HydroGEN: Solar Thermochemical Hydrogen (STCH) Water Splitting

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Project ID # p148d

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
**Goal:** Accelerate foundational R&D of innovative materials for advanced water splitting (AWS) technologies to enable clean, sustainable and low-cost (< $2/kg H₂) hydrogen production.

**HydroGEN is focused on early-stage R&D in H₂ Production**
Overview – STCH and Hybrid STCH Technologies

Thermochemical Cycle

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

R&D effort focused on MO\textsubscript{x} materials discovery.

\begin{align*}
MO\textsubscript{x} & \rightarrow MO\textsubscript{x}-\delta + \frac{\delta}{2}O\textsubscript{2} \\
MO\textsubscript{x}-\delta + \delta \cdot H\textsubscript{2}O & \rightarrow MO\textsubscript{x} + \delta \cdot H\textsubscript{2} \\
\delta \cdot H\textsubscript{2}O & \rightarrow \frac{\delta}{2}O\textsubscript{2} + \delta \cdot H\textsubscript{2}
\end{align*}

(1) Reduction

(2) Oxidation

(3) Thermolysis

Hybrid Cycle

Sulfur is redox active element in two-step cycle.

HydroGEN: Advanced Water Splitting Materials
Principal Material Challenges for Non-Stoichiometric Oxides: Reduction Temperature ($T_R$) and Solid State O-atom Activity ($\mu_{O,\text{solid}}$)

- Oxygen storage materials with a twist.
  - O-atom “harvested” from H$_2$O not air
  - Bulk phenomena largely govern O-atom exchange with environment
- Material subject to extreme environments.
  - Redox cycling on the order of seconds
  - Large thermal stress per cycle
    - $800 \, ^\circ\text{C} < T < 1450 \, ^\circ\text{C}$; $\Delta T_{\text{RATE}} \sim 100 \, ^\circ\text{C}/\text{sec}$
  - Large chemical stress per cycle
    - $10^{-14} \, \text{atm} < p_{O_2} < 10^{-1} \, \text{atm}$
- Water splitting at extremely low $p_{O_2}$.
  - Strongly reducing “oxidizing” atmosphere

```
"O" activity in H$_2$O:H$_2$  $\mu_{\text{gas}} > \mu_{\text{solid}}$  $\mu_{\text{gas}} \sim 10^{-13}\text{atm}$
```
Approach – HydroGEN EMN

Barriers
- Cost
- Efficiency
- Durability

Support through:
- Personnel
- Equipment
- Expertise
- Capability
- Materials
- Data

STCH Node Labs
- Sandia National Laboratories
- Idaho National Laboratory
- NREL
- SRNL
- Lawrence Livermore National Laboratory

STCH FOA Projects
- Arizona State University
- Colorado School of Mines
- UC San Diego
- Northwestern University
- UF University of Florida
- Greenway Energy LLC
## Collaboration: HydroGEN STCH Node Utilization

### FY20 Projects

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<thead>
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<th>Node</th>
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- **HydroGEN:** Advanced Water Splitting Materials

- **Computation:**
  - Materials Synthesis
  - Characterization
  - Analysis

- **Hy2.0:** NSF
Project Accomplishments, Seedling Summary and Examples of Node Collaborations

STCH Node Labs

Support through:
Personnel
Equipment
Expertise
Capability
Materials
Data

STCH FOA Projects

ASU
Arizona State University

Mines
Colorado School of Mines

Northwestern University

UF
University of Florida

Greenway Energy LLC
STCH Seedling Projects are Fulfilling the Vision of the Consortium/EMN Model (HPC, ML, theory guided material design)

• Found RP phases that modify redox thermo.
  – DFT screening of defect formation energy
  – Thin film combinatorics for compound discovery
  – High throughput colorimetric screening

• Incorporate second redox active sublattice to modify thermo.
  – DFT method to predict $\Delta\delta$ a priori using simple sublattice model formulations
  – Discover compounds with optimized thermo ($\delta H$, $\delta S$)

• Use machine-learned models coupled to DFT to discover new redox materials.
  – Rapidly screen materials based on machine-learned predicted stability
  – Formulate descriptor(s) for predicting reaction network energetics and equilibrium

• Use high-throughput Density Functional Theory to discover new redox materials.
  – Screen $>10^4$ known compounds for ground state stability/synthesizability and favorable thermo at reduction $T<1400$ °C

• One dozen potential STCH compounds have been “discovered” using HPC, ML, and DFT

• Water splitting functionality has been verified in several of these predicted formulations

• Validated high-throughput computational tools are now in place to rapidly expand the known STCH material space
Hypothesis for material formulation.
- Simultaneously reducible cations on separate sublattices will increase reduction entropy leading to higher performing material
- Engineer a perovskite to tolerate low $p_{O_2}$ during water splitting like CeO$_2$ in order to achieve HIGH capacity and HIGH yield

Major constraints limit possible perovskite compositions for $(A,A')$BO$_3$.
- Structure, charge neutrality, reduction enthalpy and redox activity constrain selection to Ca$^{2+}$ and Ce$^{(4+/3+)}$ on A-site, and M$^{(3+/2+)}$ on B-site to ensure enthalpy is in target region

Workflow considered 24 structures using DFT.
- $M =$ Sc, Ti, V, Cr, Mn, Fe, Co, Ni
- Evaluate $E_{VaO}$ of CaMO$_3$, CeMO$_3$, and Ca$_{0.5}$Ce$_{0.5}$MO$_3$
- Mn and Fe satisfy all criteria for B-site.
ASU Seedling Project: HydroGEN Node Support Provided by NREL (w/ SLAC) and SNL

- ASU predicts new material family: Ca$_{0.5}$Ce$_{0.5}$XO$_3$ with A-site redox activity.
  - https://doi.org/10.1021/acs.chemmater.0c02912
- NREL: Synthesized and characterized crystal structure and cation redox.
  - SLAC confirmed structure of predicted and enhanced stability material with cation Y substitution – “CCXY”
  - Confirmed dual-cation reduction mechanism during redox by XAS
- SNL: Characterized water splitting and A-site cation redox.
  - Confirmed CCXY splits water at low p$_{O2}$
  - Confirmed Ce$^{4+/3+}$ redox in CCXY phase as predicted

CCXY H$_2$ prod capacity > SLMA >> BCM

CCXY exhibits high-yield water splitting with same relative yield as BCM (75%) @1333:1
UCSD Seedling Project: High Entropy Perovskite Oxides with Increased Reducibility for STCH

Potential benefits of high entropy perovskites oxides (HEPOs) as a new class of water splitting materials:

- Vast composition space: A and/or B site mixing, tunability, enhanced reducibility and stability

- Modulate oxygen reduction enthalpy and increase oxygen reduction entropy.
  - Vibrational entropy: increased soft vibrational modes, larger defect volume
  - Electronic and magnetic entropy: Fe cation configurations, long range electron transfer
Compositional heterogeneity in \( \text{La}_{0.8}\text{Sr}_{0.2}(\text{Mn}_{0.28}\text{Fe}_{0.28}\text{Co}_{0.16}\text{Al}_{0.28})\text{O}_3 \) found by STEM-EDS.

- Found regions containing bulk stoichiometry
- Found Sr-, Co-, Al-, and Mn-rich regions

Co-reduction of Mn and Co observed in bulk phase via EELS during in situ thermal reduction at 700 °C in vacuum.

Redox activity is very sensitive to composition; Mn does not reduce at Mn:Co of 0.5
CUB Seedling Project: HydroGEN Node Support Provided by NREL and SNL

- Computationally accelerate discovery of high-performance materials for STCH.
  - Utilize machine-learned models coupled with ab initio thermodynamic and kinetics screening calculations to accelerate material discovery
- Predict defect formation energies from supercell calculations, predict defect equilibria phase diagrams with ideal gas law $\Delta \mu$ for H$_2$, O$_2$, H$_2$O.
  - Defect pairs ($V_O$-$Fe_{Al}$) are essential (solid line vs dashed line)
  - Fe-rich off-stoichiometry facilitates $V_O$ formation
- Model capacity ($\Delta \delta$) vs yield (H$_2$/H$_2$O).
  - Desirable (moderate) reduction conditions limit capacity
  - FeAl$_2$O$_4$ splits water only under low yield (low H$_2$) conditions

- Reduction conditions
  - $T = 1400^\circ$ C
  - $pO_2 = 10^{-4}$ atm
- Fe-rich oxide
  - Fe/(Fe+Al) = 0.4

Defect pair mechanism enables O deficiency, but reduces the reduction entropy
Project Accomplishments, STCH Supernode

**Supernode Goal:**
Principal research outside scope of seedling projects

Atomistic Understanding of MnO₆ Arrangements that Influence WS Activity

**Project Accomplishments, STCH Supernode**

- **Ba₄PrMn₃O₁₂ (BPM)**
  - Pr for Ce

- **Ba₄CeMn₃O₁₂ (BCM)**
  - Nb for Ce

- **Ba₄NbMn₃O₁₂ (BNM)**

**Important Interrelationships:**
- **electronics**
- **defects**
- **structure**
- **performance**

**Objectives:**
- Discover and synthesize model perovskite system
- Develop and exercise multi-length-scale observation platforms and methods
- Apply first principles theory to derive atomistic understanding of WS activity

**HydroGEN: Advanced Water Splitting Materials**

- **BXM (X = Ce, Pr, Mn) identical space group symmetry**
  - Perfectly ordered 12R-phase @ full stoichiometry

- **Oxidation state Pr⁺⁶ = Ce⁺⁴; Δ_{radii} ~ -2%; Mn⁺⁴**

- **Oxidation state Nb⁺⁵ ≠ Ce⁺⁴; Δ_{radii} ~ -25%; Mn⁺³⁺/⁺⁴**
Accomplishment: Unraveling where Electrons go during Thermal Reduction using XAS

• Redox capacity and high yield behavior vary with X in BXM (Ce, Nb, Pr).
  – BCM > BNM > BPM H₂ production (bar graph)
  – BCM < BNM < BPM O₂ redox (residual mass graph)
• BCM and BPM O K-edge are very similar in the oxidized state but differ significantly with reduction.

understanding how electronic structure influences redox behavior is critical to designing better materials
Accomplishment: Multiple Levels of Theory Used to Interpret XAS and EELS Experiments

- **Many-Body X-ray Absorption Spectroscopy** theory accounts for multiple electron processes in the excited core-hole.
  - Collaboration with BES Molecular Foundry

- **Electron density of states (DOS)** calculated by DFT+U.

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<td>Mn 3d</td>
<td>Ce 4f</td>
<td>Ce 4f</td>
<td>O 2p</td>
</tr>
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assign specific O-orbital interactions

build a molecular orbital picture of electron distribution in defected BXM

Full Spectrum
- O1
- O2 down
- O2 up
Accomplishment: High Temperature X-Ray Diffraction Reveals Complex Phase Behavior in BXM during Redox

**HT-XRD on BaX_{0.25}Mn_{0.75}O_3 (X = Ce, Nb, Pr)**

- 12R to 6H polytype transition in BCM and BNM is reversible.
  - MnO_6 trimer reduced to a dimer, partial occupancy of Mn on Ce site increases configurational entropy
- BPM clearly exhibits more complicated redox phase behavior.

12R-BaX_{0.25}Mn_{0.75}O_3 (X = Ce, Nb, Pr)

Mn

Ce, Nb, Pr

Ba

12R-BCM reduction

12R-BCM → 6H-BCM

BaMnO_{2.59}

Ba_3Mn_2O_8

BaCeO_3

12R-BNM reduction

12R-BNM → 6H-BNM

12R-BPM reduction

12R-BPM → ???

6H-Ba_{0.75}Ce_{0.25}Mn_{2.25}O_9

Fixed from initial 6H, and maintains 12R-BCM cation ratio

Unclear how phase transitions affect water splitting
Accomplishment: HR-STEM Reveals Important Structural Transformations in BCM

- DFT calculations predict a lower oxygen vacancy formation energy at the twins.
- Nucleation and growth of twinned regions may be important mechanisms for 6H formation and stabilization of oxygen defects.
- BCM’s redox kinetics relatively fast despite structural rearrangements.
Project Accomplishments, STCH 2.0

EVALUATE

DISCOVER

HydroGEN: Advanced Water Splitting Materials
Goals: A comprehensive validation of known STCH material properties and a focused, theory-guided material design effort addressing 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).
- Find new materials using the ML model and characterize by detailed calculations, synthesis, and experimental validation.

<table>
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<th>State of the Art (Point A)</th>
<th>End of Project Milestone (Point B)</th>
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<tr>
<td>Materials evaluation protocols are absent. Rigorous assessment of the potential for materials to meet DOE STCH technology performance targets also absent.</td>
<td>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.</td>
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<td>Materials that efficiently and cost effectively produce ( \text{H}<em>2 ) remain elusive because increasing both capacity (( \Delta \delta ) at lower ( T</em>{\text{RED}} )) and reaction yield in non-stoichiometric oxides has not been demonstrated.</td>
<td>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 (&gt;1000) of compositions and structures. Identify and validate materials that optimize the capacity/yield tradeoff.</td>
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Approach: Critically Assess STCH Pathway Viability

- Develop and validate testing protocols.
  - Synthesis + mapping $\delta$-T-pO$_2$ equilibrium state space
  - Leverage Benchmarking project deliverables

- Develop computational toolset to establish material performance targets.
  - Generate equilibrium model from raw data and DFT
  - Formalism to derive optimal cycle dynamics
  - Standard platform to predict cycle performance

- Rigorously assess selected material formulations.
  - Establish optimal material-dependent cycle conditions
  - Model cycle performance
  - Evaluate potential to meet DOE technology performance targets
Approach: Develop a Materials Search Strategy for Optimizing the Capacity/Yield Tradeoff

**Perform High-Throughput Calculations**
(NREL)

- Bulk calculations and existing databases
- Defect calculations

**DFT Calculations**
- Oxides: TMs, Lanthanides, group I and II as alloying elements
- Stoichiometry families: Binaries, ternaries and quaternaries in possible crystal structures
- Oxidation State, Magnetic moment, Stability, Enthalpy of formation, Bandgap, Dielectric constant, Density of States, Bulk Modulus, etc.
- Defect formation energy
  - O vacancies, cation off-stoichiometry, Isovalent and non-isolavent dopants

**Develop Machine Learning Model**
(SNL)

- Training the ML Model
  - Regression-based and other algorithms

**Optimize Property**
(STCH)

- Identify correlations
- Validate and develop knowledge

**Capacity vs. yield trade-off**

H₂ production (μmol/gm)

Yield \( \log(\frac{P_{H_2O}}{P_{H_2}}) \)

Neutral O vacancy \( (V_0^0) \)

Yield \( \frac{P_{H_2O}}{P_{H_2}} \) vs. Capacity \( (\Delta \delta) \),
O vacancy concentration vs. \( T, pO_2 \)
• Properties of a defected material (structure, $\Delta H_{\text{defect}}$) are encoded in ground state crystal structure.

• Graph Convolution Neural Network model will be trained on relaxed structure, bulk properties, and targeted defect properties.
  – Use ML to predict defect structures outside training set

• Writing and testing code to implement workflows.
Summary & DOE Targets

Summary:

• HydroGEN supported 7 STCH FOA projects with 13 nodes.
• Computational tools created by seedling projects for materials discovery.
  – Validated high-throughput computational tools are in place to rapidly expand the known STCH material space
  – Several new water splitting materials have been discovered
• Advanced experimentation and atomistic theory gain insight into the behavior of BaX$_{0.25}$Mn$_{0.75}$O$_3$ (X=Ce, Nb, Pr) based water splitting materials.
  – Experiments reveal different redox behaviors within BXM family; X=Ce best performer
  – XAS and EELS show electronic structural changes in BXM under reduction
  – HT-XRD and hot stage HR-STEM reveal crystallographic changes in BXM under reduction
  – DFT methods used to model and interpret core-hole spectroscopies
• STCH 2.0 will assess potential for technology to meet DOE targets and develop a DFT-Machine Learning approach to material discovery.
  – Materials search strategy tailored for optimizing the capacity/yield tradeoff

DOE Targets:

• This project is focused on discovering redox active materials with sufficient H$_2$ production yield, capacity, and durability to meet the following ultimate STCH Technical Targets:
  – Cost = $2/kg; Solar to Hydrogen (STH) Energy Conversion Ratio = 26%; 1-Sun Hydrogen Production Rate = 2.1E-6 kg/s m$^2$
Future Work

• Leverage HydroGEN Nodes at the labs to enable successful completion of Phase 1 seedling projects and successful continuation of two STCH seedling projects.

• Complete STCH Supernode R&D.
  – Determine the most significant difference between features in BCM and BPM that results in BPM losing 80% of its H₂ production capacity when oxidized in mixture of H₂O:H₂
  – Features include type of polymorphism, structural and/or electronic effects of Ce vs Pr on Mn-O bonding environment, and the role of charge defects
  – Publish results in peer reviewed literature (several manuscripts in preparation)

• Demonstrate a STCH material downselect process on exemplar materials.
  – Combine detailed thermodynamic data with computational methods that incorporate necessary and sufficient reactor conditions needed to predict best-case material performance
  – Rigorous assessment and ranking of a material’s likelihood to meet DOE STCH technology performance targets

Any proposed future work is subject to change based on funding levels.
# Acknowledgements

## HydroGEN
**Advanced Water Splitting Materials**

## Authors
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- Northwestern University
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**Energy Materials Network**

U.S. Department of Energy
1. X. Qian et al., Outstanding Properties and Performance of CaTi$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ for Solar-Driven Thermochemical Hydrogen Production. *Matter.* **4**, 688–708 (2021).


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