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PREDICTING AND EVALUATING NEW WATER SPLITTING MATERIALS FOR SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION

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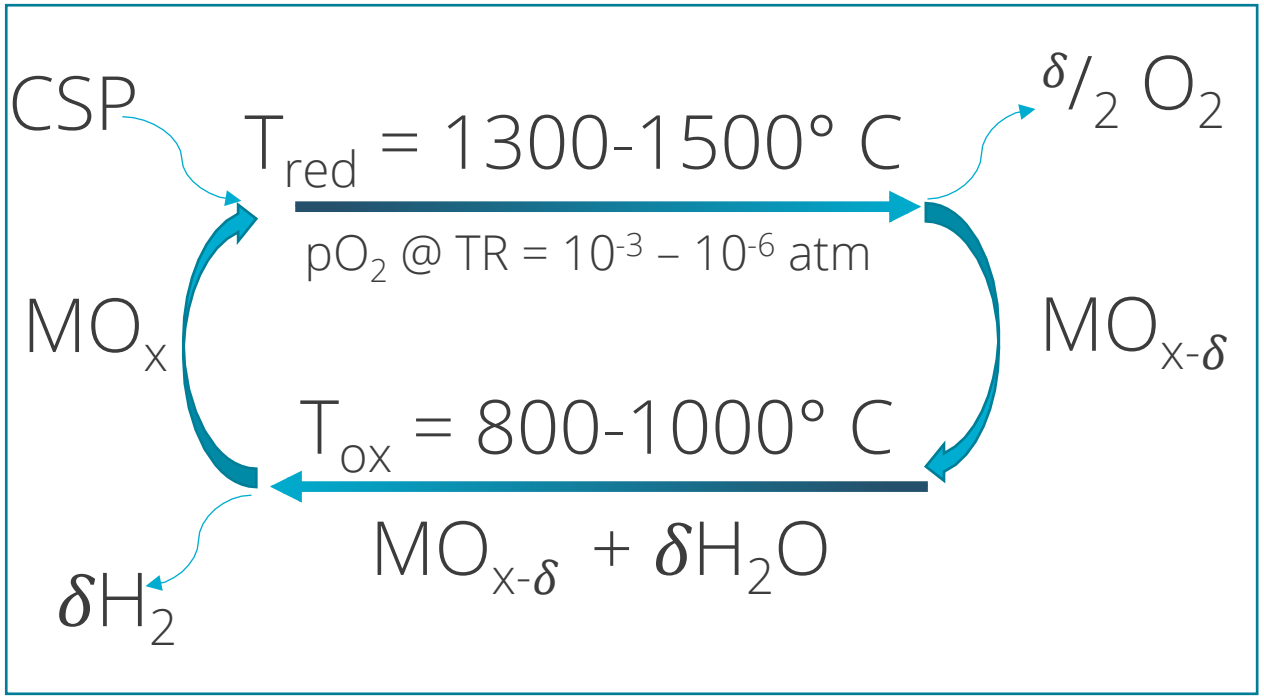
24th International Conference on Solid State Ionics, London, UK
3C2 Catalysis
11:15 am – 11:45 am, Wednesday, July 17, 2024 (Room Fleming) - Keynote

Outline

- Solar thermo-chemical hydrogen production (STCH) background and the US DOE HydroGEN consortium
- Addressing needs for STCH community
  - Identification of benchmarking metrics and applying them to exemplar materials
  - New materials identification aided by computational discovery with machine learning approach
  - Revisiting oxygen non-stoichiometry in $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ at STCH reducing temperatures (>1200 ^{o}C), and new High Entropy Perovskite Oxide (HEPO)

Solar Thermo-Chemical Hydrogen Production (STCH)

Sunlight (heat) + water → Hydrogen



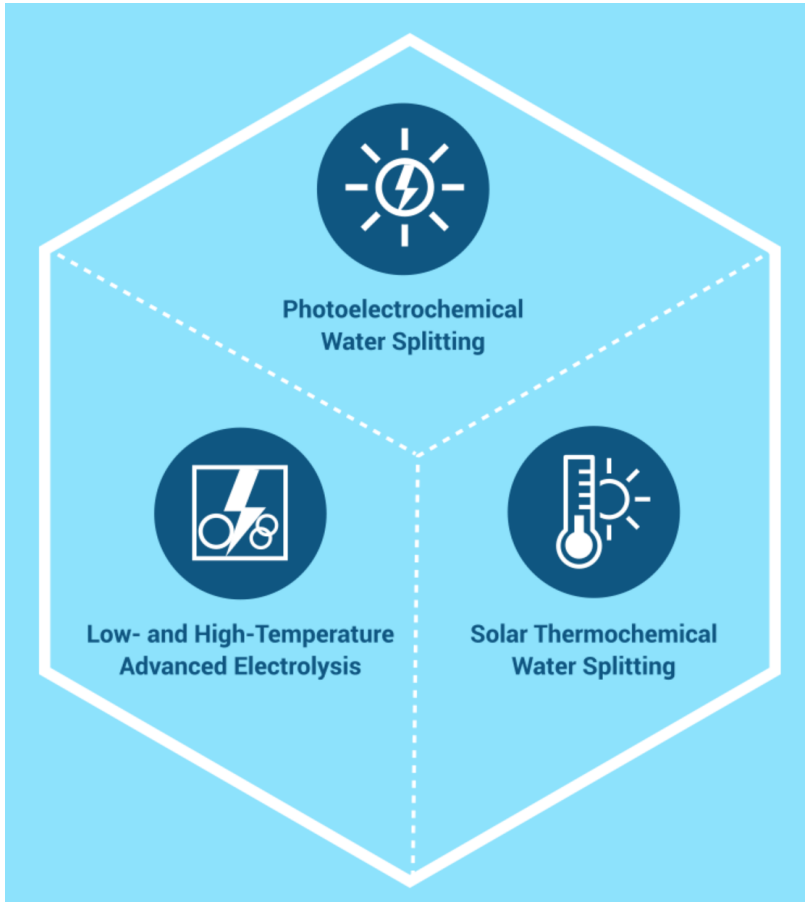
National Solar Thermal Test Facility at Sandia National Labs

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

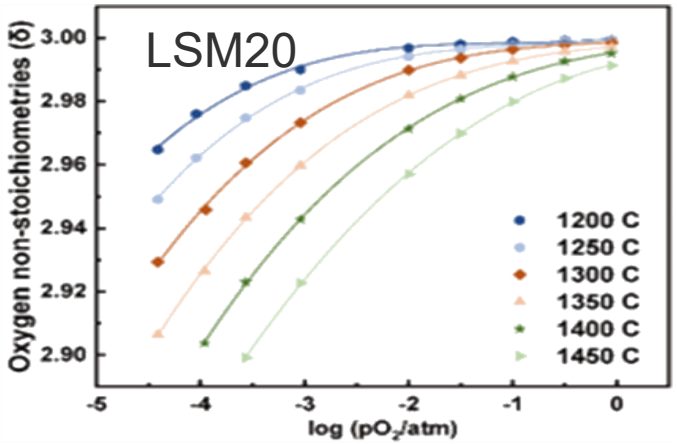
Sandia node capabilities used for this presentation:

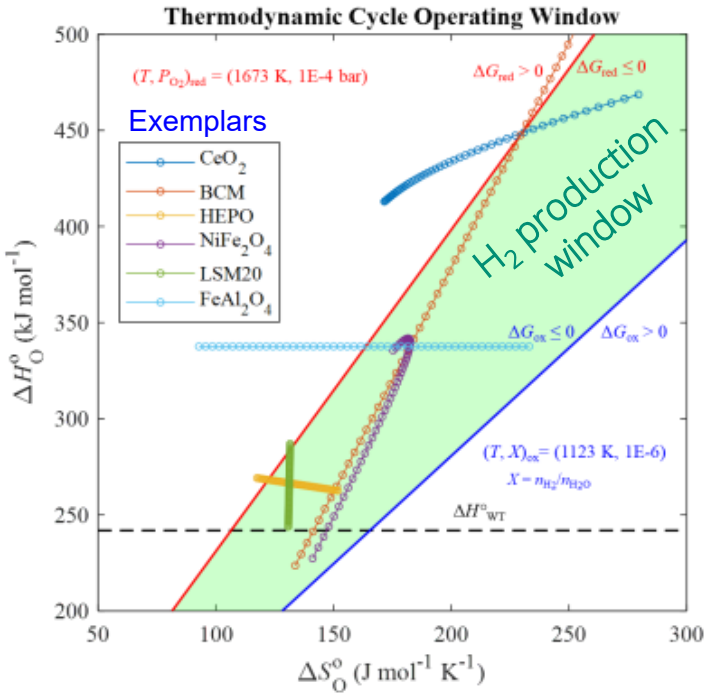
- Thermo-gravimetric analysis (Sean Bishop)
- STCH reactor (Tony McDaniel)
- Electron microscopy and composition analysis (Josh Sugar)

Exemplar Material Viability Study

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

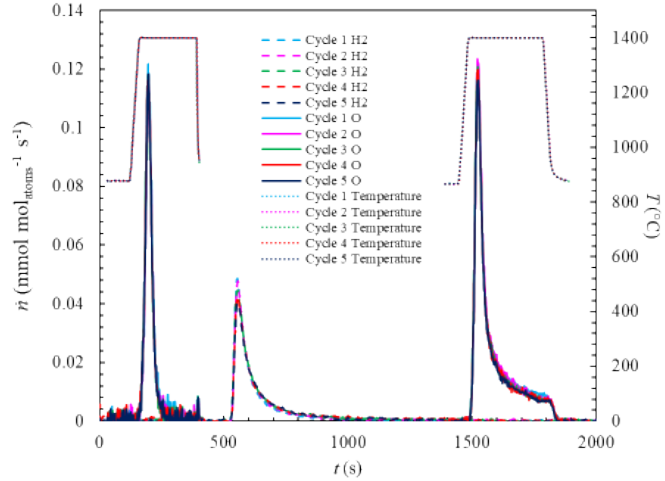
Thermodynamic parameters (from thermo-gravimetric analysis)



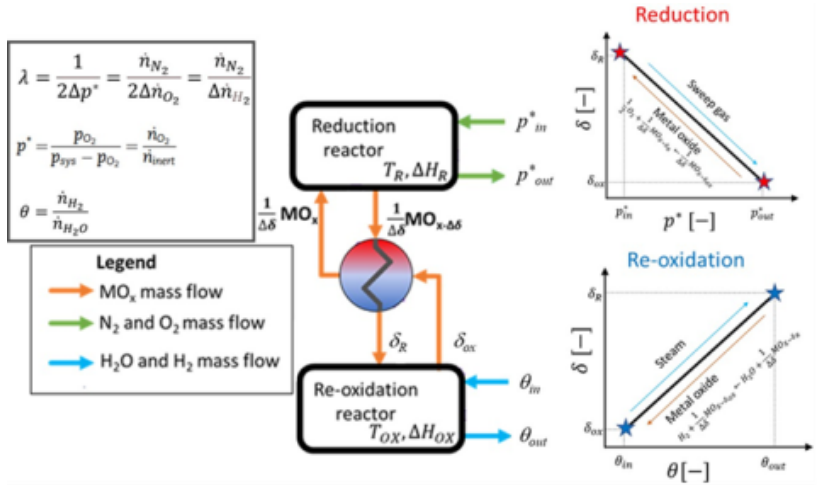


BCM: $BaCe_{0.25}Mn_{0.75}O_3$
HEPO: $La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Ba_{1/6}Sr_{1/6})MnO_3$
LSM20: $La_{0.8}Sr_{0.2}MnO_3$

Hydrogen production and kinetic parameter (from flow reactor)



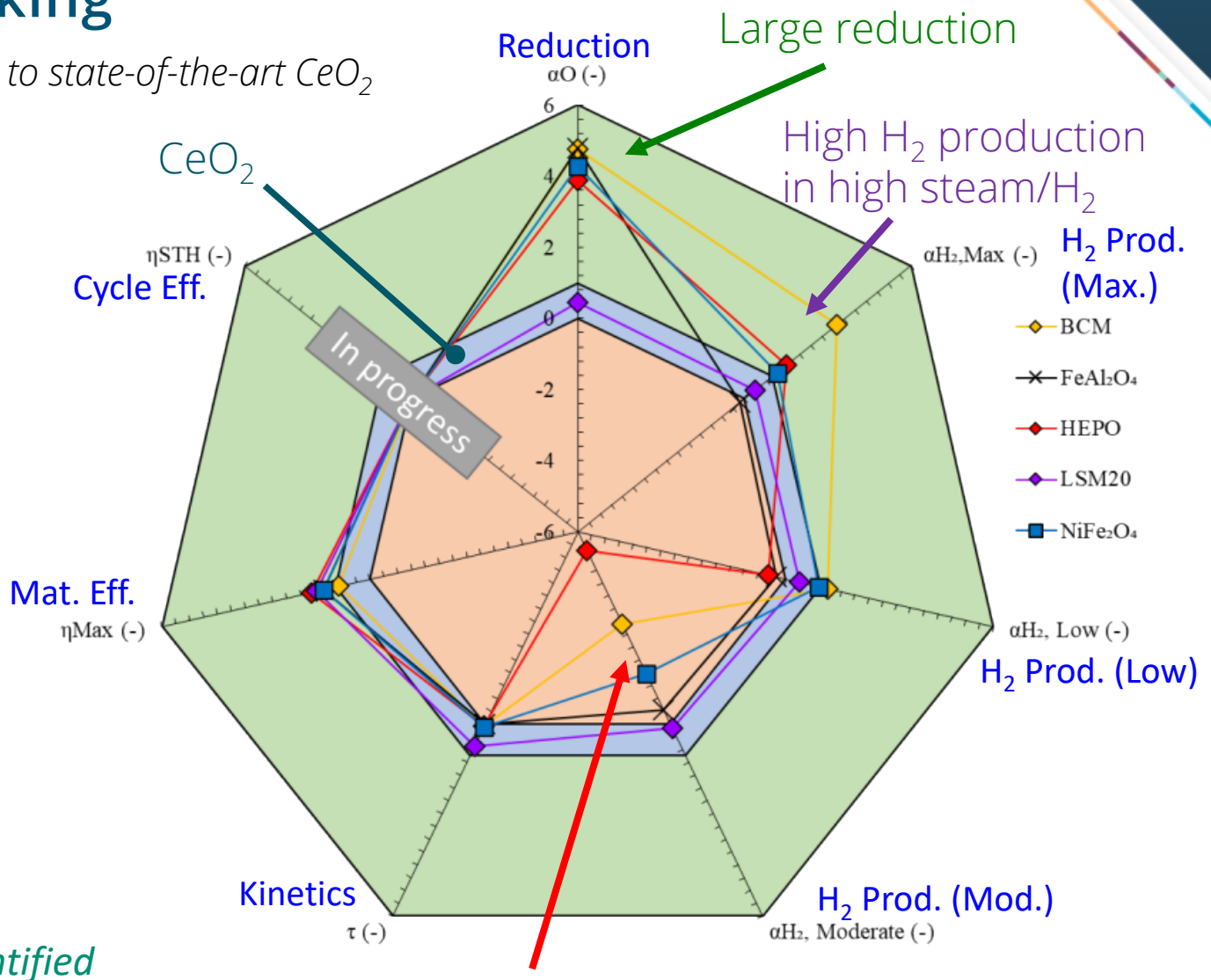
Cycle efficiency estimation



Metrics and Exemplar Benchmarking

Exemplars normalized to state-of-the-art CeO_2

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	$\frac{\Delta G^{o}_{WS}}{\Delta H^{o}_{S}}$ 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	$\alpha_{O} > 5$
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	$\tau > 0.20$

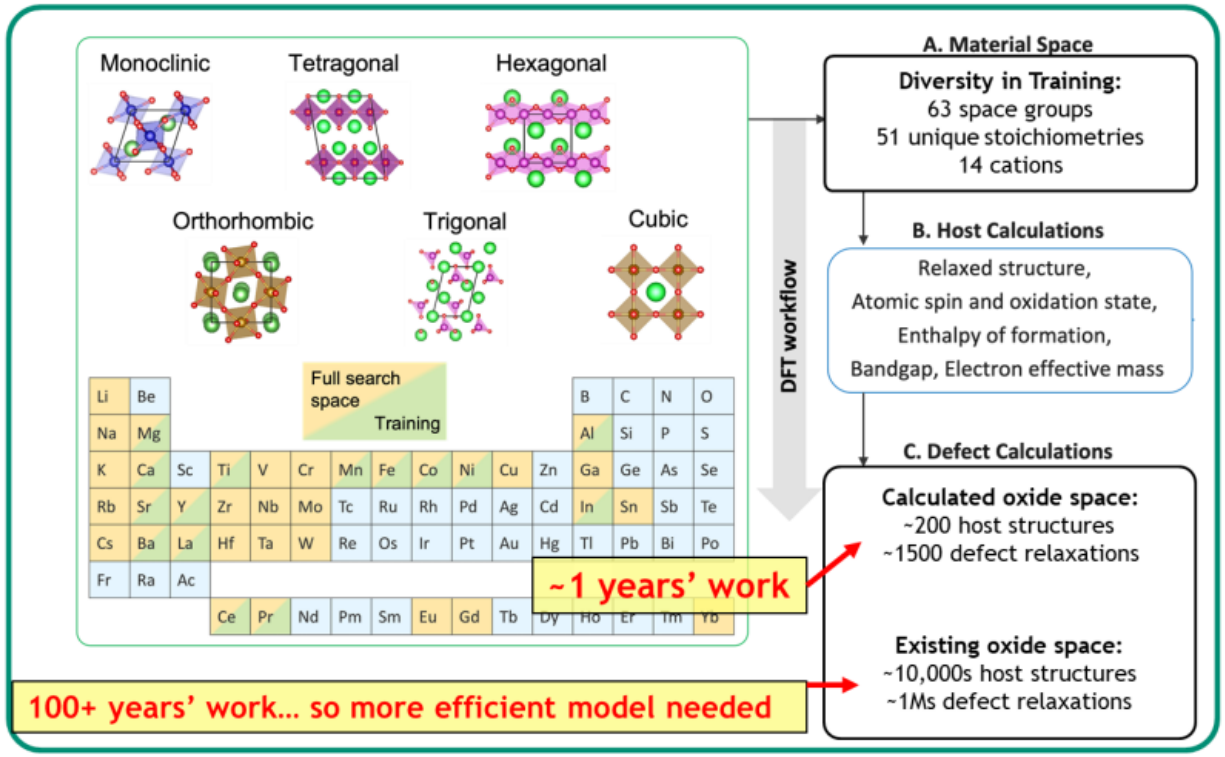


- *Evaluation framework created and metrics identified*
- *Weakness of exemplars in low steam/H_2 ratio → **critical need for new materials***

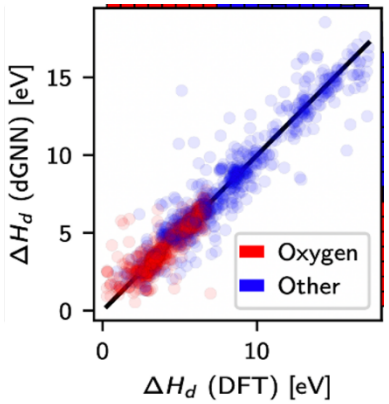
…but H_2 "consumption" in low steam/H_2 → only LSM20 competitive with CeO_2

Discovery of New STCH Materials Aided by Machine Learning

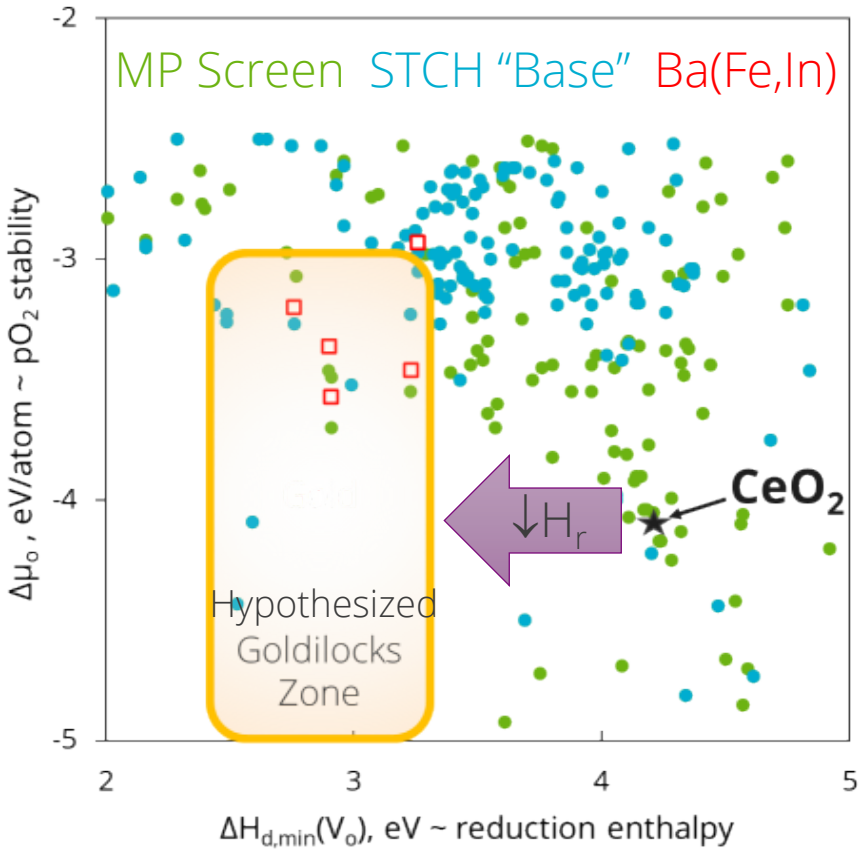
First-principles DFT workflow is robust but costly (using NRELMatDb hosts)



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).



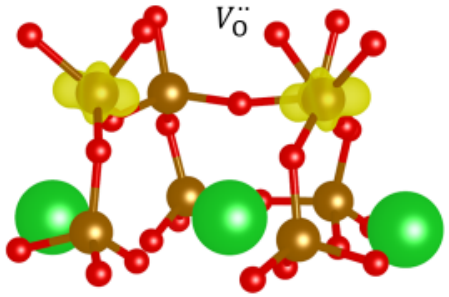
→ *Examples:* Identified $Ba(Fe,In)_2O_4$ and $(Ba,Sr)_6(La,Y)_2Fe_4O_{15}$

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

$BaFe_2O_4$: $V_O^{\cdot\cdot}$ Point Defect Mechanism, and Al Addition to Increase Temperature Stability

$BaFe_2O_4$

Orthorhombic (Bb21m) phase



DFT → oxygen vacancy preferred vs. cation defects

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

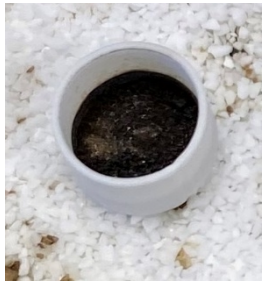
→ Enables higher reduction temperature and resistance to densification

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

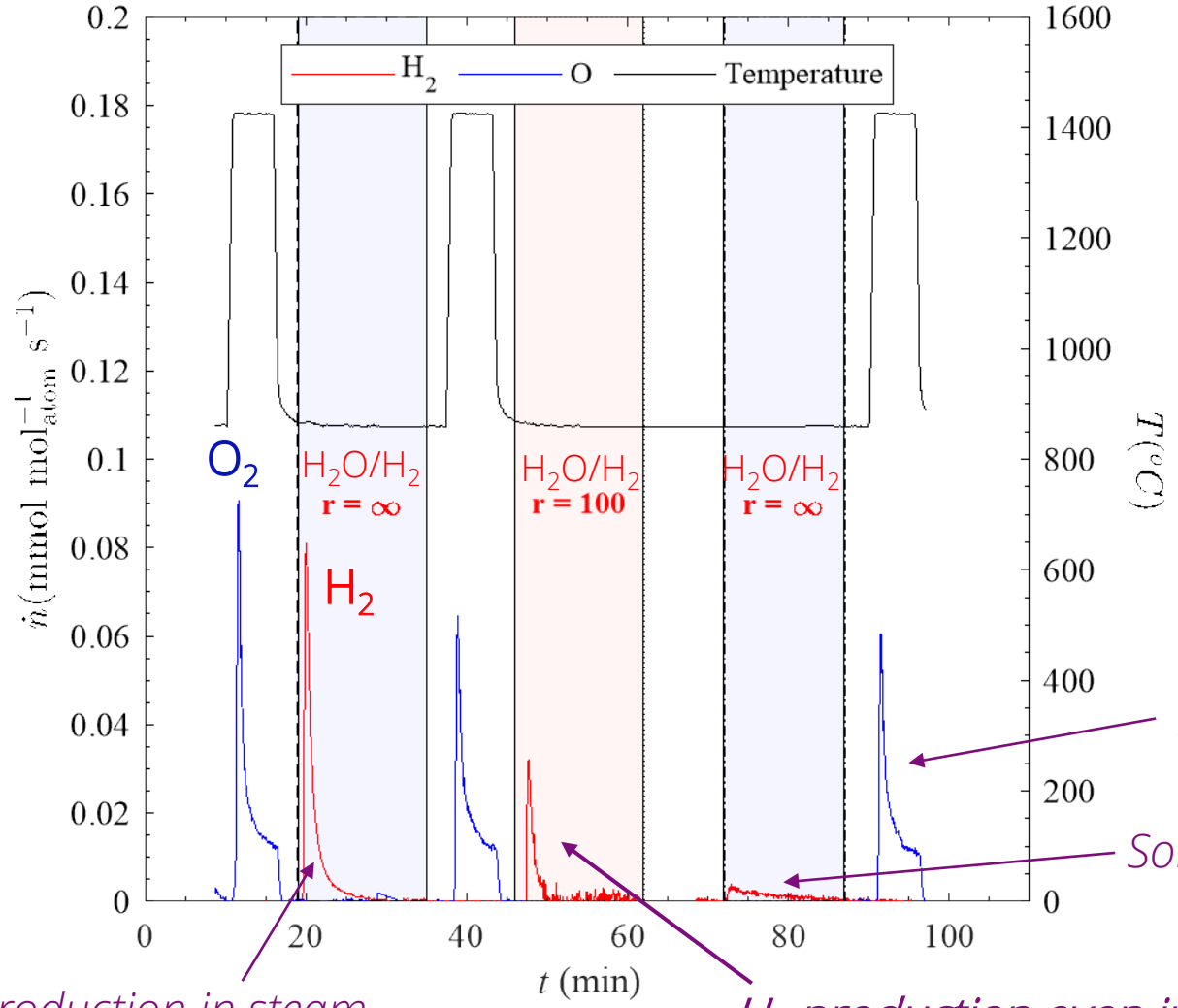
$BaAl_{0.4}Fe_{1.6}O_4$ stable at 1450 °C in air!

$BaFe_2O_4$ $T_{melt,air}$~1420 °C



$BaAl_{0.4}Fe_{1.6}O_4$: Water Splitter 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

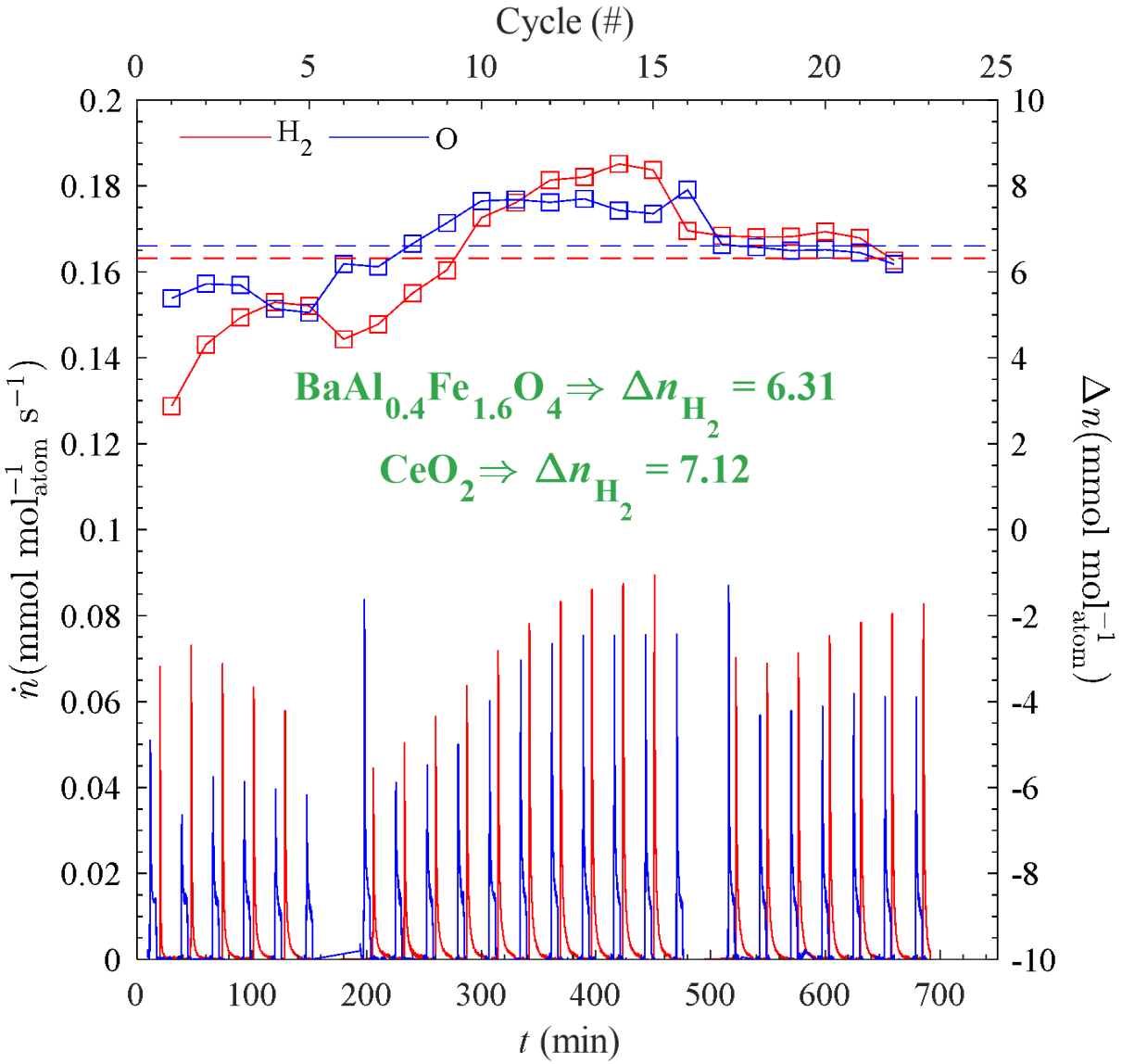
Reduction largely reproducible after cycle

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

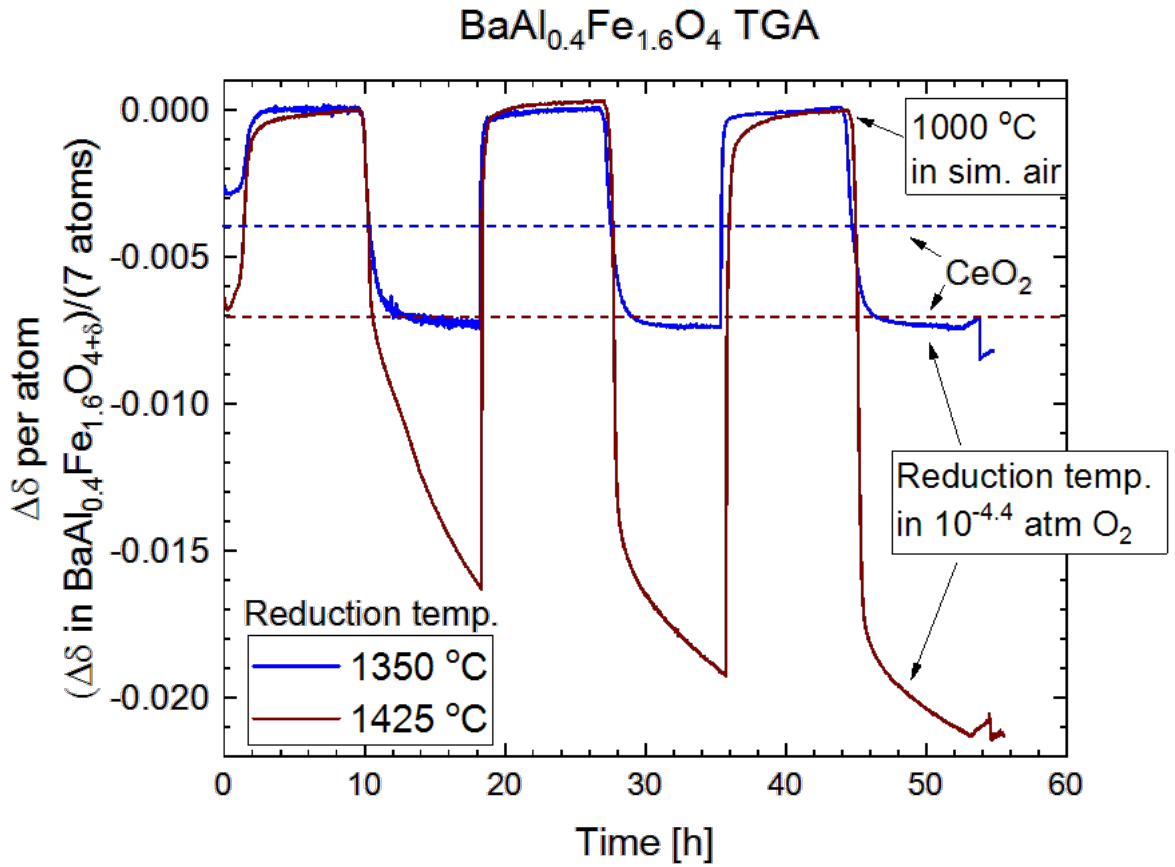
After 20 redox cycles

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%

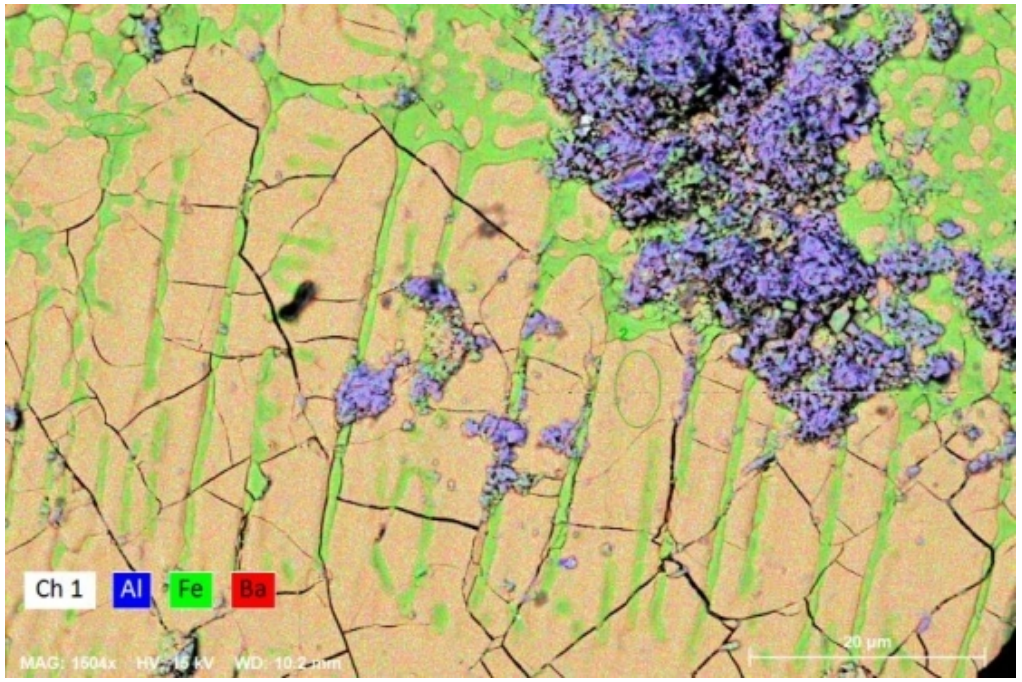
} Decomposition products

Long-term reduction at 1425 °C
→ continuous oxygen release



Detailed Compositional Analysis – 3-phases

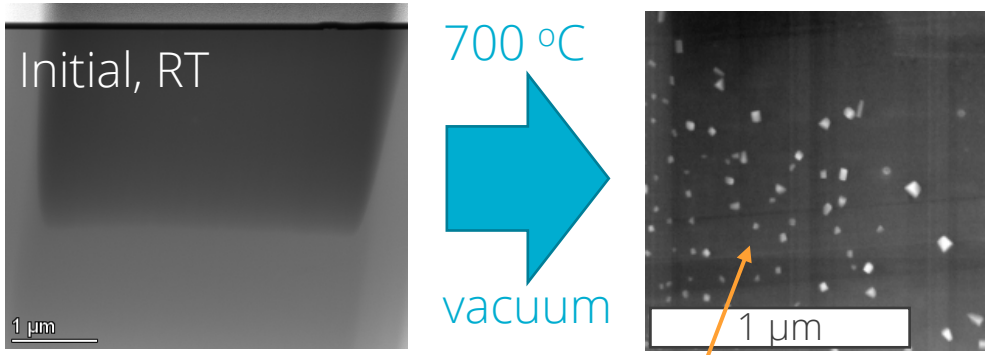
EDS map of post-20 cycled sample



- Purple phase consistent with ~$BaAlFeO_4$ (the expected $P6_3$ structure)
- Tan phase consistent with ~$BaFeO_3$, with possible melting
- Green phase consistent with ~$BaFe_2O_4$, with possible melting

In situ reduction in TEM → evolution of decomposition

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



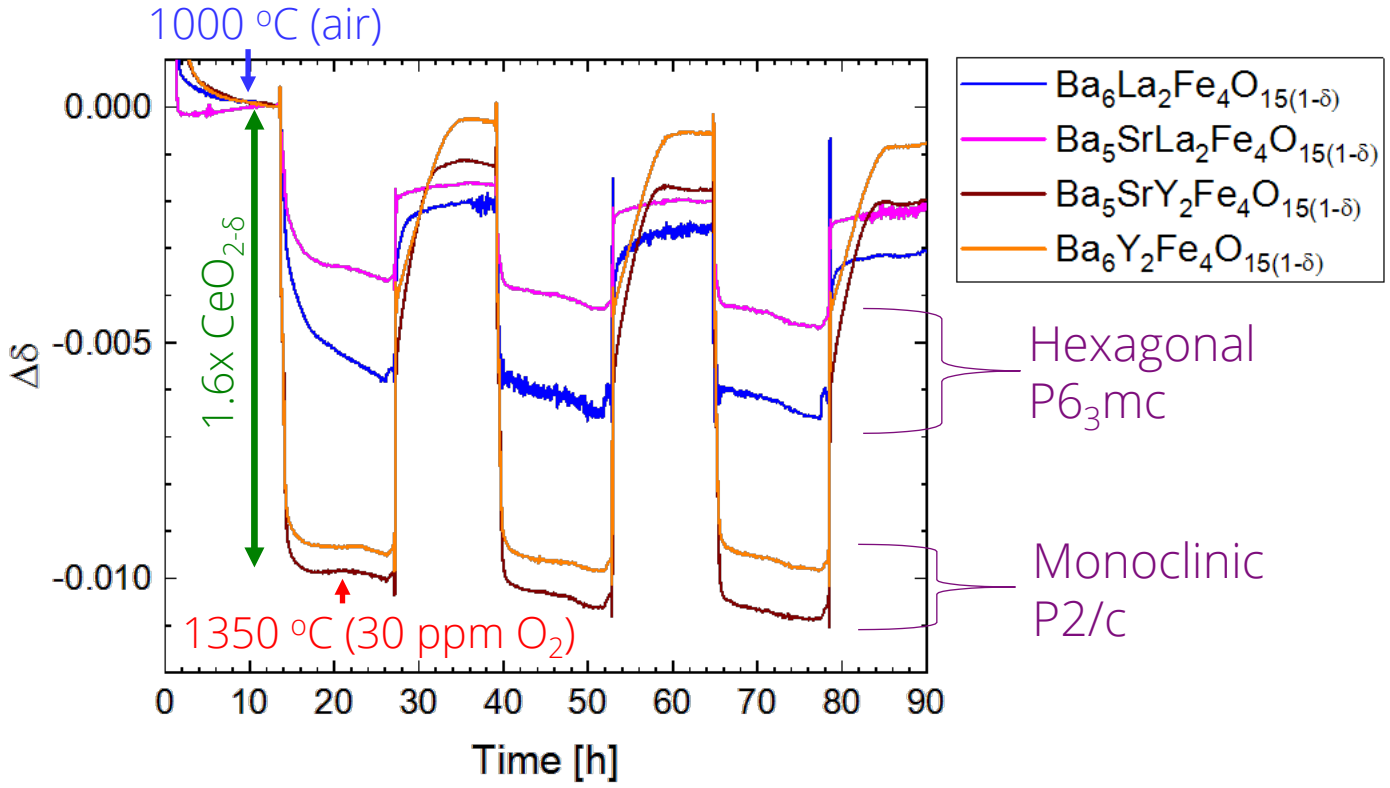
Fe-rich particles formed

Future Work:

→ *investigating role of each phase in water splitting and durability*

→ *HTXRD in simulated water splitting conditions*

$(Ba,Sr)_6La_2Fe_4O_{15}$ and $(Ba,Sr)_6Y_2Fe_4O_{15}$ ML Predicted Water Splitters



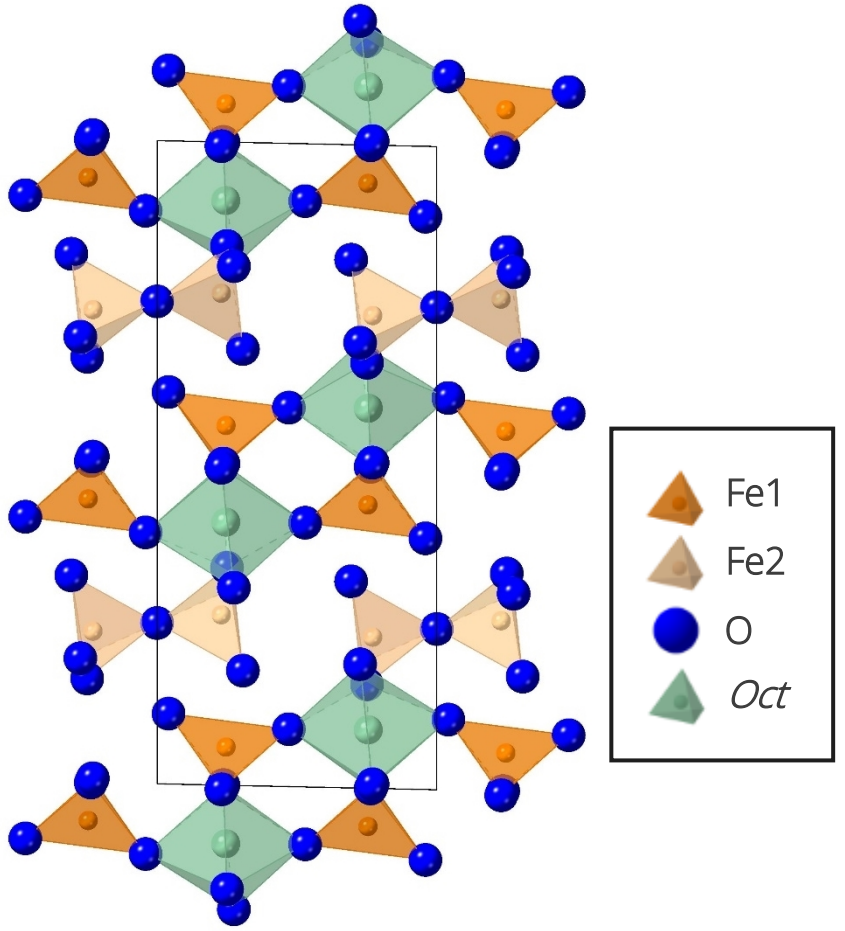
STCH screening protocol[1] → $Ba_6Y_2Fe_4O_{15}$ is best

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

Monoclinic → Δδ > CeO_2

Generalized monoclinic structure (excluding Ba,Sr)

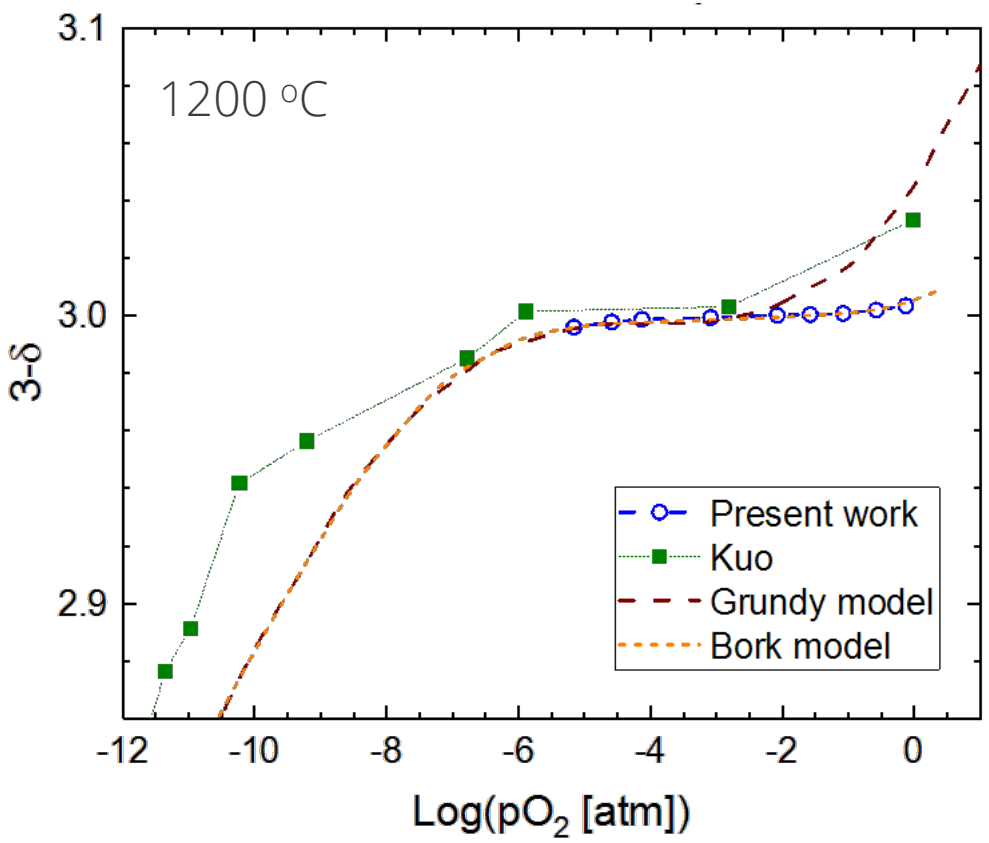
Fe apex sharing dimers (not in hexagonal structure)



Future Work → Flow reactor measurements

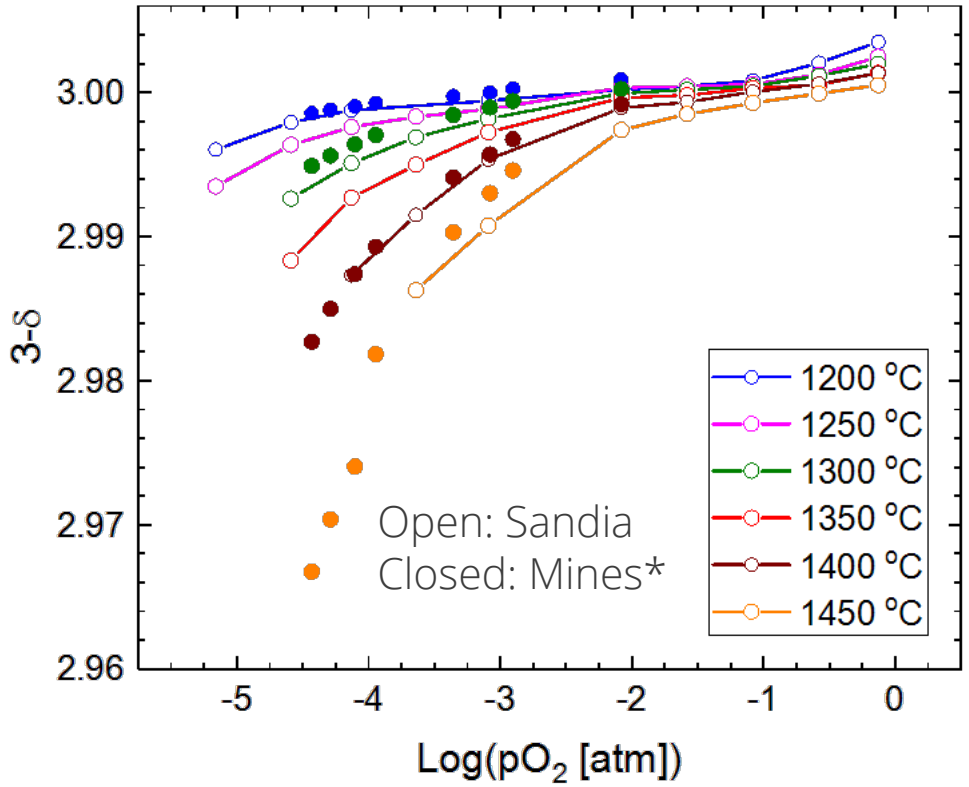
Re-Visiting $La_{0.8}Sr_{0.2}MnO_3$: Oxygen Stoichiometry at High Temp.

Limited δ data above 1200 °C → evaluate at higher temperatures (e.g., STCH conditions)



Less super-stoichiometry than previously estimated, in agreement with Bork model

Increase in δ with temperature, as expected

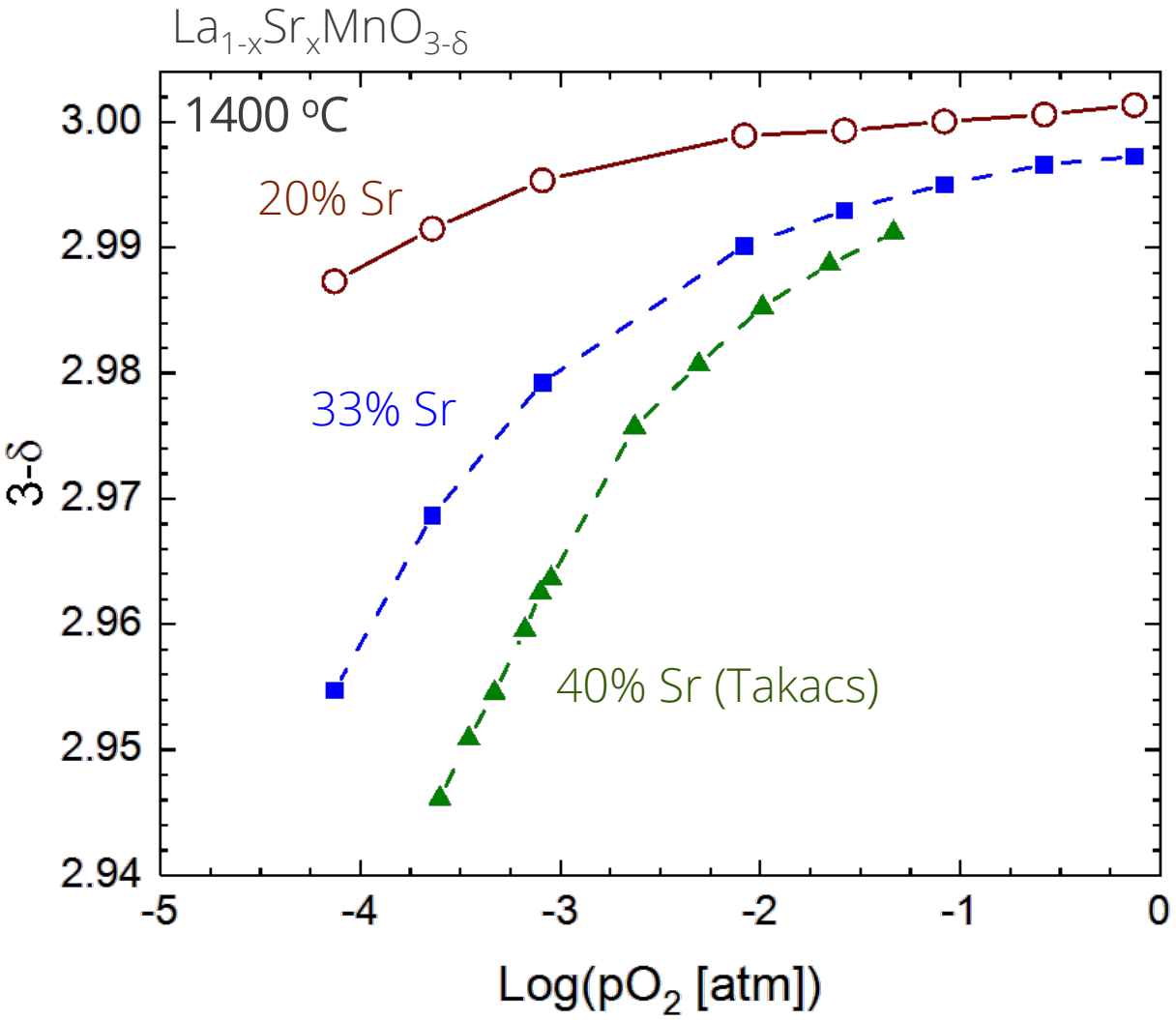


**Mines: In collaboration with M. Sanders at CSM*

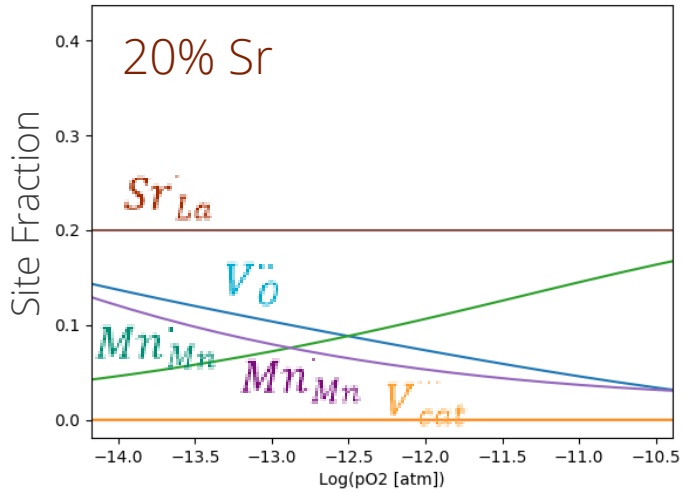
Kuo et al., J. Sol. State Chem., 83 (1989) 52
Bork et al., Adv. Energy Mater. 7 (2017) 1601086
Grundy et al., CALPHAD 28 (2004) 191

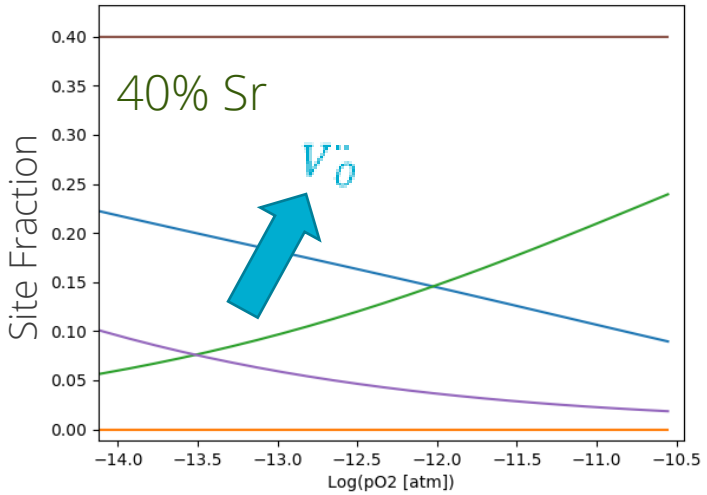
Future Work → Defect equilibria modeling

Impact of Acceptor Dopant Content on Reducibility



Takacs, et al., Acta Mater., 103 (2016) 700





Increasing [Sr] → more oxygen vacancies due to charge compensation

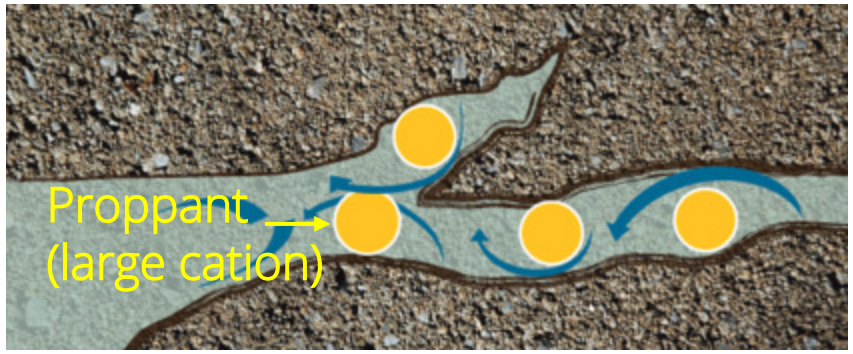
*33% Sr in collaboration with X. Liu and J. Luo (WVU and UCSD)

Enhanced Reducibility of High Entropy Perovskite Oxide (HEPO)

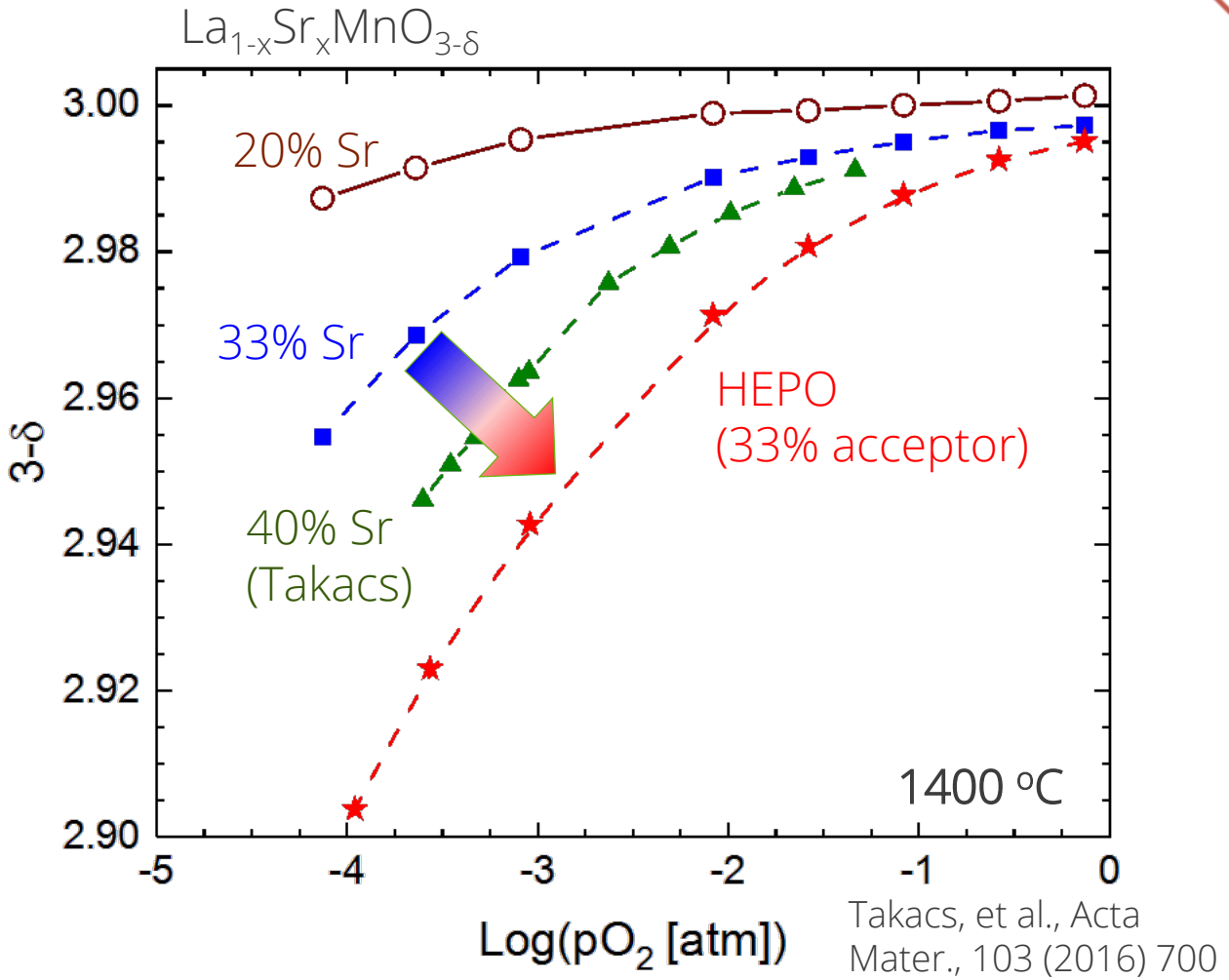
$(La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Ba_{1/6}Sr_{1/6})MnO_{3-\delta}$ (HEPO)*

- HEPO and LSM33 have similar
  - Average A-site ionic radius
  - Lattice parameter
  - Total acceptor dopant content
- Even more reducible than LSM40

Explanation?: Large cations "fracked" LSM (small cation – oxygen bonds weakened)



Shale Oil and Gas Handbook (2015)

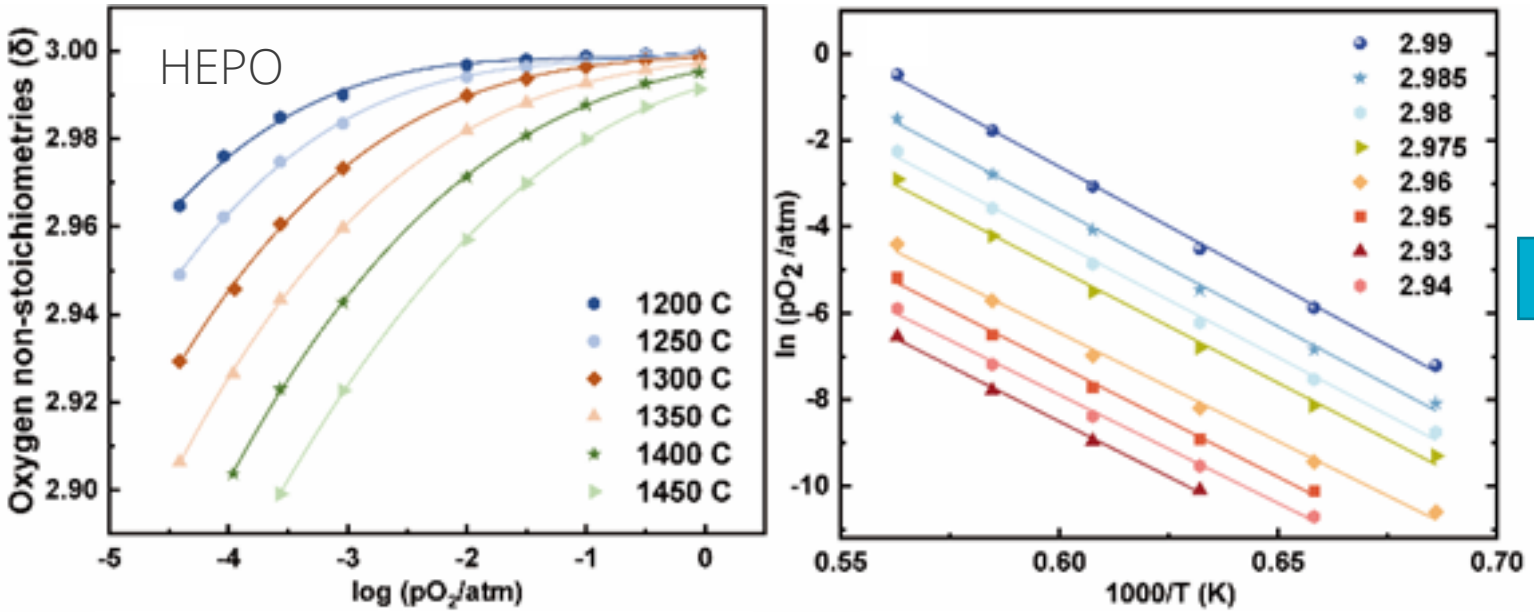


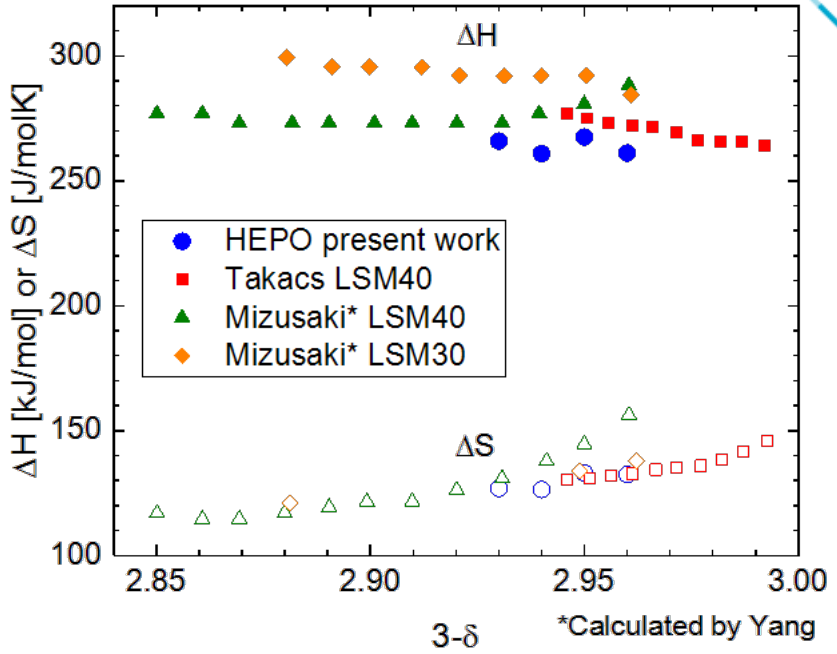
Takacs, et al., Acta Mater., 103 (2016) 700

S. Bishop et al., ECS Trans. (2023)

*In collaboration with X. Liu (WVU) and J. Luo (UCSD)

H_r Decrease for HEPO





Van't Hoff analysis

$$\frac{1}{\alpha}\mathrm{ABO}_{3-\delta} \leftrightarrow \frac{1}{\alpha}\mathrm{ABO}_{3-\delta-\alpha} + \frac{1}{2}\mathrm{O}_2(\mathrm{g})$$

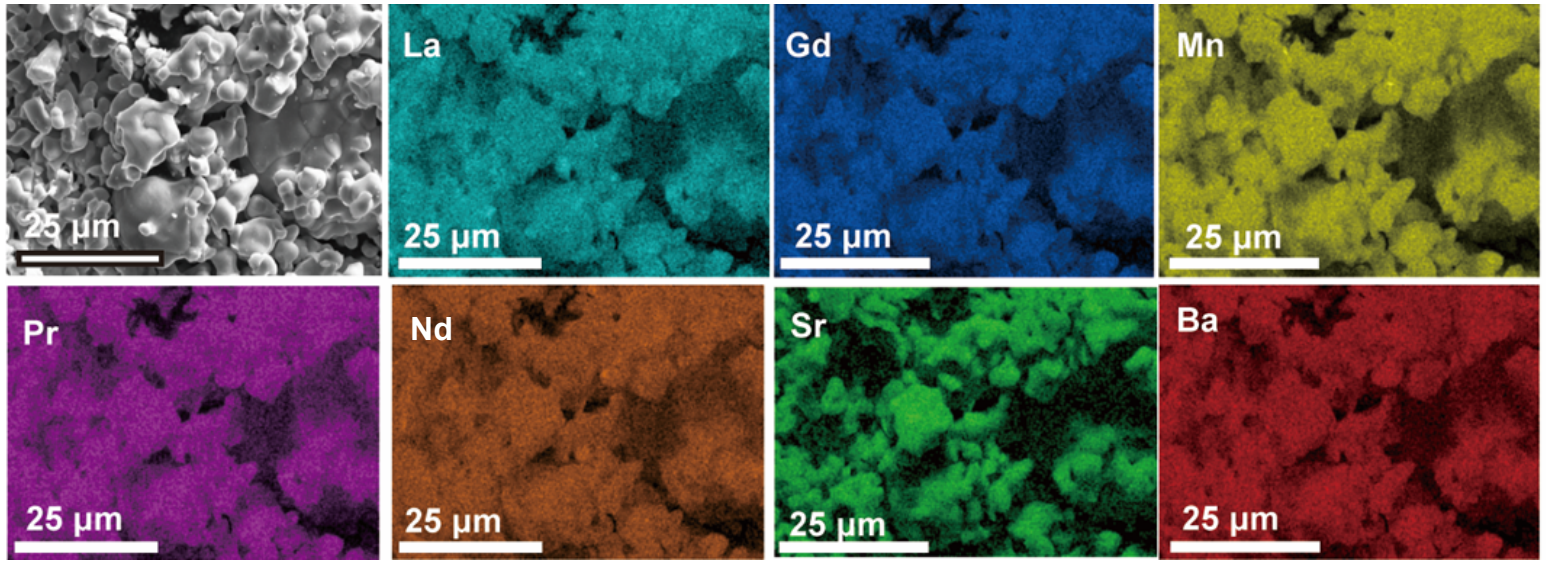
$$K_{\mathrm{redox}} = \left(pO_2^*\right)^{1/2} = \exp\left(-\frac{\Delta H^0_{\mathrm{redox}} - T\Delta S^0_{\mathrm{redox}}}{RT}\right)$$

Takacs, et al., Acta Mater., 103 (2016) 700
Mizusaki, et al., Solid State Ionics, 129 (2000) 163
Yang, J. Mater. Chem. A, 2 (2014) 13612

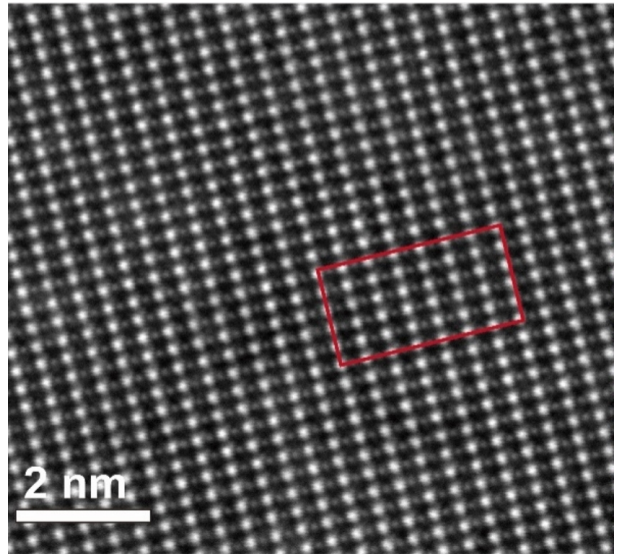
- *Lower H_r for HEPO compared to LSM*
- Entropy similar

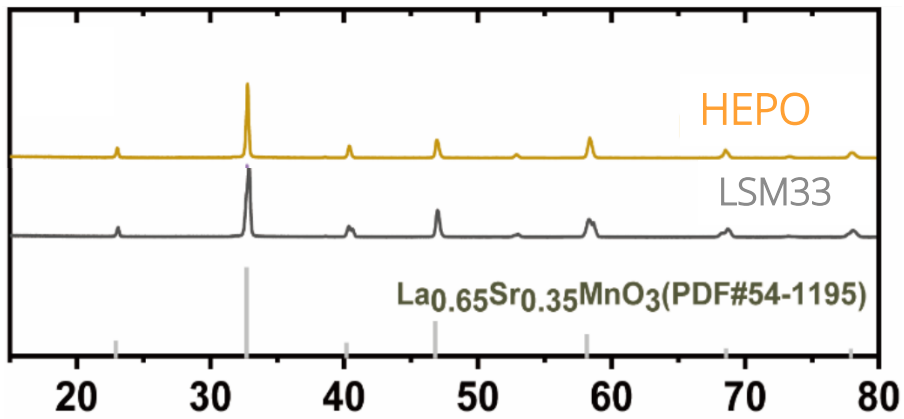
Homogeneous Composition and Disordered Atomic Structure

SEM/EDS: No significant evidence of compositional heterogeneity



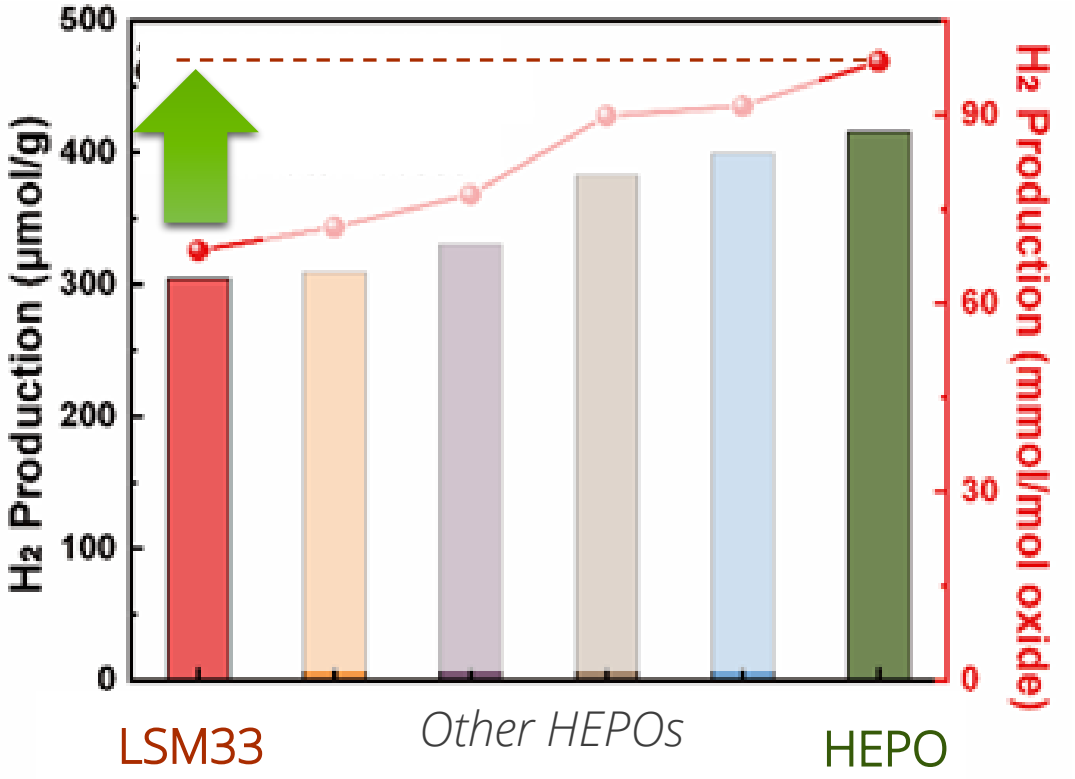
HAADF-STEM: No significant evidence of A-site cation ordering





- Expected perovskite structure of HEPO and LSM33
- HEPO ~0.2% smaller cell volume

Dramatic Increase in STCH H_2 Production



1350 °C N_2 reduction; 1100 °C 40% steam oxidation

46% increase in H_2 production with HEPO compared to LSM33!

Cijie Liu et al., J. Mater. Chem. A, 2024,12, 3910-3922

Summary

- Presented exemplar STCH materials and key STCH metrics
  - Identified significant gap in H_2 production in low steam/H_2 ratio materials
- Demonstrated successful water splitting with ML predicted compound
  - 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
- Examined high temperature (>1200 ^oC) oxygen non-stoichiometry in LSM20
  - Experimental differences from thermodynamic predictions in high pO_2
- Discussed new $(La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Ba_{1/6}Sr_{1/6})MnO_{3-\delta}$ (HEPO) STCH material with much lower reduction enthalpy than LSM of same acceptor content

Acknowledgements

- U.S. Department of Energy (DOE)/ Hydrogen and Fuel Cell Technologies Office (HFTO) HydroGEN Advanced Water Splitting Materials Consortium (h2awsm.org)
- DOE, Office of Energy Efficiency and Renewable Energy (EERE), under the Agreement Number DE-EE0008839

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