo. into cycle efficiency model

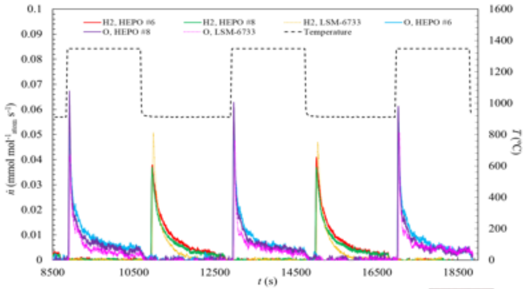
# Accomplishments: Seedling Projects

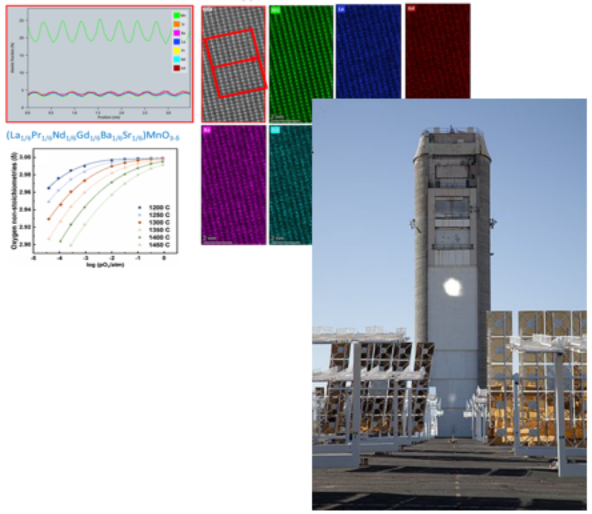
**Node thrusts for seedling support in Hy3.0:**

- **SNL (ASU, CU, St. Gobain, WashU):** Advanced electron microscopy, HTXRD and DSC, $H_2$ flow reactor, on-sun testing
- **NREL (ASU, CU, St. Gobain, WashU):** Techno-economic analysis and thermo-chemical modeling, materials synthesis, combinatorial thin film fabrication
- **INL (ASU):** Scaled up materials fabrication
- **LLNL (St. Gobain):** Computational interface kinetics

***Recent Interactions and Accomplishments***

- **St. Gobain seedling - LLNL:** computed energy barriers for water splitting process on STM
- **CU, St. Gobain, WashU seedlings - SNL**: Performed preliminary analysis of on-sun reactor testing





# 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.

## 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

# Proposed Future Work

- STCH Lab R&D
  - 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 current and new seedling projects.

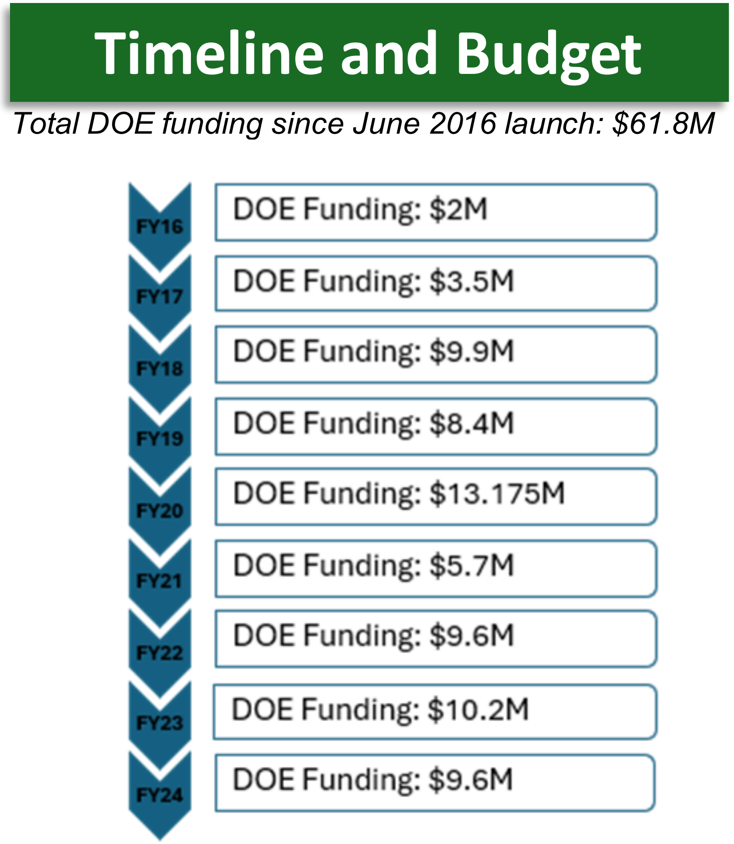
(future work subject to available funding)

# Project Summary

- Seedling project successes on discovering new STCH materials enabled by collaboration with HydroGEN by providing experimental and theoretical results using advanced methods.
- 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.

# Timeline and Budget

## Timeline and Budget for entire HydroGEN consortium (includes STCH, PEC, HTE, LTE)



**Timeline and Budget**

*Total DOE funding since June 2016 launch: $61.8M*

| | |
|---|---|
| FY16 | DOE Funding: $2M |
| FY17 | DOE Funding: $3.5M |
| FY18 | DOE Funding: $9.9M |
| FY19 | DOE Funding: $8.4M |
| FY20 | DOE Funding: $13.175M |
| FY21 | DOE Funding: $5.7M |
| FY22 | DOE Funding: $9.6M |
| FY23 | DOE Funding: $10.2M |
| FY24 | DOE Funding: $9.6M |

Core Lab R&D: $5.1M
FOA- & lab-awarded project support: $4.5 M

# Safety Planning and Culture

- HydroGEN is NOT required to submit a safety plan for review by the Hydrogen Safety Panel
- Every National Lab has a rigorous DOE-approved Safety Procedure which is regularly reviewed and monitored by cognizant DOE Field Offices
  - **SNL:** Work Planning and Control (WPC) which uses Integrated Safety Management (ISM)

**Integrated Safety Management (ISM) Process can be described:**

- Define the scope of work
- Analyze hazards associated with the work
- Develop and implement hazard controls
- Perform work within controls
- Provide feedback and continuous improvement

## Engineered Control Strategies Utilized *For Hydrogen*

- ***Prevent a release***—Use high quality stainless steel tubing, fittings, and components to resist hydrogen embrittlement;
- ***Detection***—use robust point and area detection to detect leaks***;***
- ***Process control***—interlock detection system with process controls to shut off system; low-V heat tape controllers
- ***Ventilation***—robust ventilation to quickly evacuate areas***;***
- ***Control of ignition sources***—use protected electrical systems that prevent gas ignitions; over-temperature protection for heat tapes
- ***Defense in depth.*** Uses layers of controls in the design. For instance, the ventilation system design for hydrogen generation laboratory is redundant so if one exhaust system fails a redundant system will take the load.

## Safety Culture Principles

- Everyone is personally responsible for ensuring safe operations
- Leaders value the safety legacy they create
- Staff raise safety concerns because trust permeates the organization
- A questioning attitude is cultivated
- Learning does not stop.
- Hazards are identified and evaluated for every task, every time
- A healthy respect is maintained for what can go wrong