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Evaluation of $Ba(Al,Fe)_2O_4$, a Machine Learned Compound, for Solar Thermochemical Hydrogen Production

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34th Rio Grande Symposium on Advanced Materials, Albuquerque, NM
Energy/Nuclear Materials & Sustainability
2:00 pm – 2:30 pm, October 21, 2024 (Alvarado H) - Invited

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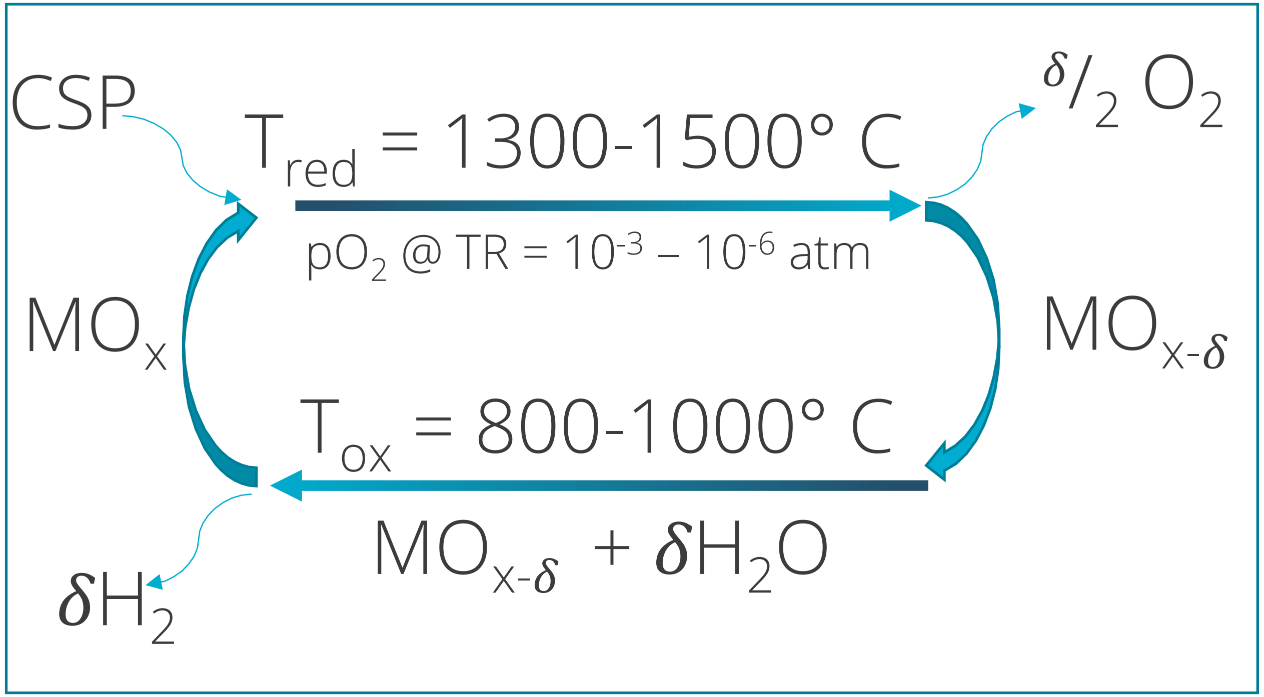
Outline

- Solar thermo-chemical hydrogen production (Solar-TCH) background and the US DOE HydroGEN consortium
- Addressing needs for TCH community
  - Identification of benchmarking metrics and applying them to exemplar materials
  - New materials identification aided by computational discovery with machine learning approach

Solar Thermo-Chemical Hydrogen Production (Solar-TCH)

Sunlight (heat) + water → Hydrogen



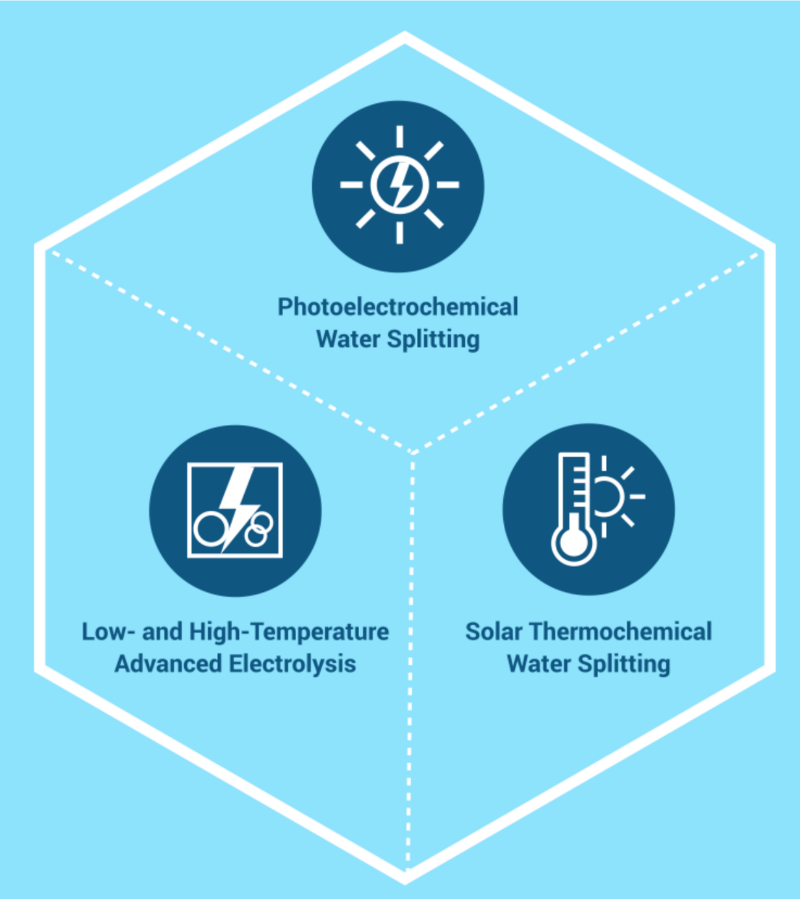
National Solar Thermal Test Facility at Sandia National Labs

energy.sandia.gov

- Single phase materials to avoid cycling degradation
- Oxides that “breathe” oxygen needed → non-stoichiometric oxides
- Goldilocks reduction enthalpy (H_r)
- Also use heat from other sources → *Thermo-chemical hydrogen production (TCH)*

Department of Energy HydroGEN Consortium (H2AWSM.org)

Research focus areas



Leverage capabilities at national laboratories

- National Renewable Energy Laboratory (Lead)
- Lawrence Berkeley National Laboratory
- Sandia National Laboratories
- Idaho National Laboratory
- Lawrence Livermore National Laboratory

Collaboration with industry and academia seedlings supported by HydroGEN funding opportunities

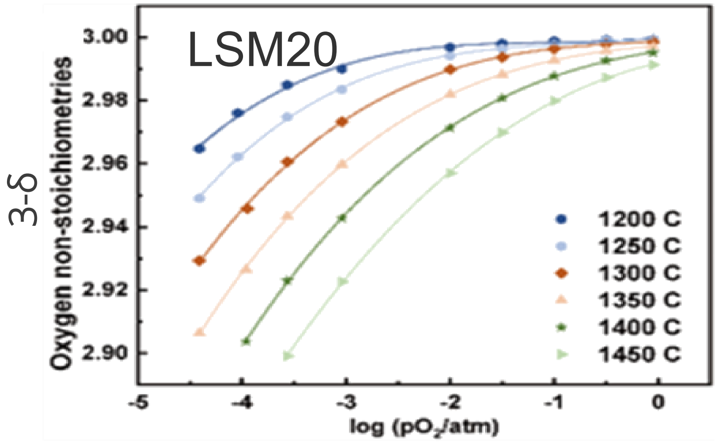
Sandia node capabilities used for this presentation:

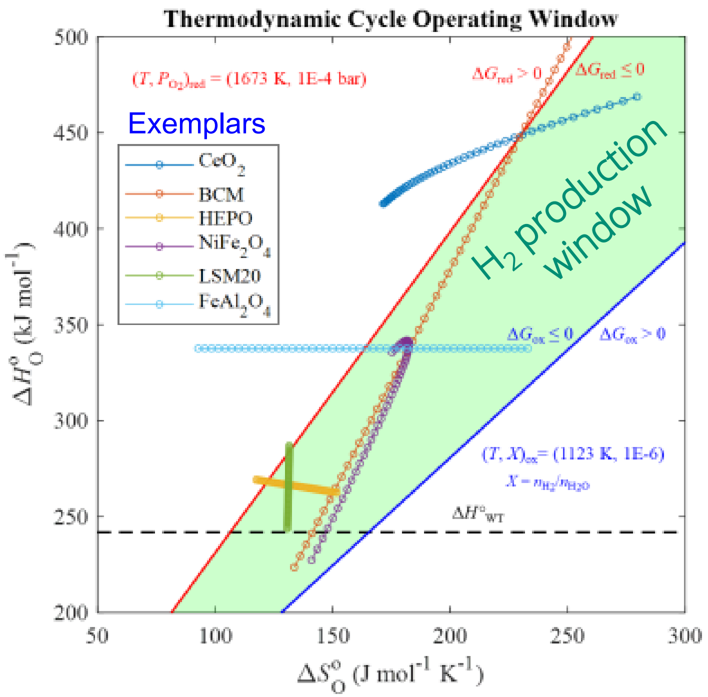
- Thermo-gravimetric analysis (Sean Bishop)
- TCH reactor (Tony McDaniel)
- Electron microscopy and composition analysis (Josh Sugar)

Exemplar Material Viability Study

- Define TCH metrics
- Benchmark exemplar materials against state of the art (CeO_2)
- Identify technology gaps

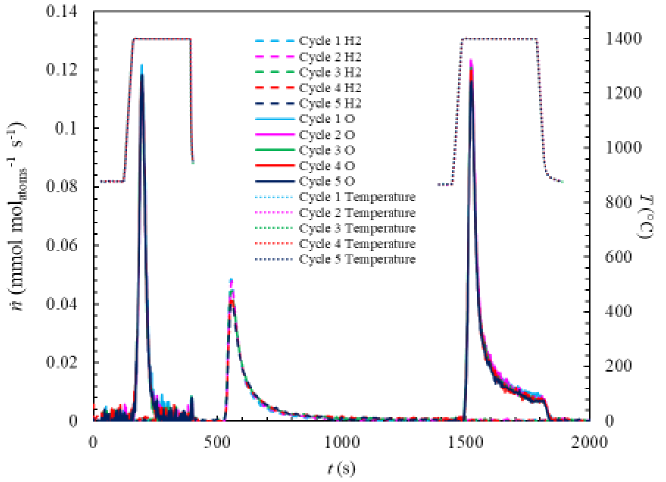
Thermodynamic parameters (from thermo-gravimetric analysis)



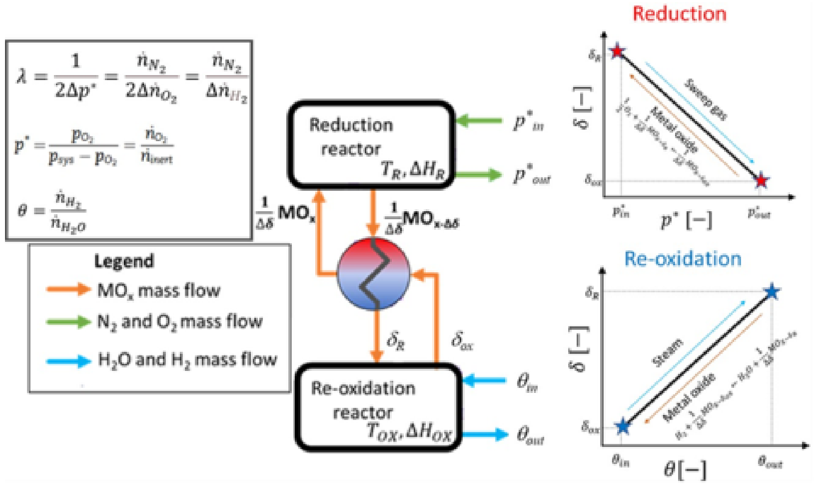


BCM: $BaCe_{0.25}Mn_{0.75}O_3$
HEPO: $La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Ba_{1/6}Sr_{1/6})MnO_3$
LSM20: $La_{0.8}Sr_{0.2}MnO_3$

Hydrogen production and kinetic parameter (from flow reactor)



Cycle efficiency estimation



$$\lambda = \frac{1}{2\Delta p^*} = \frac{\dot{n}_{N_2}}{2\Delta \dot{n}_{O_2}} = \frac{\dot{n}_{N_2}}{\Delta \dot{n}_{H_2}}$$

$$p^* = \frac{p_{O_2}}{p_{sys} - p_{O_2}} = \frac{\dot{n}_{O_2}}{\dot{n}_{inert}}$$

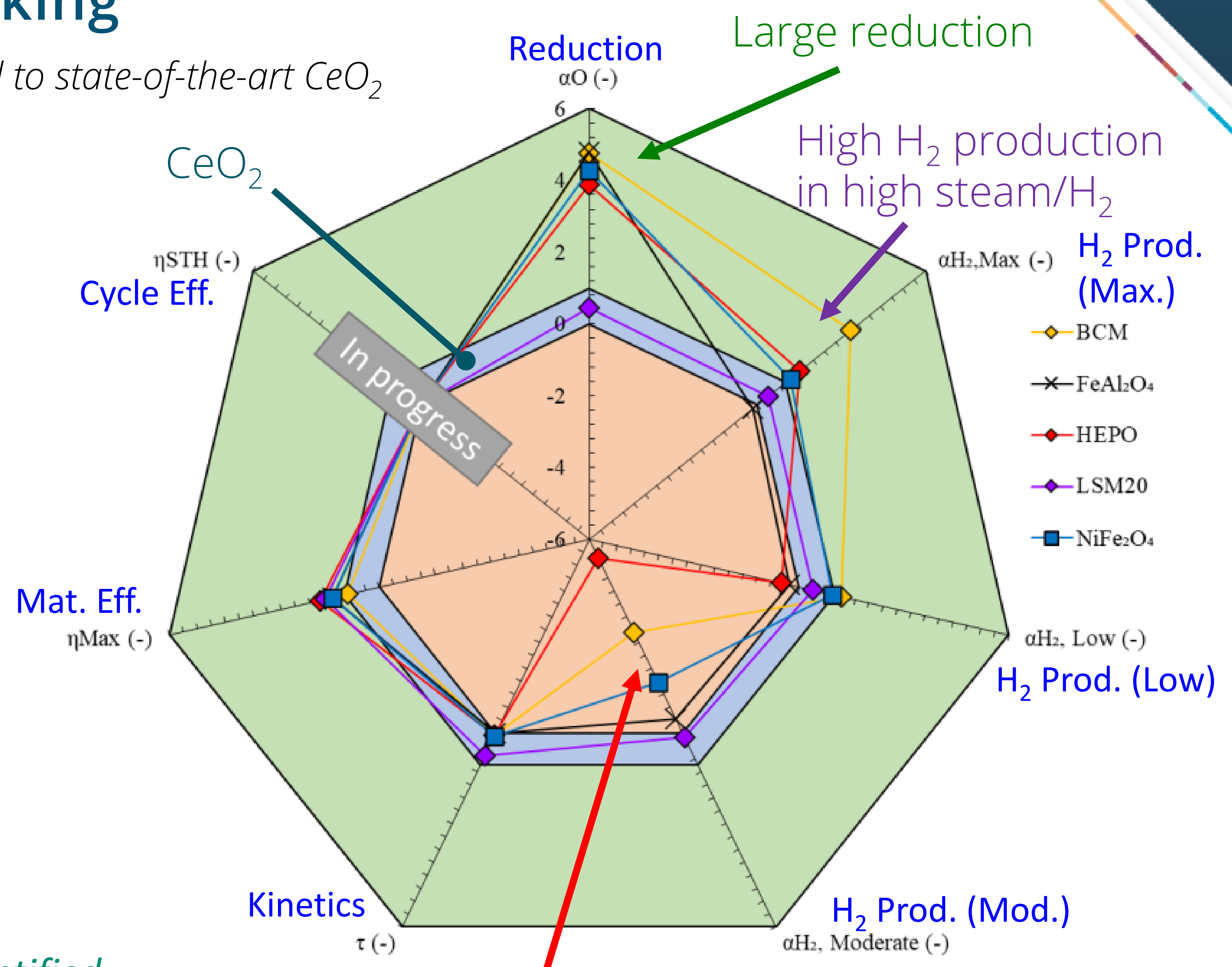
$$\theta = \frac{\dot{n}_{H_2}}{\dot{n}_{H_2O}}$$

Metrics and Exemplar Benchmarking

Exemplars normalized to state-of-the-art CeO_2

Metrics

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	$\frac{\Delta G^o_{WS}}{\Delta H^o_8}$ 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	$\alpha_O > 5$
TCH Capacity (Maximum Yield)	mmol H_2 / mol atom in solid reduced @ neutral low condition, oxidized in pure H_2O @ optimal T_{OX} for material	$\alpha_{H2,Max} > 5$
TCH 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	$\alpha_{H2,Low} > 2.5$
TCH 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	$\tau > 0.20$

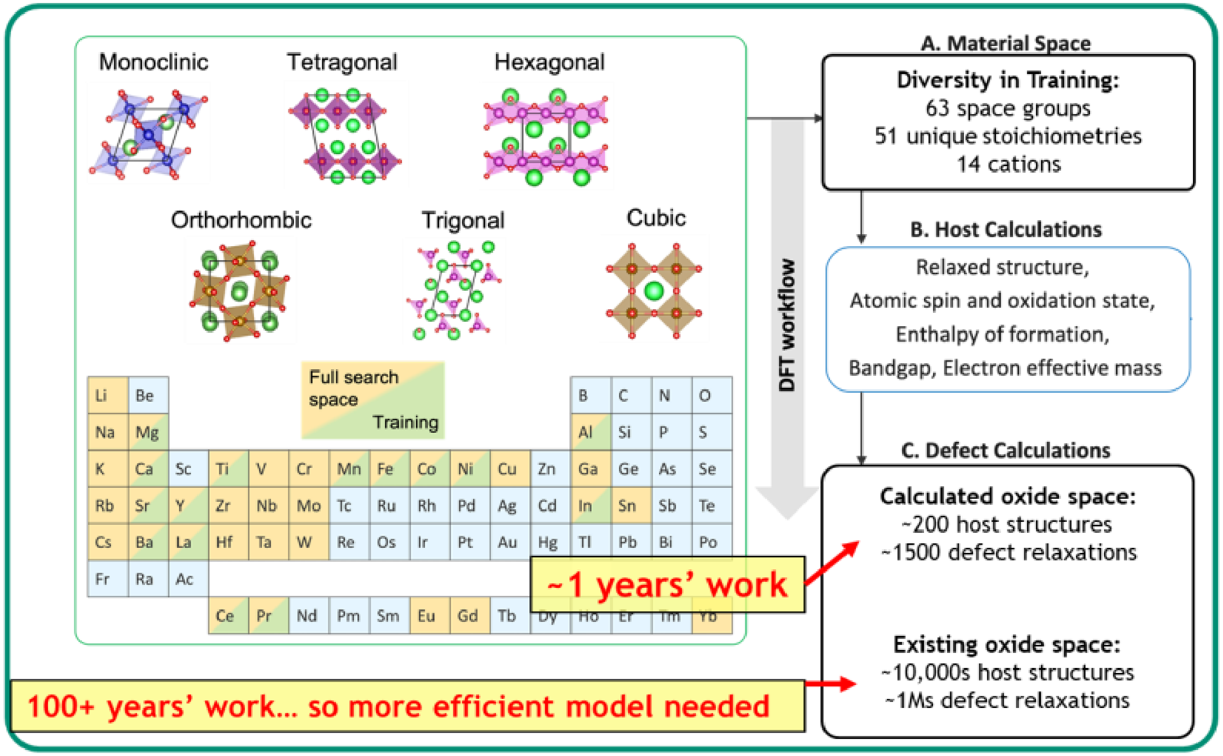


...but H_2 "consumption" in low steam/H_2 → only LSM20 competitive with CeO_2

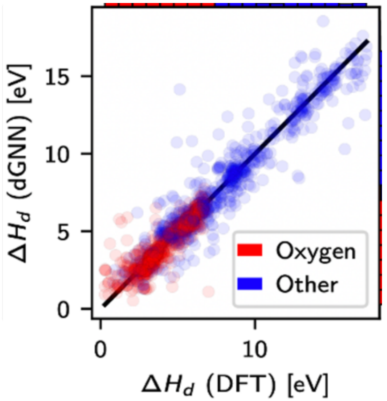
- *Evaluation framework created and metrics identified*
- *Weakness of exemplars in low steam/H_2 ratio → **critical need for new materials***

Discovery of New TCH Materials Aided by Machine Learning

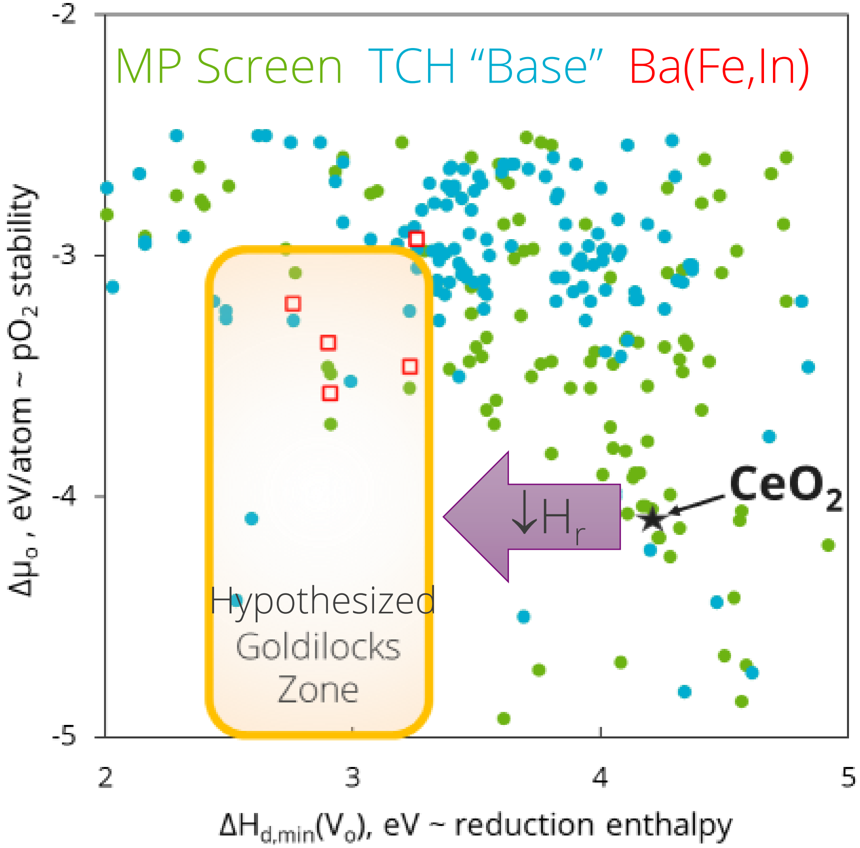
First-principles DFT workflow is robust but costly (using NRELMatDb hosts)



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



Expected $\Delta H_{0,d}$ MAE for unseen compounds < 450 meV (threshold for ML to be predictive).



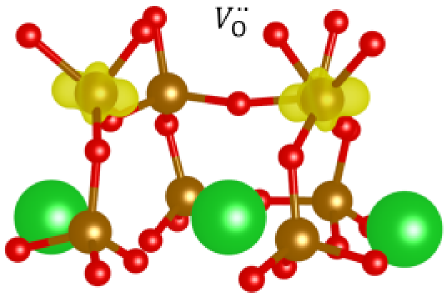
→ Identified $BaFe_2O_4$

M. Witman, Nature Computational Science, 3 (2023) 675

$BaFe_2O_4$ – Oxygen Vacancies Predicted, but it Melts

$BaFe_2O_4$

Orthorhombic (Bb21m) phase



DFT → oxygen vacancy preferred vs. cation defects

Calcined $BaCO_3$ and Fe_2O_3 at 1400 °C in air in alumina crucible

→Orthorhombic $BaFe_2O_4$ (Bb21m) phase with 2 wt% $BaFe_{12}O_{19}$ hexagonal (P_{63}/mmc) impurity

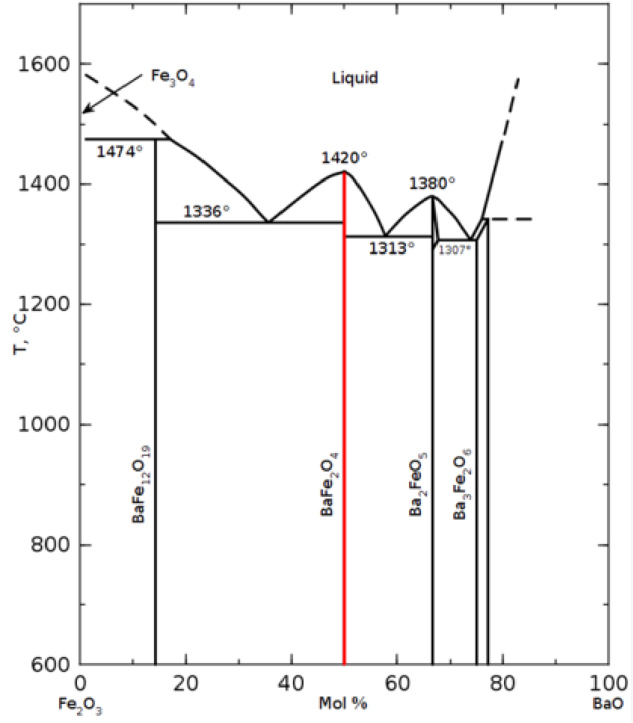
$BaFe_2O_4$

1400 °C (2 h) air
→ sintering

1400 °C (2 h) 1% O_2
→ slight melting

1400 °C (2 h) Ar (~20 ppm O_2)
→ significant melting

Alumina crucible



→ TCH reduction extent limited by solid phase stability

Stabilize $BaFe_2O_4$ with Al

Melting of BFO in low pO_2 mitigated by Al substitution!

1400 °C in Ar (~20 ppm O_2)

$BaAl_{0.4}Fe_{1.6}O_4$ – Hexagonal ($P6_3$) phase

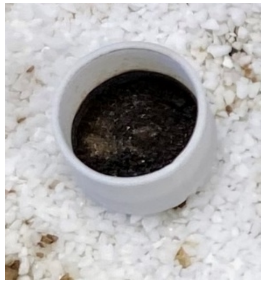
→ Enables higher reduction temperature and resistance to densification

Higher melting point expected with Al

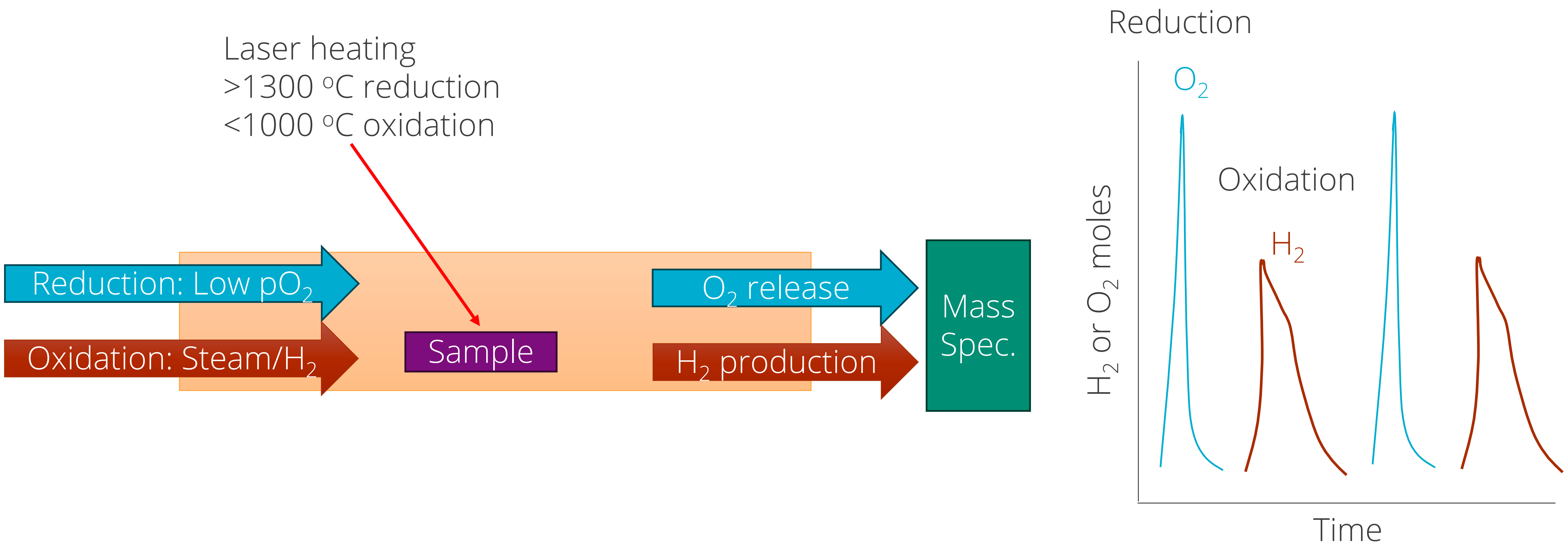
- $BaAl_2O_4$ (hexagonal $P6_3$, stuffed tridymite) melting point ~1820 °C
- $MgAl_2O_4$ (cubic Fd-3m, spinel) melting point ~2130 °C

$BaAl_{0.4}Fe_{1.6}O_4$ stable at 1450 °C in air!

$BaFe_2O_4$ $T_{melt,air}$~1420 °C

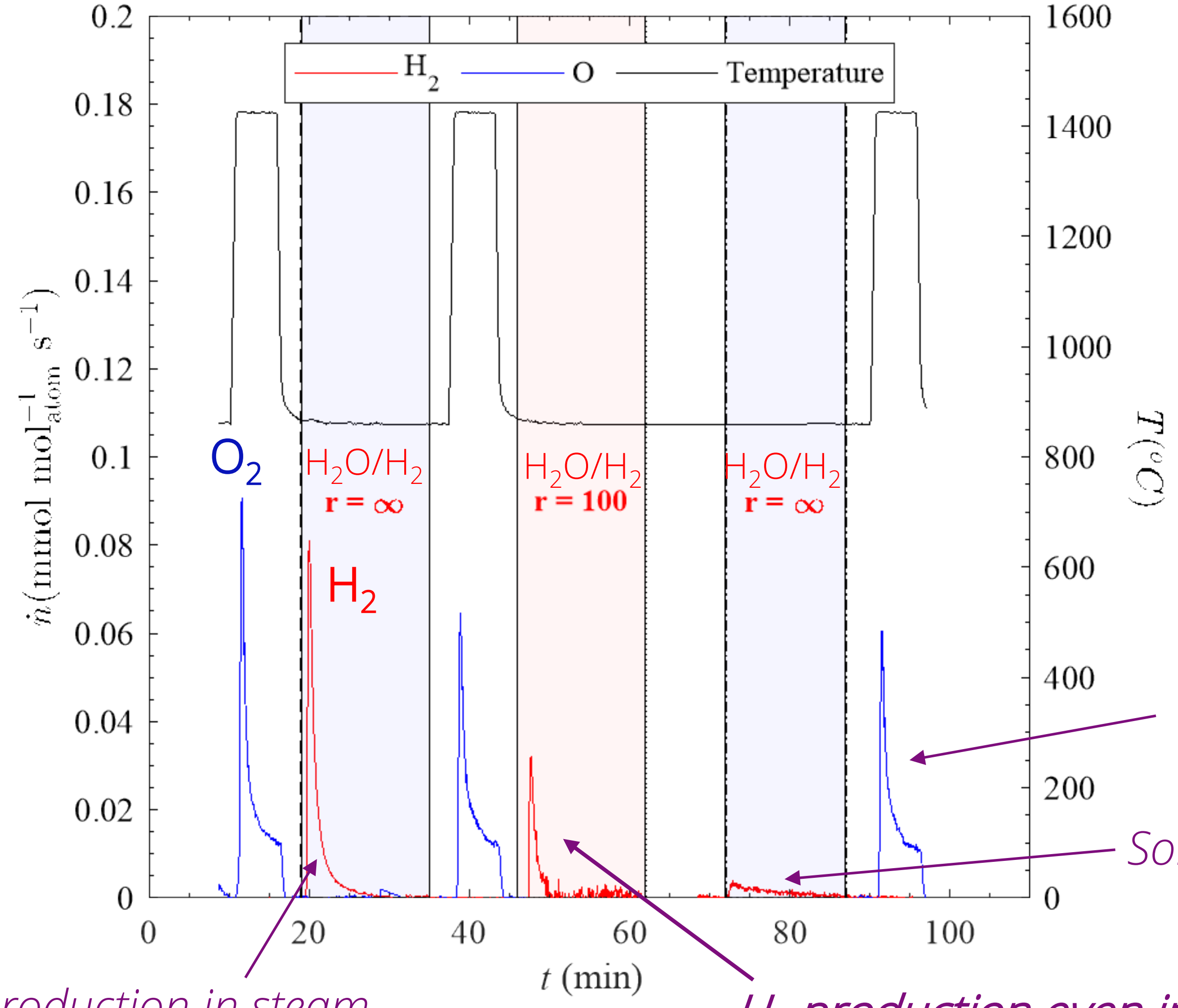


Hydrogen Production Measurement – Flow Reactor



$BaAl_{0.4}Fe_{1.6}O_4$: Water Splitter, even in Low Steam/H_2!

H_2 production measurement using flow reactor



- Reduction at 1425 °C in ~1 ppm O_2
- Oxidation at 850 °C in steam or 1% H_2 in steam

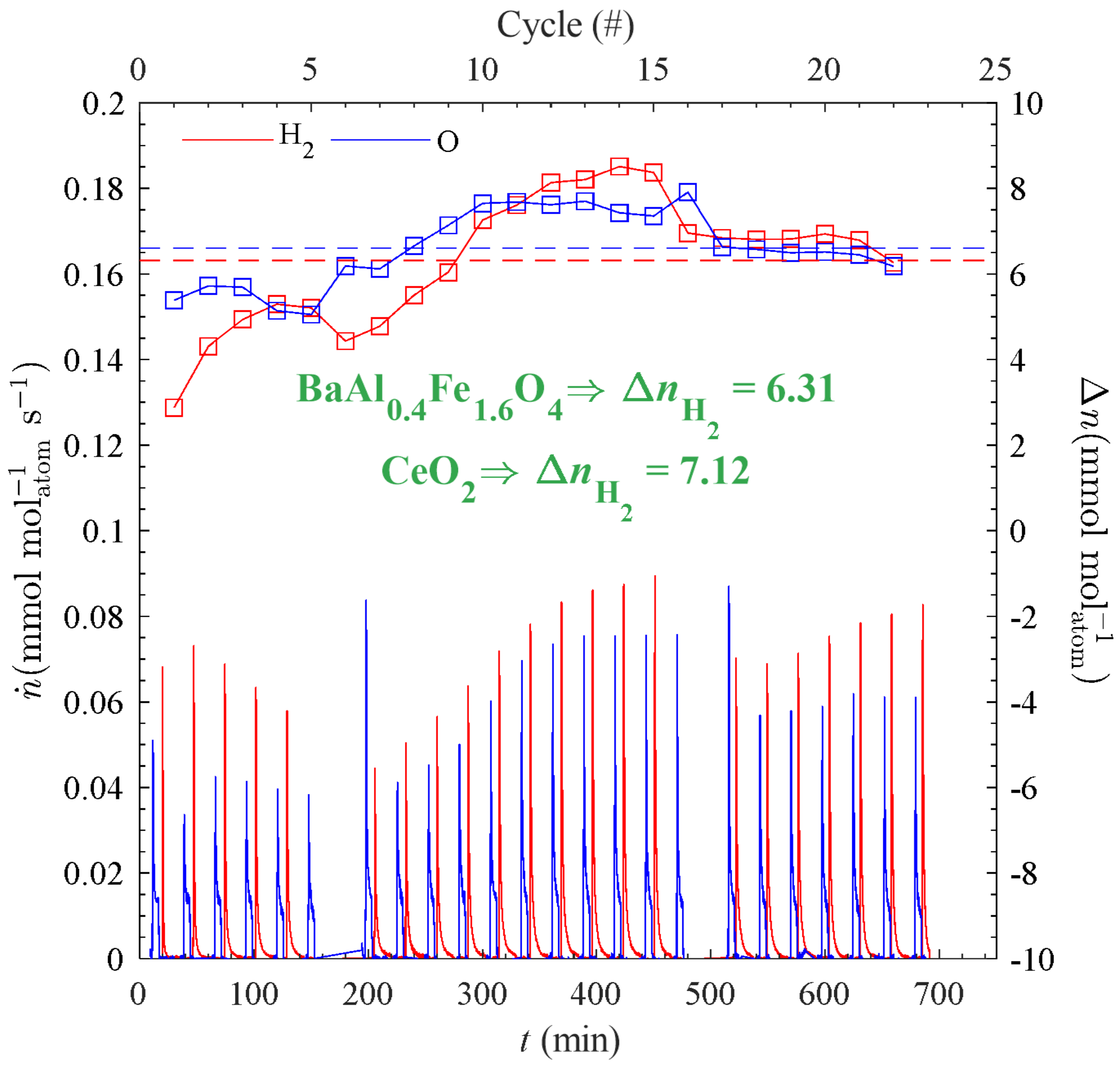
Reduction largely reproducible after cycle

Some continued H_2 production in pure steam

H_2 production in steam

H_2 production even in 1% H_2 environment!

H_2 Production Over 20 Cycles



- Reduction at 1425 °C in ~1 ppm O_2
- Oxidation at 850 °C in steam

Comparable H_2 production performance to CeO_2 retained for 20 cycles!

Severe Change in Morphology and Phase After Cycling

Initial powder

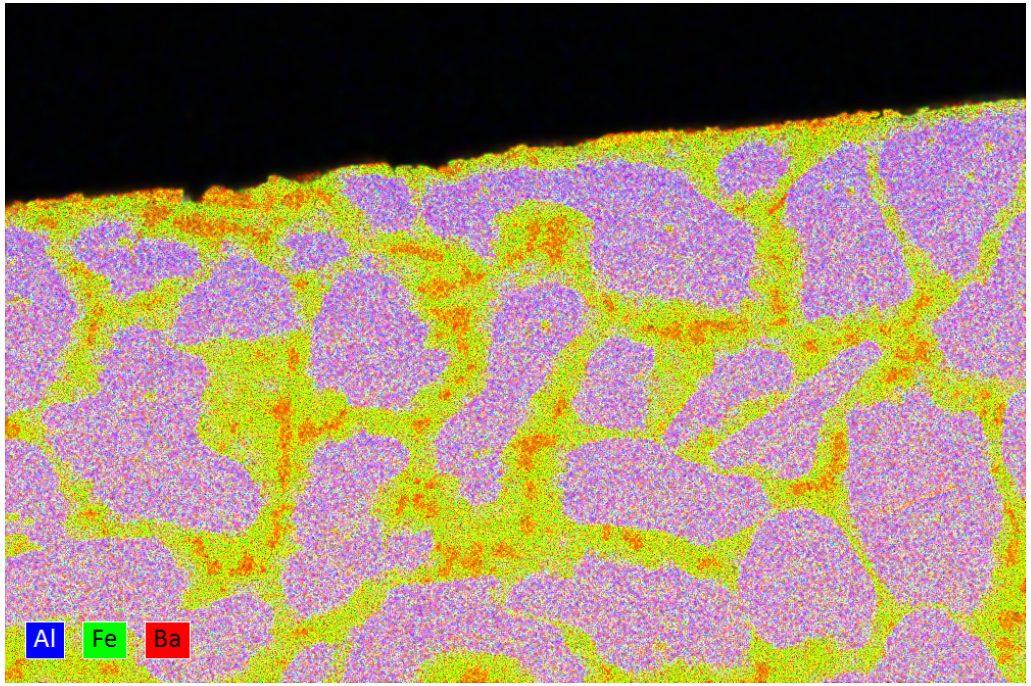
After 20 redox cycles

Post-cycled sample initial diffraction analysis at SLAC

- $BaAl_2O_4$ ($P6_3$) is 20.34 wt% → starting phase
- $BaFe_2O_4$ (Cmc21) is 75.17 wt%
- $BaFeO_3$ ($P6_3$/mmc) is 4.48 wt%

Decomposition products

EDS map of post-20 cycled sample

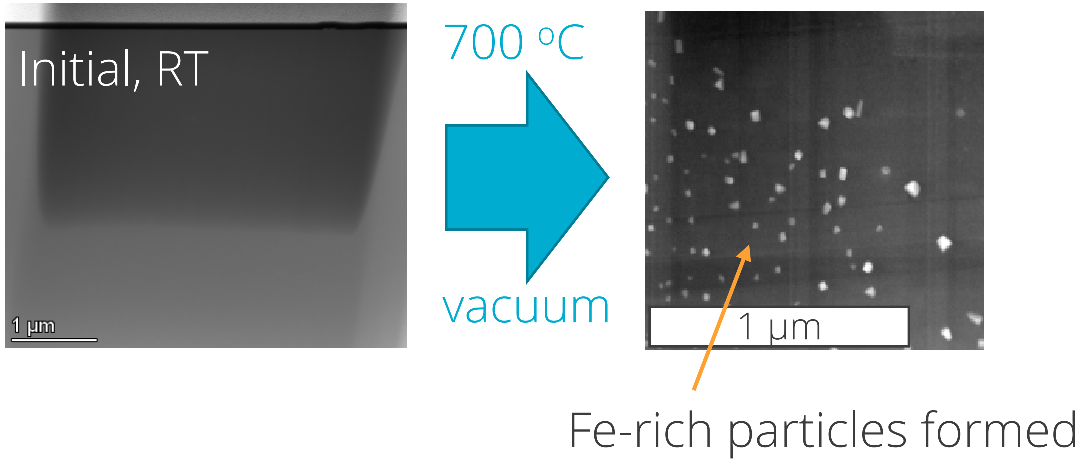


- Purple phase → ~$BaAlFeO_4$ (expected $P6_3$ structure)
- Yellow phase → ~$BaFe_2O_4$, with possible melting
- Red phase → ~$BaFeO_3$ (or $Ba_2Fe_2O_5$), with possible melting

Decomposition Evidence with ***in situ*** TEM

In situ reduction in TEM → evolution of decomposition

FIB cross-section of $BaAl_{0.4}Fe_{1.6}O_4$



Identify most TCH active $BaFe_2O_4$ Decomposition Phase

Fabricated decomposition products estimated from EDS

EDS Composition	Nominal Composition	Fabricated Structure Prototype
$BaAl_{0.02}Fe_{0.99}O_x$	$BaFeO_3$ or $Ba_2Fe_2O_5$	$Ba_2Fe_2O_5$
$BaAl_{0.1}Fe_{1.6}O_x$	$BaFe_2O_4$	$BaFe_2O_4$ with some $BaFeO_3$
$BaAlFeO_x$	$BaAlFeO_4$	$BaAl_2O_4$

- $BaFe_2O_4$, $BaAlFeO_4$, and $BaFeO_3$ observed in post-cycled XRD
- $BaFeO_3$ impurity in "$BaFe_2O_4$" consistent with (Al+Fe)/Ba<2
- $Ba_2Fe_2O_5$ unexpected from post-cycled XRD → possible sample size and detection limit challenge

→ *Measure reduction oxygen capacity to compare TCH activity*

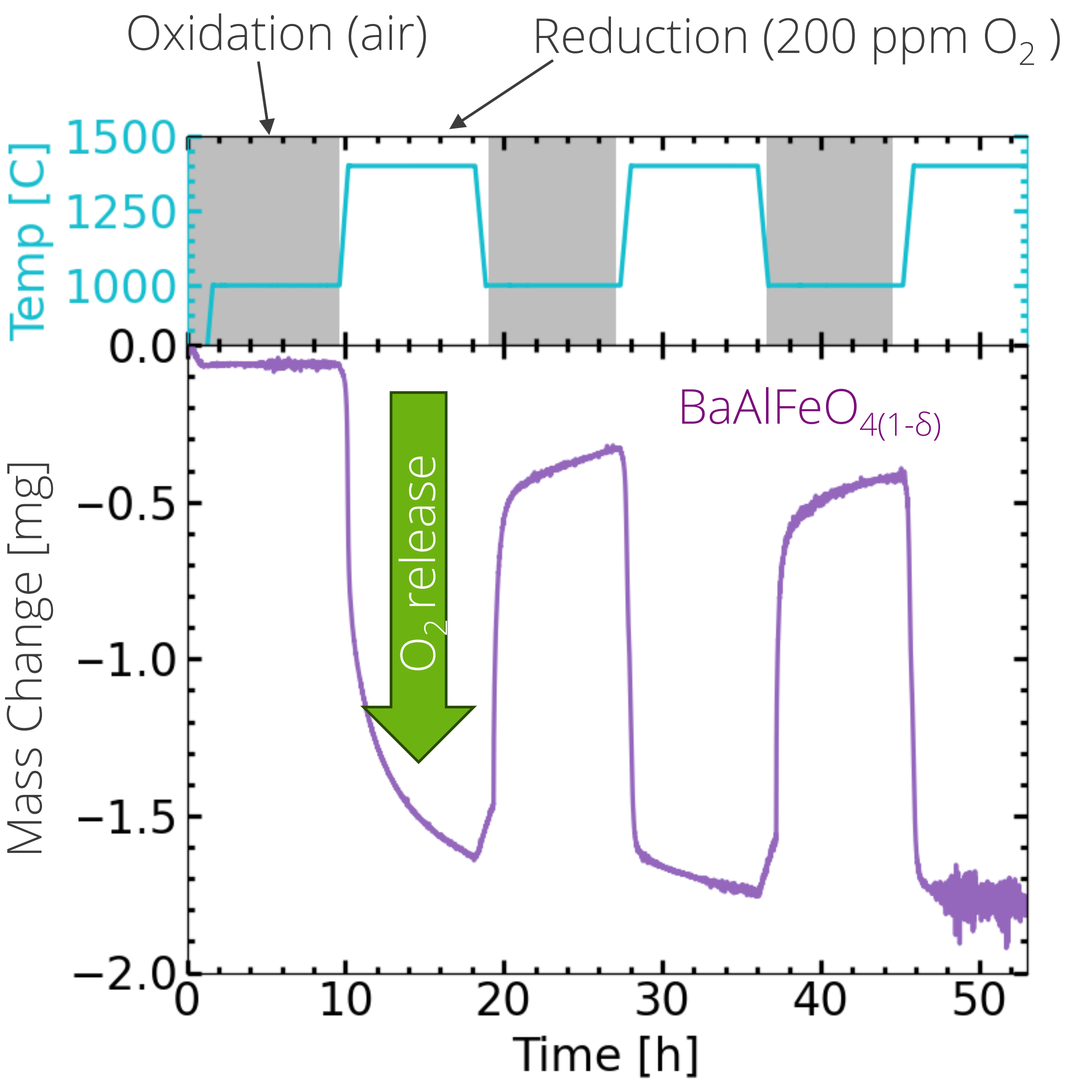
Oxygen Non-Stoichiometry in TCH Cycling

Netzsch STA 449 F1
thermo-gravimetric analyzer

netzsch.com

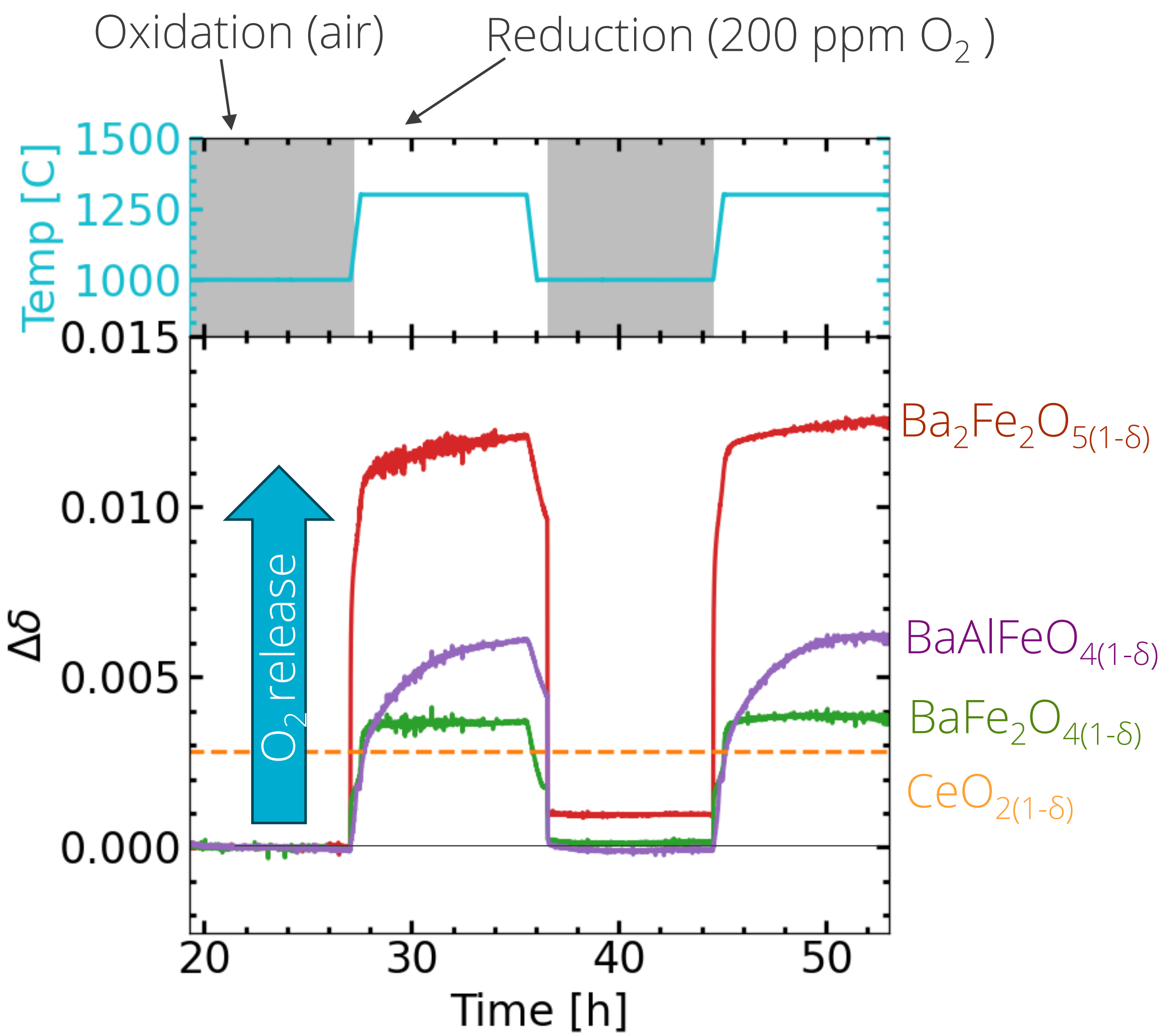
Gas out

Zirox oxygen sensor → pO_2



Convert mass loss to non-stoichiometry (δ)

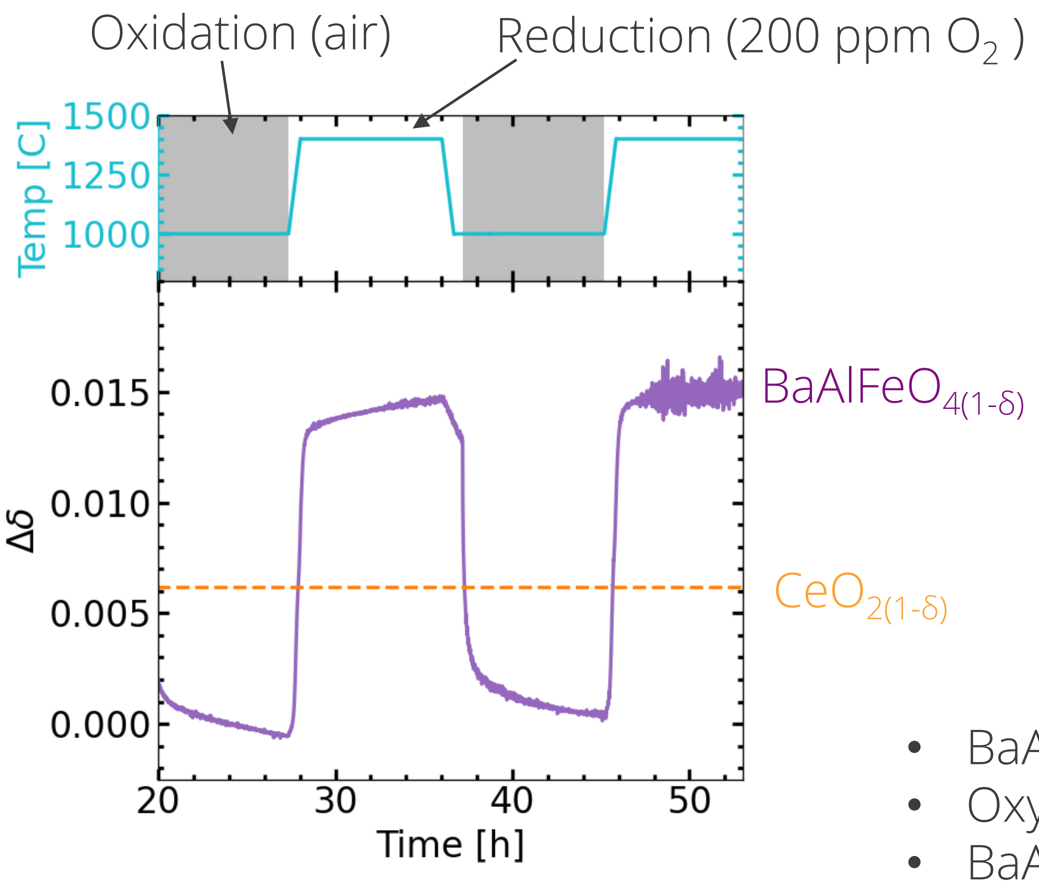
Oxygen Non-Stoichiometry Comparison

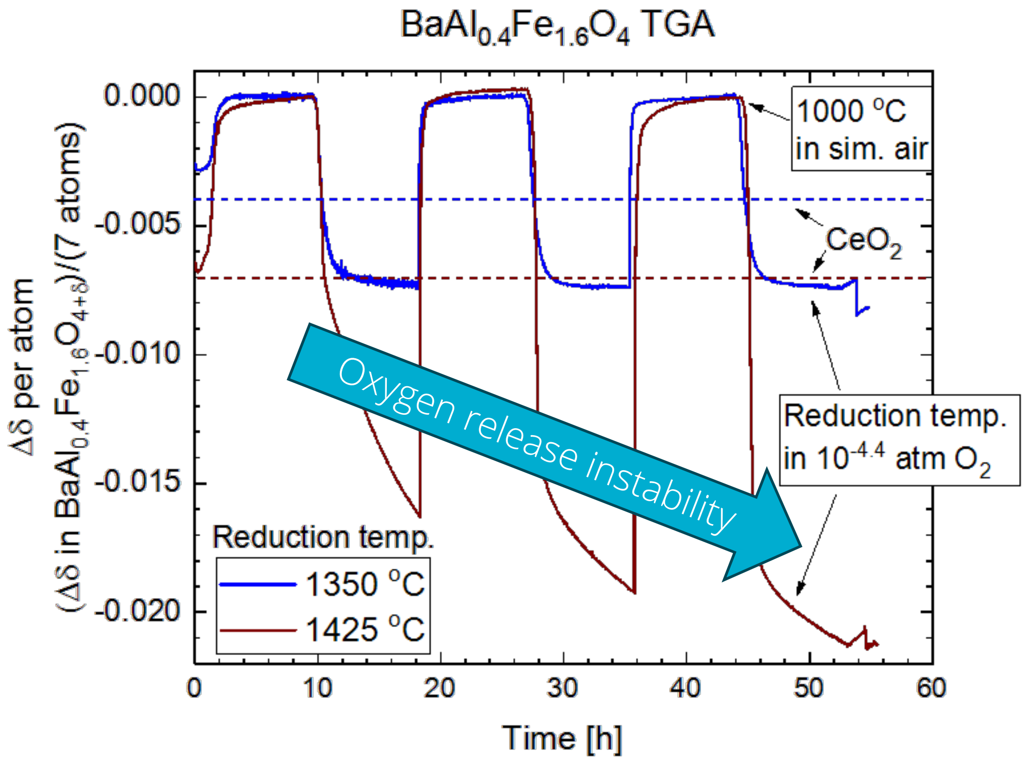


- $Ba_2Fe_2O_5$ → most oxygen release, indicating attractive TCH activity
- $BaFe_2O_4$ → least oxygen release, possibly lowest TCH activity
- After test, only $BaFe_2O_4$ showed partial decomposition to $BaFe_2O_4$, $Ba_2Fe_2O_5$, and $BaFeO_3$

- All three composition have more oxygen release than state-of-the-art CeO_2 → **Ba ferrite is a strong hydrogen production contender**

Increasing Oxygen Release at Higher Temperature with $BaAlFeO_4$





- $BaAlFeO_4$ high temperature stability → greater reduction
- Oxygen release exceeds state-of-the-art CeO_2
- $BaAlFeO_4$ mitigates oxygen loss instability and decomposition compared to $BaAl_{0.4}Fe_{0.6}O_4$

Future work: *Evaluate hydrogen production with flow reactor (are some of the compositions too reducible?)*

Summary

- Presented exemplar Solar-TCH materials and key Solar-TCH metrics
  - Identified significant gap in H_2 production in low steam/H_2 ratio materials
- Demonstrated successful water splitting with ML predicted compound $BaFe_2O_4$
  - Improved thermal stability with Al addition
  - Competitive H_2 production to CeO_2 in low steam/H_2
  - Despite severe morphological and phase changes, maintains H_2 production after many cycles
  - Demonstrated attractive oxygen release for decomposition products, with greater stability at high temperature

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