Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

# HydroGEN: Solar Thermochemical Hydrogen Production

**A. McDaniel*, S. Wan, S. Lany**

**Date: 4/30/2019**

**Venue: 2019 DOE Annual Merit Review**

Project ID # p148D

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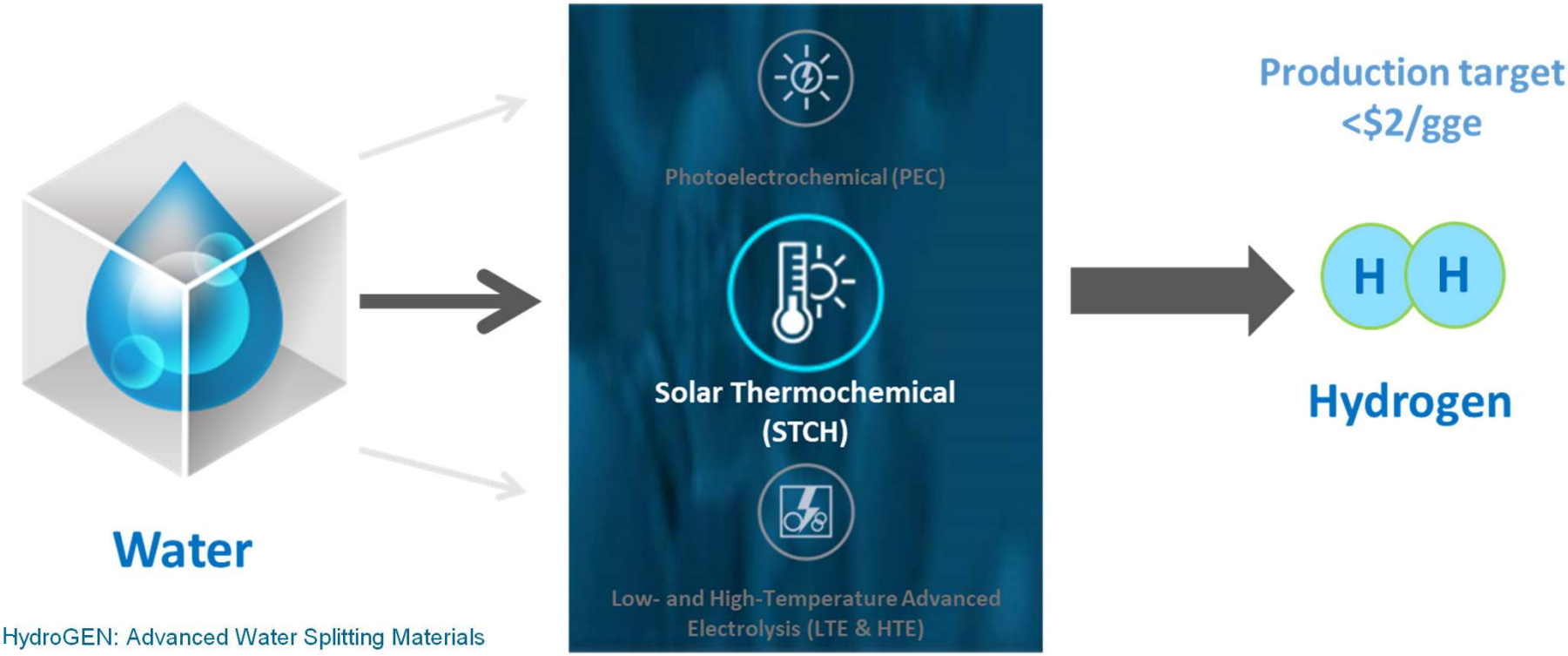
NREL · BERKELEY LAB · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

# Advanced Water-Splitting Materials (AWSM) Relevance, Overall Objective, and Impact

**AWSM Consortium 6 Core Labs:**

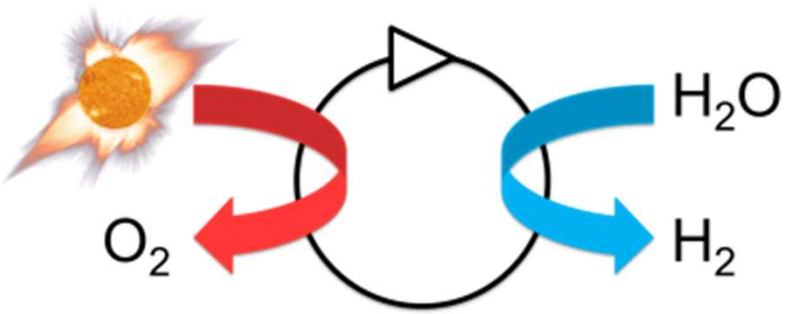
NREL National Renewable Energy Laboratory
Berkeley Lab
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

**<u>Accelerating R&D</u> of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost $H_2$ production, including:**



# Thermochemical and Hybrid Water Splitting Technologies

## Thermochemistry



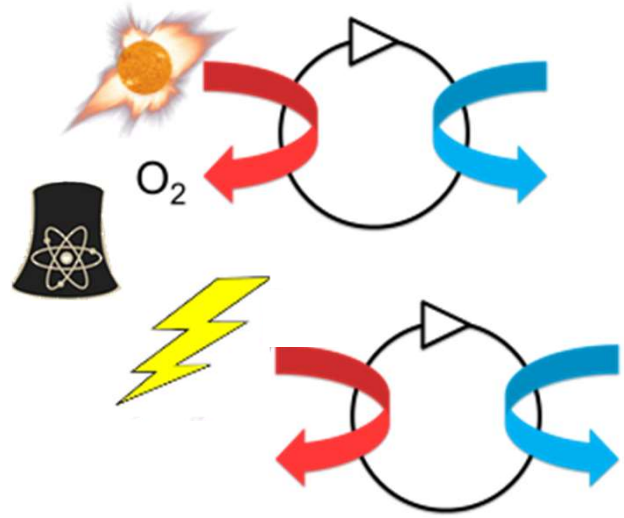

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \qquad \text{(1) Reduction}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \qquad \text{(2) Oxidation}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \qquad \text{(3) Thermolysis}$$

- Metal cation is redox active element in two-step cycle.

## TC + Electrochemistry

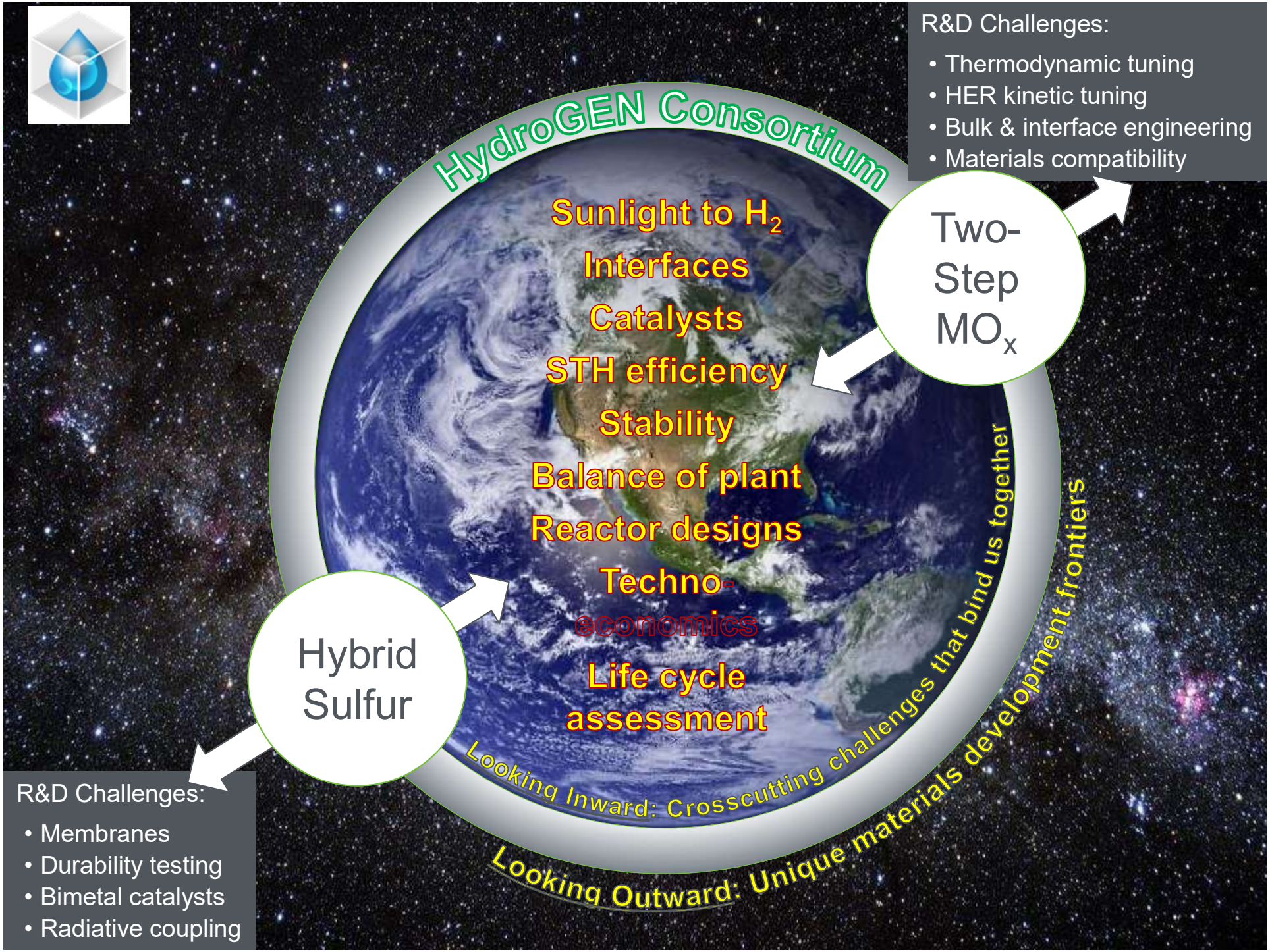



$H_2SO_4 \leftrightarrow H_2O + SO_2 + ½\ O_2$
(thermochemical; 800-900 °C)

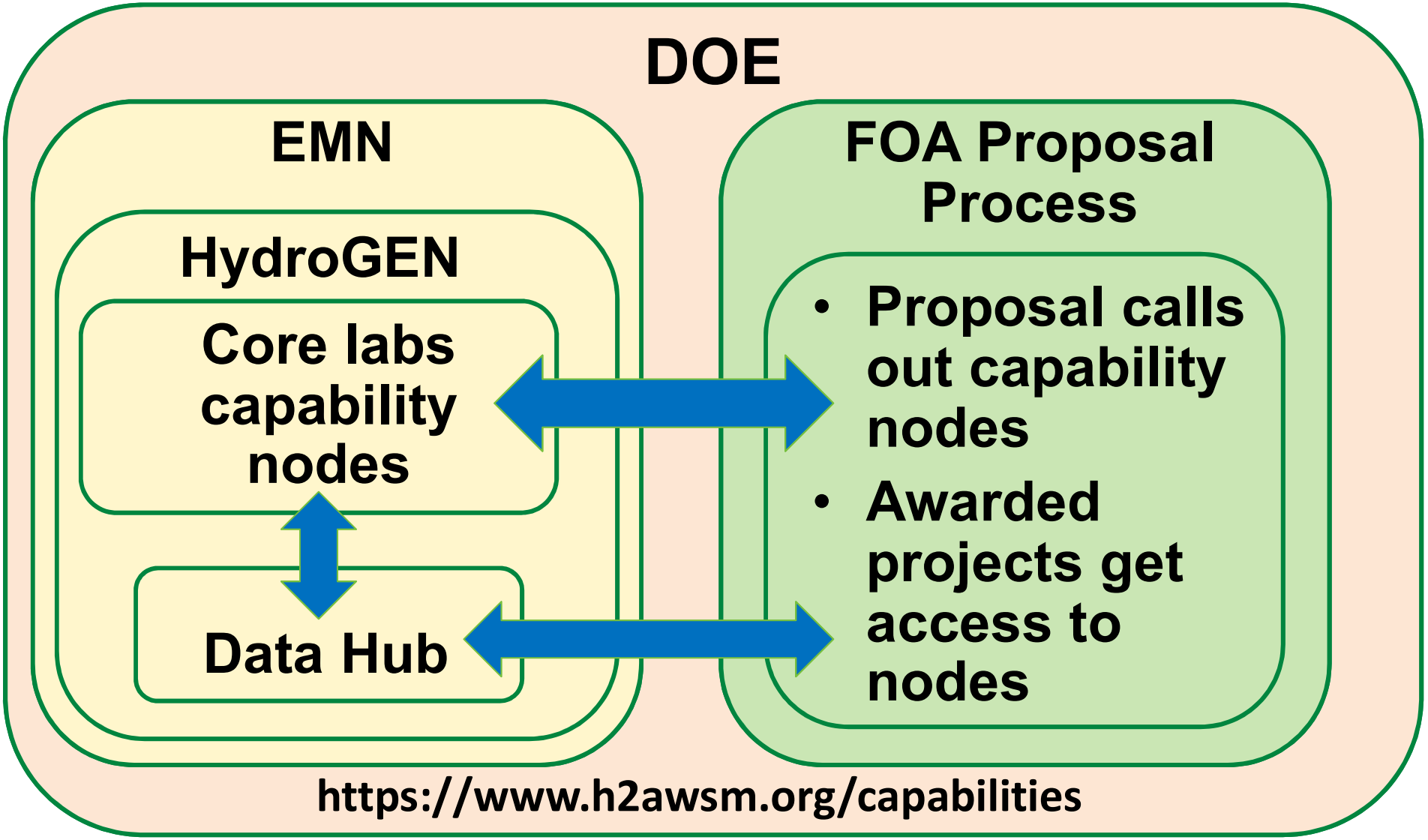
$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$
(electrochemical; 80-120 °C)

Net Reaction: $H_2O \rightarrow H_2 + ½\ O_2$

- Sulfur is redox active element in two-step cycle.


HydroGEN Consortium
Sunlight to $H_2$
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle assessment
Two-Step $MO_x$
Hybrid Sulfur
R&D Challenges:
• Thermodynamic tuning
• HER kinetic tuning
• Bulk & interface engineering
• Materials compatibility
R&D Challenges:
• Membranes
• Durability testing
• Bimetal catalysts
• Radiative coupling
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers

# Approach – HydroGEN EMN



# Approach – HydroGEN EMN

**STCH: Solar Thermochemical & Hybrids**

**Barriers**
- Cost
- Efficiency
- Durability

## STCH Node Labs

Sandia National Laboratories
Idaho National Laboratory
NREL NATIONAL RENEWABLE ENERGY LABORATORY
SRNL SAVANNAH RIVER NATIONAL LABORATORY
Lawrence Livermore National Laboratory

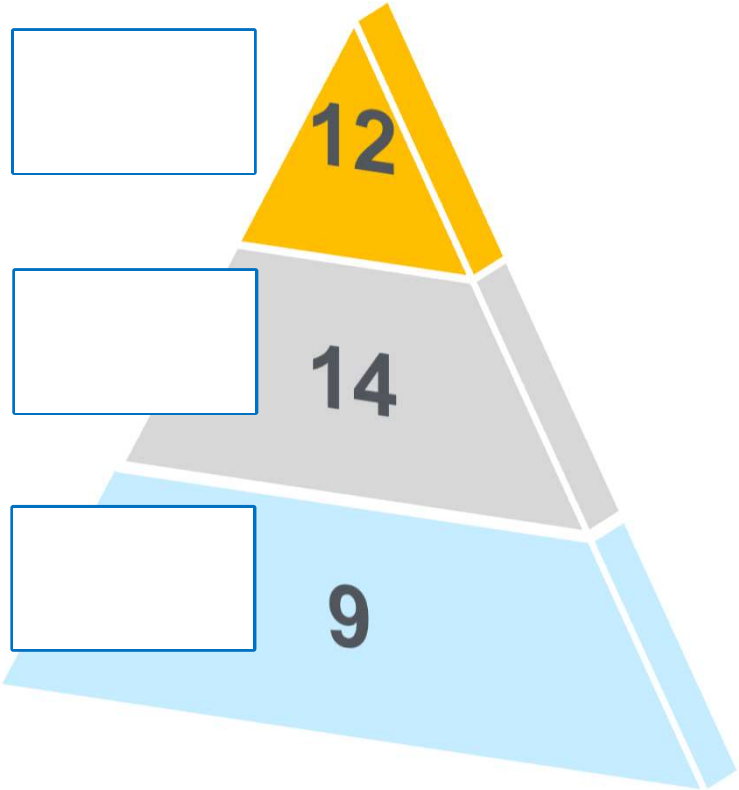
**Support through:**

**Personnel**
**Equipment**
**Expertise**
**Capability**
**Materials**
**Data**

## STCH Projects

Greenway Energy LLC
Engineering consultant in Aiken County, South Carolina
Northwestern University
Arizona State Sun Devils

# Collaboration: 35 STCH Nodes, 1 Supernode




**Analysis: 2**
**Characterization: 6**
**Computation: 3**
**Synthesis: 1**

Node is **fully developed** and has been used for AWSM research projects

**Analysis: 3**
**Characterization: 5**
**Computation: 6**
**Synthesis: 2**

Node requires some development for AWSM

**Analysis: 2**
**Characterization: 5**
**Computation: 4**
**Synthesis: 1**

Node requires significant development for AWSM

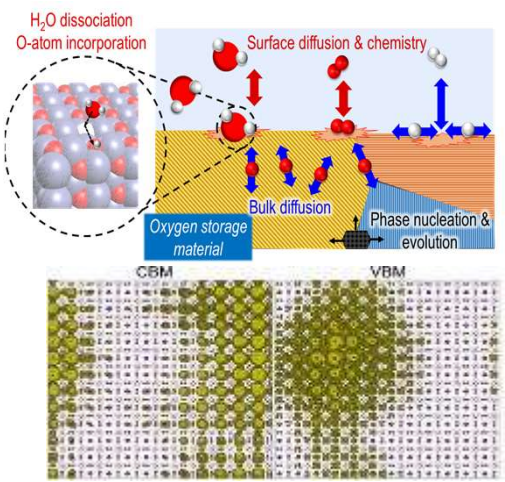
- Nodes comprise equipment and expertise including uniqueness.
- Category refers to availability and readiness.
- Many nodes span classification areas.

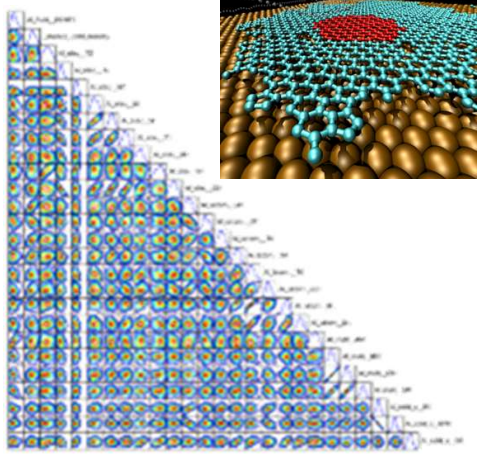
**13 (11 by FOA) Nodes utilized**
**15 Lab PIs engaged**
**Hundreds of files on Data Hub**

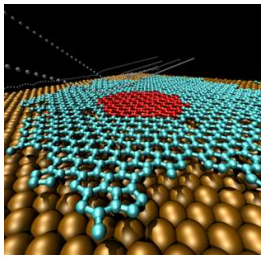
# Collaboration: HydroGEN STCH Node Utilization

| Lab | Node | ASU | CSM | CUB | NWU | GWE | Super | NSF |
|---|---|---|---|---|---|---|---|---|
| LLNL | Mesoscale Modeling | | | | ✓ | | | |
| | | | | | | | | |
| NREL | Defect Modeling | | ✓ | ✓ | | | ✓ | ✓ |
| | | | | | | | | |
| NREL | Defect Engineering | ✓ | | | ✓ | | ✓ | ✓ |
| | | | | | | | | |

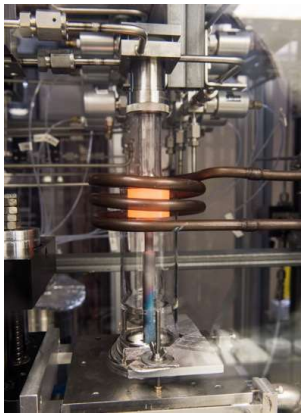
Computation

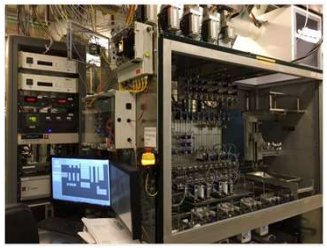


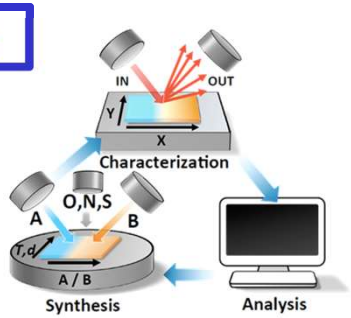





Material Synthesis



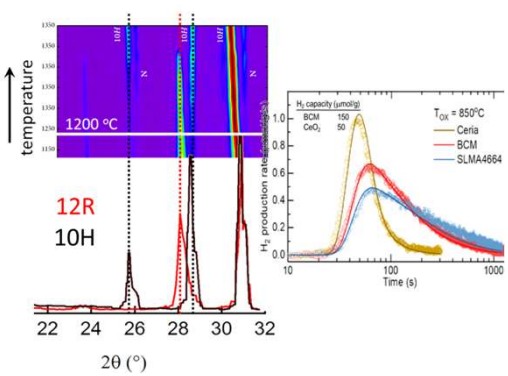


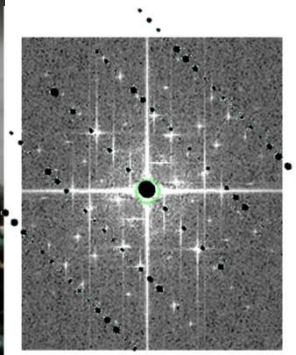


# Collaboration: HydroGEN STCH Node Utilization

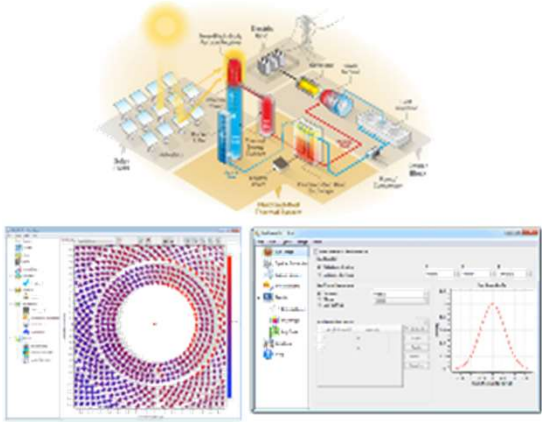
| Lab | Node | ASU | CSM | CUB | NWU | GWE | Super | NSF |
|---|---|---|---|---|---|---|---|---|
| INL | Catal. Harsh Environment | | | | | ✓ | | |
| | | | | | | | | |
| SNL | Adv. Electron Microscopy | | | | | | ✓ | |
| | | | | | | | | |
| NREL | Engineering BOP | | | | | ✓ | | |
| | | | | | | | | |
| SRNL | AWSM Requirements Flow Sheet TEA | | | | | ✓ | | |

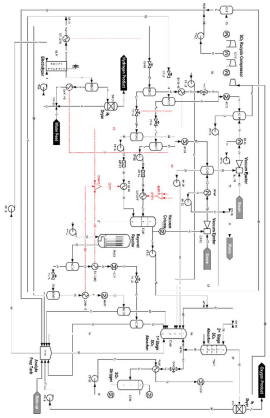
Characterization





Analysis



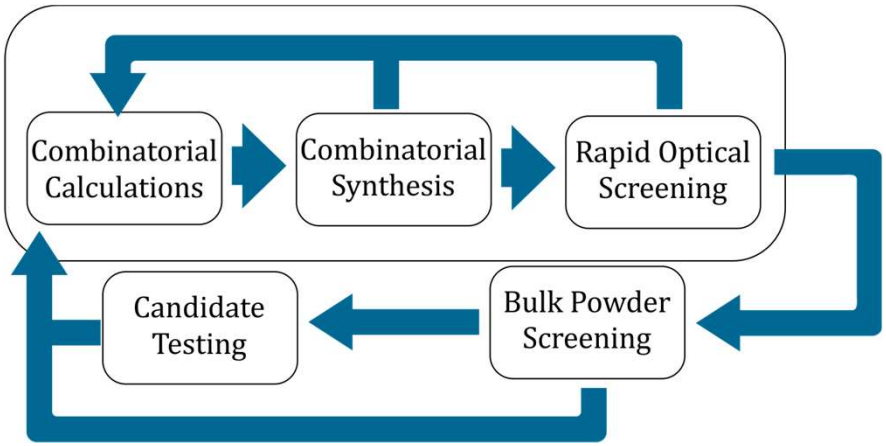


# Accelerated discovery of STCH hydrogen production materials via high-throughput computational and experimental methods

Colorado School of Mines — Ryan O'Hayre and Michael Sanders #P165

## Goals:

- Integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH.
- Accelerate the discovery of STCH compounds and gain a broader understanding of the property and behavior relationships for redox oxide-cycle water splitting.




## Accomplishments in BP1

| Milestone Number | Milestone Verification Process |
|---|---|
| GNG1.3 | Extent of reduction measurements on five compositions from different oxide families and more than three across a single family ✓ |
| GNG3.2 | 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. ✓ |

**$Ce_{0.2}Sr_{1.8}MnO_4$ (CSM2) produced 247 µmol $H_2$/g sample at $T_R$ of 1400 °C**

## Focus of BP2

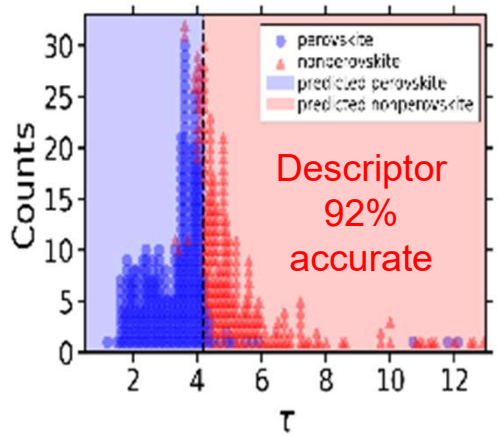
- Expand computational and combinatorial search to more complex compositions (quaternary perovskites, single-dopant layered perovskites, and random structures).
- Focus efforts on a number of more likely constituent elements identified during BP1.

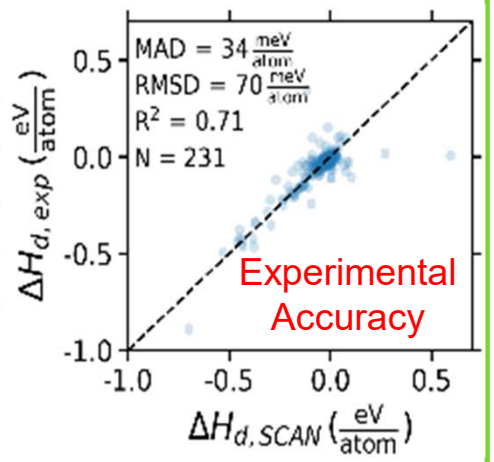
# Computationally accelerated discovery and experimental demonstration of high-performance materials for advanced solar thermochemical hydrogen production

University of Colorado Boulder — Charles Musgrave #P166

## Goals:

- Develop and utilize a computationally accelerated, accurate, and experimentally validated materials-by-design approach involving ab initio and machine-learned models.
- Design and demonstrate durable materials with optimum thermodynamic and kinetic properties for solar thermochemical water splitting (STWS) that meet DOE targets.



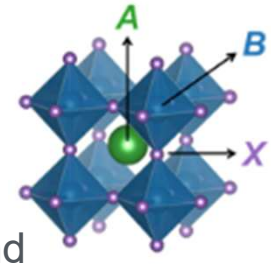




## Accomplishments in BP1

Go/No-Go #1: Four materials have been demonstrated to have hydrogen productions >200 μmol/g/cycle at $T_{red}$ =1450 °C and Δ T=250 °C and results compared to computational predictions.

Go/No-Go #2: Two new machine learning descriptors developed to rapidly predict materials stability and perovskite formation. New approach developed to accurately assess materials stability of materials screened using descriptors. Approach to rapidly assess kinetics of reduction and oxidation developed. Computational material screening in progress to determine materials to test experimentally.

## Focus of BP2




Predict and validate defects in metal oxides that mediate STWS including oxygen vacancies, oxygen interstitials and neutral and charged defects. Use approaches developed in BP1 and predicted defect energetics to screen binary and ternary perovskites for stability and for STWS capacity and kinetics.

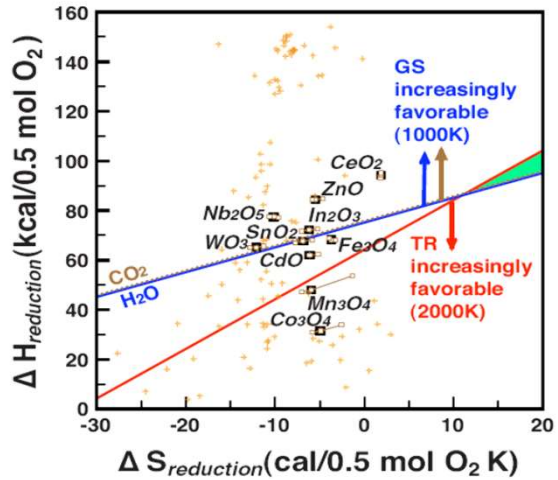
# Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

Northwestern University — Christopher Wolverton

#P167

## Goals:

- Combine high-throughput computation and experiment to study the properties of novel, predicted STCH materials.
- Explore the enormous combinatorial space of materials, to "tune in" desired STCH enthalpy and entropy of reduction.
- Design materials with reduced temperatures of reduction but sufficient gas-splitting rates.




## Accomplishments in BP1

Go/No-Go #1:

- Experimentally measured the enthalpy and entropy of twelve predicted perovskites and validated the high-throughput DFT calculation approach.

## Focus of BP2

Significantly expand range of chemistries consider for potential double-perovskites, compare TGA experiments to calculations of reduction entropy using experimental data from Year 1 to validate more refined thermodynamic models.

Execute high throughput DFT screening of oxygen vacancy formation energy of double perovskites, tailoring oxygen vacancy formation energy by A- and B-site doping; alloying B-site metals with different reduction energies, e.g., $BaMn_xCe_{1-x}O_3$; alloying A-site metals to control octahedral rotation.

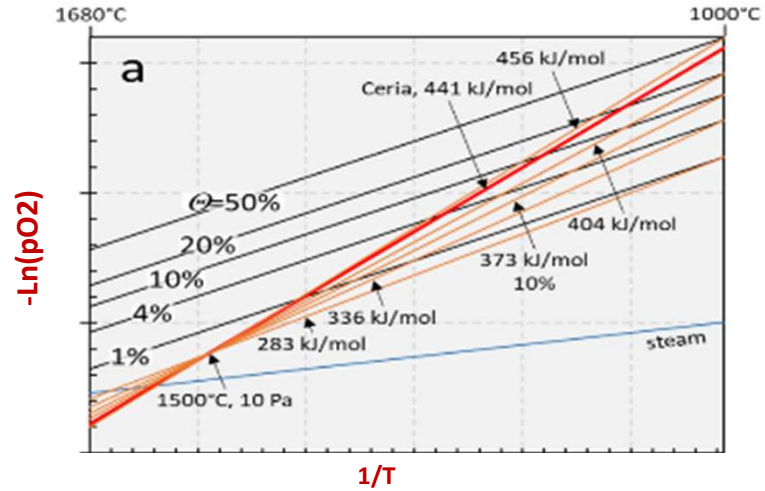
# Mixed ionic electronic conducting quaternary perovskites: materials by design for STCH $H_2$

Arizona State University — Ellen Stechel

#P168

## Goals:

- Construction of chemical potential maps decouples gas and solid phases within a thermochemical cycle, but predicting chemical potentials in solid phases is not trivial.
- The goal is to construct sub-lattice models, with energy values from DFT (with SCAN+U functionals) and predict off-stoichiometry across temperatures and partial pressures of oxygen by equating solid state chemical potential with gas phase chemical potential.
- The goal is to identify new candidate materials in silico based on derived understanding.




## Accomplishments in BP1

Go/No-Go #1:

- We have validated our methodology with $CeO_2$ and with $(La,Sr)MnO_3$.
- We have identified a promising pathway to improve capacities by calculating cation couples that can be simultaneously redox-active.
- We have identified the relationship between off-stoichiometry and chemical potentials and between $H_2$ yield and enthalpy of reduction.

## Focus of BP2

- Sublattice models for candidate quaternary and quinary perovskites with two redox active cations on different sublattices.
- Uncertainty quantification on DFT formulation
  - No temperature dependent DFT calculations
  - Temperature/$pO_2$ dependent off-stoichiometry
  - Optimized reduction enthalpy considering yield, and full operating cycle characteristics

# High temperature reactor catalyst material development for low cost and efficient solar driven sulfur-based processes

Greenway Energy — Claudio Corgnale

#P169

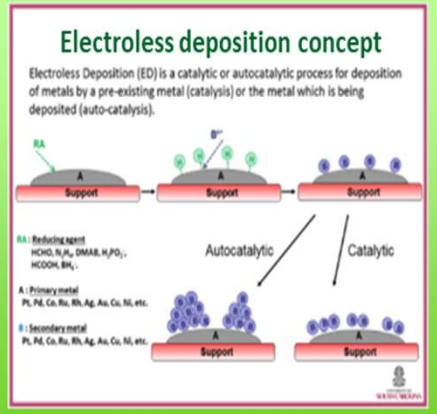
## Goals:

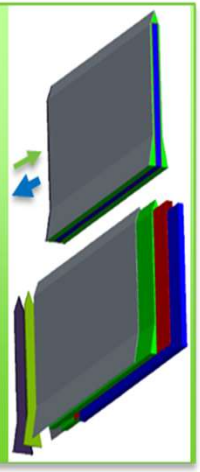
- Develop new catalyst material using our demonstrated surface free energy and electroless deposition technique.
- Design a direct solar reactor-receiver based on a demonstrated cavity solar reactor.
- Effective solar-thermochemical plant process integration.

Novel Electroless Deposition approach for bi-metallic catalyst formulations based on the Surface Free Energy of the metals

Novel direct solar cavity receiver-reactor, based on NREL concept

Novel HyS flowsheet with chemical storage and direct solar receiver



## Accomplishments in BP1

Go/No-Go #1:
Improved catalyst development and demonstrated reduced activation after 100 hours of testing.
Refined a concept for an improved solar reactor allowing for increased efficiencies and cost reduction.

Go/No-Go #2:
Completed technoeconomic analysis of the overall solar HyS plant predicting that this process can achieve solar to $H_2$ conversion efficiency > 20% and cost < 2 $/kg (both DOE technology development targets).

## Focus of BP2

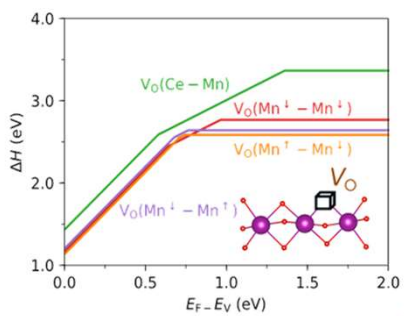
- Optimization and engineering of new catalysts
- Development of non-Ir and PGM formulations
- Long term duration tests (i.e. > 400 hours) under different T and P conditions
- Rector development, CFD analysis, scale up
- Solar plant optimization
- Optimization of the HyS process design and the storage system
- Detailed techno-economic analysis

# STCH Supernode: Approach (utilize 6 nodes)

***Goal**: Develop a fundamental understanding of how unique electronic structures induced by Mn-O ligand bond arrangements influence favorable water splitting material behavior.*

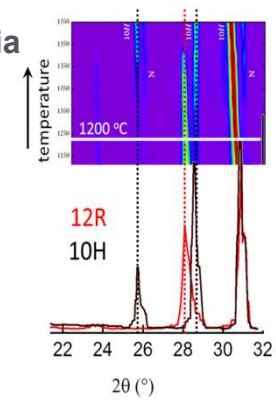
NREL NATIONAL RENEWABLE ENERGY LABORATORY

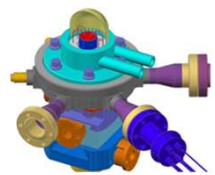
- Thermochemical properties & defect energies by DFT
- Predict defect equilibria

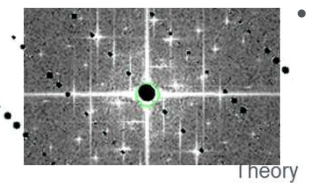



Sandia National Laboratories

- Operando measurements of atomistic behavior by x-rays and electrons

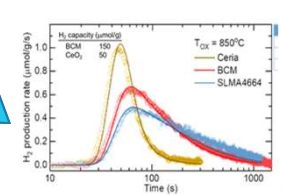


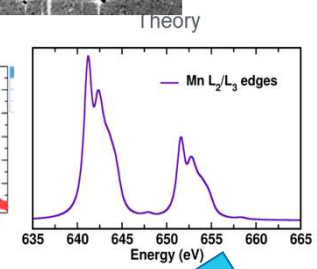



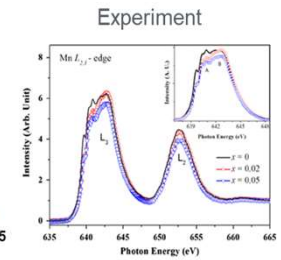


Lawrence Livermore National Laboratory

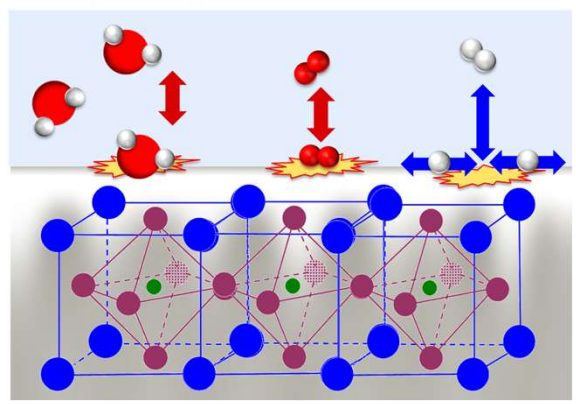
- Model core-hole spectroscopies and electron scattering by DFT

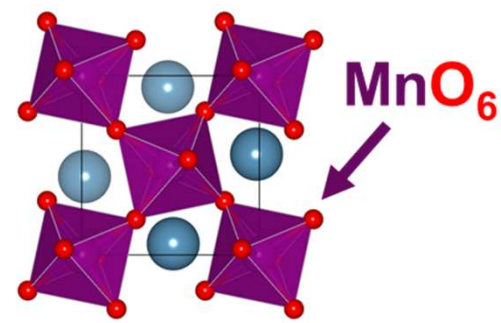


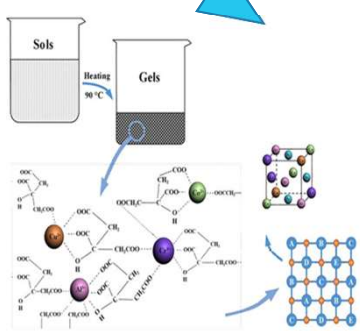




Key governing processes in STCH materials





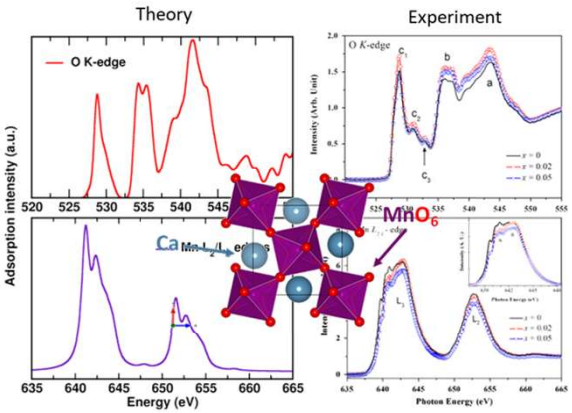

- Defect engineering & synthesis of model materials

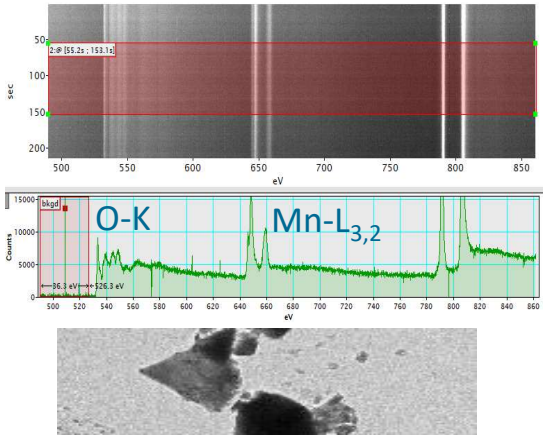


# STCH Supernode: Results

**$CaMnO_3$ model system for DFT method development.**

- Computationally expensive
- Method refinement needed

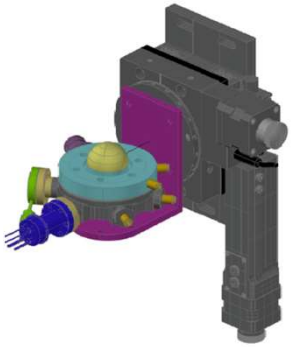



**Hot-stage EELS reveals B-site cation redox activity.**

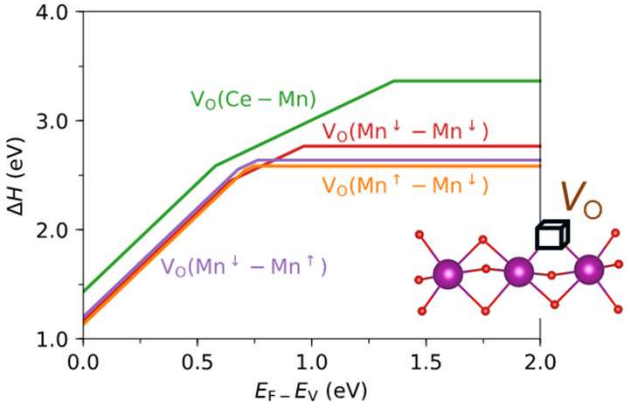
**Operando cell for x-ray scattering.**

- Synchrotron x-ray diffraction
- X-ray Absorption Spectroscopy
- SLAC campaigns pending



**DFT predicts defect formation energies in BCM.**

- Resolve the effects of $E_f$ dependence




***Accomplishments:***

- *Develop synthetic routes to "ideal" Mn-O compounds*
- *Develop DFT methods to model core-hole spectroscopies*
- *Deploy operando test cell at SLAC (x-ray scattering)*
- *Conduct HR/STEM EELS studies on "ideal" compounds*

# STCH Supernode: Future Work

- Fundamental studies of model compounds under precisely-controlled environments.
  - Operando high-temperature x-ray scattering both lab and synchrotron
  - Hot stage high resolution scanning transmission electron microscopy
  - Electron energy loss spectroscopy (EELS) of core and valence band

- Defect-thermochemistry and defect-equilibria.
  - Explore mechanisms and effects involving charged defect states, pairs, and clusters

- Ab Initio electronic structure modeling.
  - Evolution of electronic band structures induced by non-stoichiometry
  - Theory-based analysis of electron diffraction, electron energy loss spectroscopy, and x-ray spectroscopies

# Engagement with 2B Team and Data Hub

- Collaboration with 2B Team Benchmarking Project.
  - 2B working groups and annual meeting
  - Node feedback on questionnaire & draft test framework
  - Defining: baseline materials sets, testing protocols

- All HydroGEN STCH node capabilities were assessed for AWS technology relevance and readiness level.

- STCH data metadata definitions in development.

- Large number of STCH datasets uploaded to hub.
  - Designing custom APIs to facilitate error-free, auto-uploading

# Future Work

- Leverage HydroGEN Nodes at the labs to enable successful budget period 2 activities.
- Integrated research in 1 Supernode.
  - STCH resolving Mn-O ligand field effects on water splitting behavior
- Enable and work with possible new seedling projects.
- Work with the 2B team and STCH working group to further establish testing protocols and benchmarks.
- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public.

# Summary

- Developing and validating tools for accelerated materials discovery are major seedling project themes.
  - Computational material science proving effective

- Supporting 5 FOA projects with 11 nodes.
  - DFT modeling, materials characterization, synthesis, analysis, design
  - Personnel exchange: PIs and graduate students visit the labs
  - Collaboration: Node PIs meet regularly with projects

- Working closely with the project participants to advance knowledge and utilize capabilities and the data hub.

- Applying atomistic theory and advanced experimentation in STCH Supernode to understand behavior of Mn-O based water splitting materials.
  - Develop DFT methods to model core-hole spectroscopies and calculate defect thermodynamics
  - Deploy operando test cell at SLAC (x-ray scattering)
  - Conduct hot stage HR/STEM EELS studies on Mn-O compounds

# Acknowledgements

Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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# Acknowledgements

Energy Materials Network
U.S. Department of Energy

HydroGEN
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