



Energy Materials Network
U.S. Department of Energy



HydroGEN
Advanced Water Splitting Materials

New High-Entropy Perovskite Oxides with Increased Reducibility and Stability for Thermochemical Hydrogen Generation

P194

Author Name: Jian Luo

Date: 5/28/2020



Project Partners

PI: Jian Luo, University of California San Diego (UCSD)
 Co-PI: Xingbo Liu, West Virginia University (WVU)
 Co-PI: Yue Qi, Michigan State Univ. (MSU) / Brown Univ.
 HydroGEN Nodes Collaboration:
 SNL: Eric N. Coker (HT-XRD); Josh Sugar (TEM)
 NREL: Stephan Lany (First Principles)

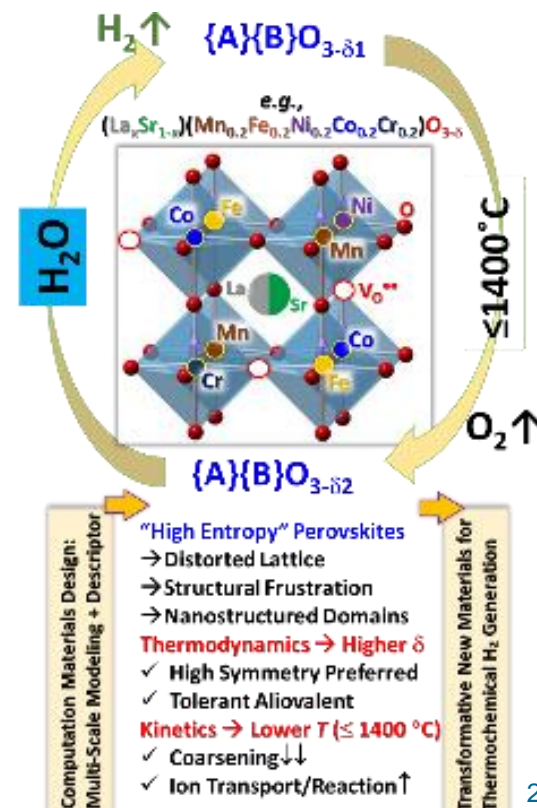
Award #	EE0008839
Start/End Date	10/01/2019 – 1/31/2023
Total Project Value*	\$1,000,000 (+ \$250 cost share)
Cost Share %	20%

Project Vision

We aim to design, synthesize and test a transformative class of **High-Entropy Perovskite Oxides (HEPOs)** as redox oxides to enable thermochemical hydrogen generation with improved stability, kinetics and efficiency.

Project Impact

To open a new field of water splitting materials via establishing a new class of high-entropy redox oxides with vast, unexplored compositional space (along with new enabling design strategies and methods).





Project Motivation

Successful synthesis of HEPOs as a new class of redox oxides with unprecedented vast compositional space and tunability.

Teaming:

MSU/Brown: Theoretical calculations to screen and select promising compositions of HEPOs
UCSD: Synthesis and characterization
WVU: Testing and STCH performance

Barriers

- Extremely vast compositional space
- Highly-complex compositions & structures
- Compositional controls in the synthesis of many-component oxides
- Flowing steam for in-situ XRD experiments

Key Impact

Metric	State of the Art	Expected Advance
k (10^{-4} cm/s)	0.516 (LSCF)	≥ 7.5
$\Delta\delta$ (dry TGA)	0.03-0.05 (CeO_2) 0.13 ($\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$)	≥ 0.15
Cycles Demonstrated	Typically ~10-20 50 @ 150 $\mu\text{mol/g}$ for $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$	≥ 50 @ 400 $\mu\text{mol/g}$ ($<20\%$ degradation)

Partnerships

SNL: Tony McDaniel

Eric N. Coker (high- T *in-situ* XRD)

Josh Sugar (advanced microscopy)

NREL:

Stephan Lany (first-principles calculations)



High-Entropy Perovskites Oxides (HEPOs):

A New and Potentially-Transformative Class of Water Splitting Materials!

Composition:

- ✓ Vast Compositional Space
- ✓ Extreme Tunability

Thermodynamics:

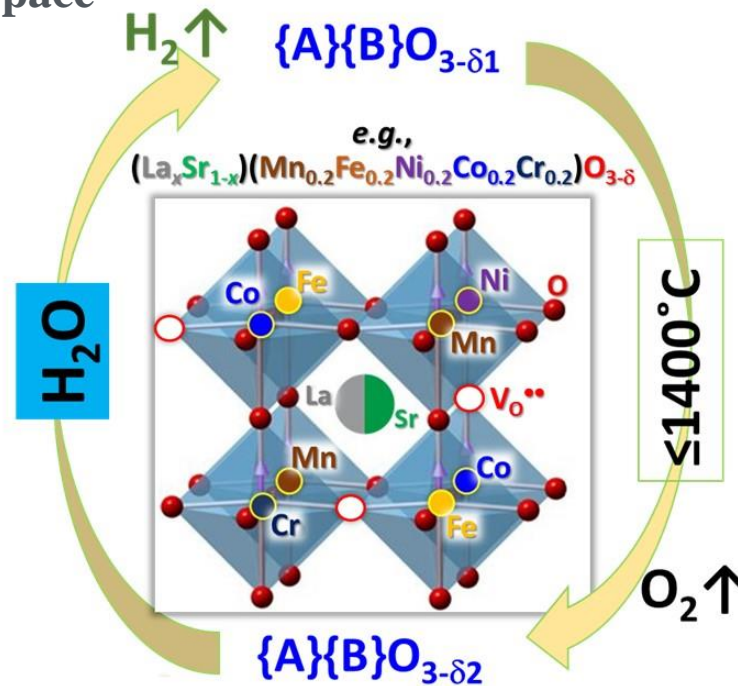
- ✓ Stability ↑
- ✓ Tolerant Aliovalent
- ✓ Reducibility ↑

Structure:

- ✓ Distorted Lattice
- ✓ Structural Frustration
- ✓ Nanodomains?

Kinetics:

- ✓ Coarsening ↓
- ✓ Ion Transport ↑
- ✓ Surface Reaction ↑





Relevance & Impact

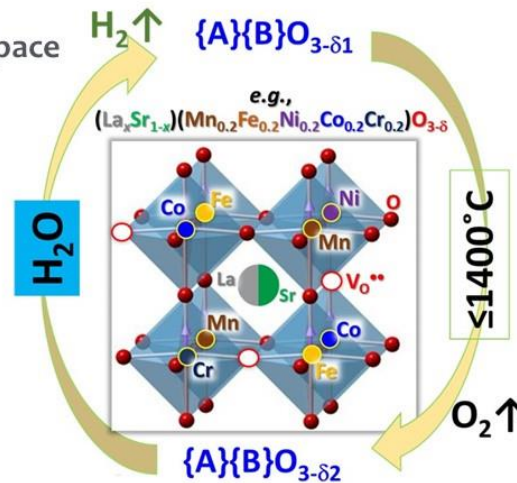
A New and Potentially-Transformative Class of Water Splitting Materials: High-Entropy Perovskites Oxides (HEPOs)

Composition:

- ✓ Vast Compositional Space
- ✓ Extreme Tunability

Thermodynamics:

- ✓ Stability ↑
- ✓ Tolerant Aliovalent
- ✓ Reducibility ↑



Structure:

- ✓ Distorted Lattice
- ✓ Structural Frustration
- ✓ Nanodomains?

Kinetics:

- ✓ Coarsening ↓
- ✓ Ion Transport ↑
- ✓ Surface Reaction ↑

Specific Project Goal: Development of HEPOs:

- ✓ H_2 yield of 400 μmol per gram of oxide
- ✓ Operating for 50 cycles with less than 20% degradation
- ✓ The total active reduction + oxidation time per cycle to be < 1 h

General/Broader Impact: To open a new field of water splitting materials via establishing a new class of high-entropy redox oxides

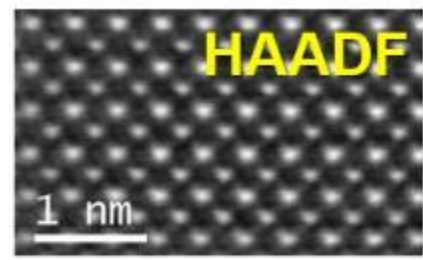
- ✓ Unprecedentedly Vast Compositional Space and Extreme Tunability
- ✓ Unique Structure, Thermodynamic, and Kinetic Characters
- ✓ Enabled by New Design Strategies and Methods



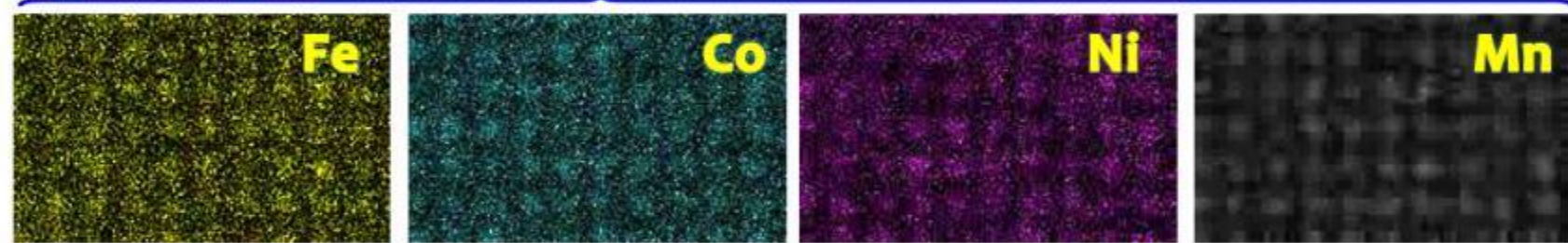
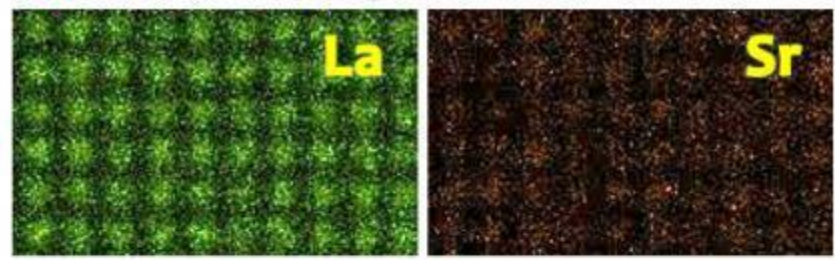
Approach- Innovation

High-Entropy Perovskites Oxides (HEPOs):

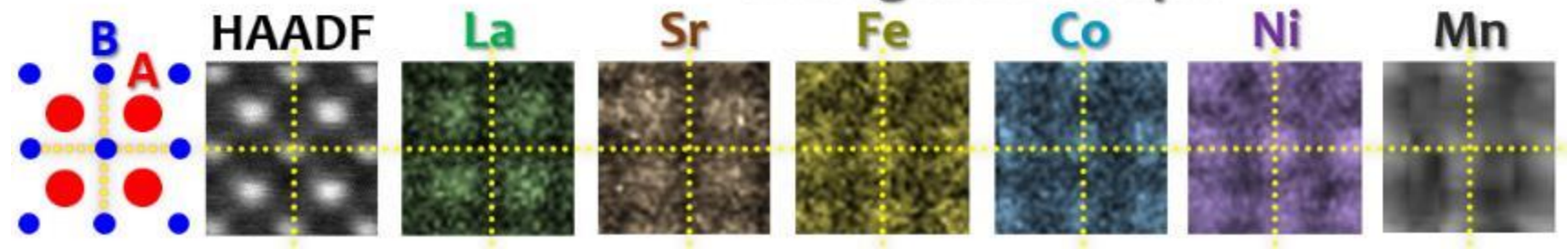
A New and Potentially-Transformative Class of Water Splitting Materials!



Raw EDS Maps:
A-Site →
B-Site



Averaged EDS Maps:





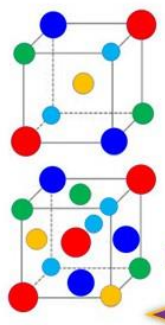
Approach- Innovation

The Rapid Expansion of High-Entropy Materials:

Enabling a New and Potentially-Transformative Class of Water Splitting Materials!

Single-Phase High-Entropy Crystal Structures First Reported by Luo Group at UCSD

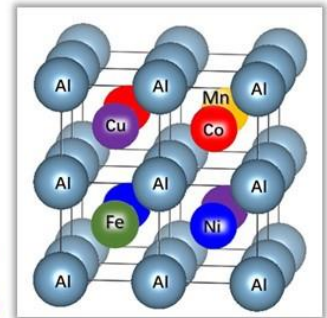
Well-Known Metallic High-Entropy Alloys (HEAs)



Bridging to...

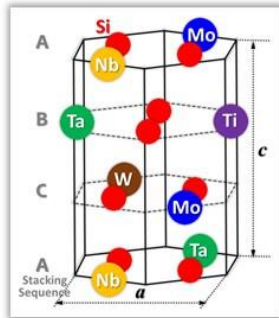
1 Lattice
More Metallic

High-Entropy Aluminide
 $(\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5}\text{Mn}_{1/5}\text{Cu}_{1/5})\text{Al}$



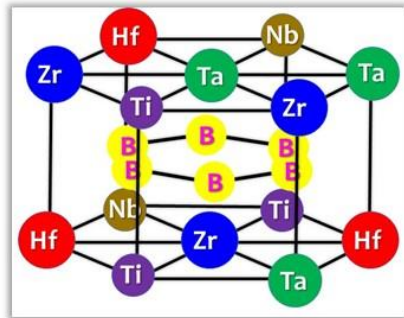
Mixing at 1 of 2 Sublattices

High-Entropy Silicide
 $(\text{Mo}_{1/5}\text{Nb}_{1/5}\text{Ta}_{1/5}\text{Ti}_{1/5}\text{W}_{1/5})\text{Si}_2$

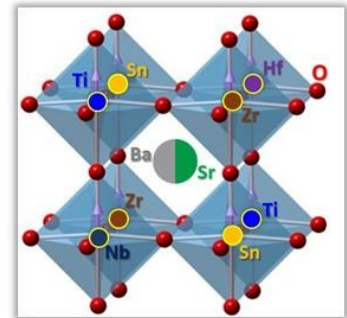


High-Entropy Mixing Only at Cation Sublattice

High-Entropy Boride
 $(\text{Hf}_{1/5}\text{Zr}_{1/5}\text{Ta}_{1/5}\text{Nb}_{1/5}\text{Ti}_{1/5})\text{B}_2$



High-Entropy Perovskite Oxide
 $(\text{Ba}_{1/2}\text{Sr}_{1/2})(\text{Zr}_{1/5}\text{Sn}_{1/5}\text{Ti}_{1/5}\text{Hf}_{1/5}\text{Nb}_{1/5})\text{O}_3$



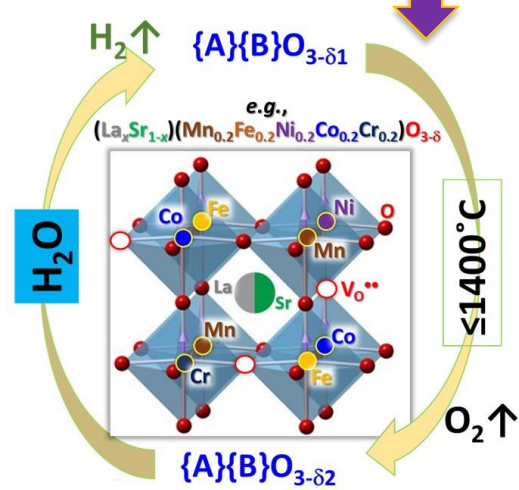
Two Cation Sublattices

Mixed Bonding

More Ionic

Potential Benefits of High-Entropy Perovskites Oxides (HEPOs) as Redox Oxides:

- ✓ Vast composition space: A- and/or B-site mixing
- ✓ Extreme tunability
- ✓ Enhanced reducibility and stability





Approach- Teaming

NREL Node:
Stephan Lany
(First-Principles Calculations)



Brown (MSU): Modelling

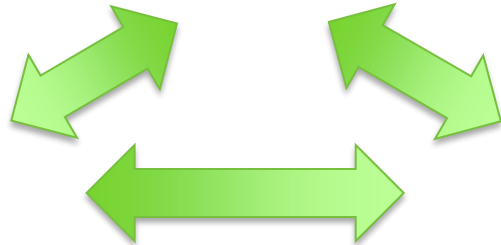
- Predicting stability and synthesizability of HEPO materials
- Screening elements for A site and B site mixing based on thermodynamics and kinetics to maximize the hydrogen production rate



UCSD: Synthesis and Characterization

- Powder synthesis techniques: high energy ball milling + sintering
- Characterization: XRD, SEM, EDS, EBSD, TEM, TGA, and XPS

UC San Diego



SNL Node (Tony McDaniel):
Eric N. Coker (High-T in-situ XRD)
Josh Sugar (Advanced Microscopy)



Sandia National Laboratories



WVU: Electrical Conductivity Relaxation (ECR) Tests and STCH Efficiency

- ECR tests of HEPO pellets
- TGA cycles of HEPO powders under flowing Ar and steam conditions
- STCH cycles to quantitatively measure H₂ yield and cyclability





Approach- Tasks

Task 1: Theoretical calculation for screening materials for HEPOs



Task 2: Synthesis and characterization of HEPOs



Task 3: Measurement of nonstoichiometry and kinetic parameters under thermal reduction/oxidation cycles



BP₃

Task 4: Thermochemical water splitting

BP₁: A-Site Mixing
BP₂: B-Site Mixing
BP₃: Both-Site Mixing





Approach- Predicting HEPO Phase Stability

Utilize first principles calculations to predict ΔH_{mix} and evaluate high entropy stabilization

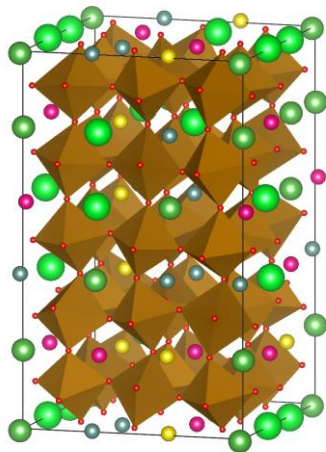
Mixing enthalpy:

$$\Delta H_{\text{mix}} = E_{\text{mix}}^{\text{DFT}} - \sum_i E_i^{\text{DFT}} > 0$$

Mixing entropy:

$$\Delta S_{\text{mix}} = -nR \sum_i \chi_i \ln \chi_i$$

Example: random A site mixing $(5A_{0.2})\text{BO}_3$



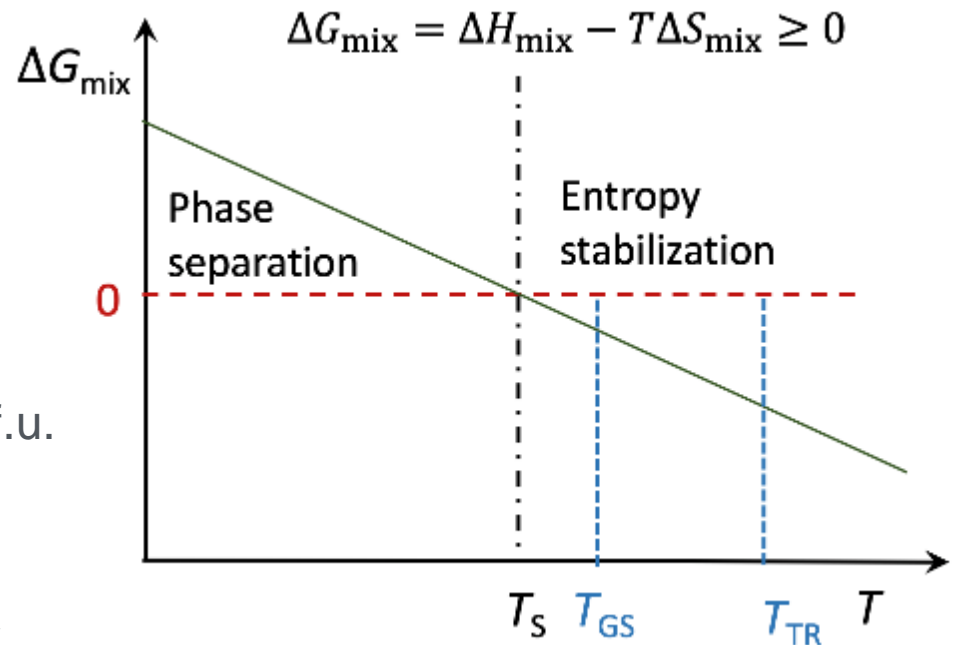
$$\Delta H_{\text{mix}} = 0.28 \text{ eV/f.u.}$$

$$\Delta S_{\text{mix}} = 1.6 k_B$$

➔ $T_S \geq 1900 \text{ }^\circ\text{C}$

High Entropy favors mixed phases and avoids phase transitions

Ideal situation is T_{GS} and T_{TR} are above T_S to avoid phase transformation during STCH process





Background

Oxygen Vacancy Concentration for Water Splitting

The TR and GS operating conditions defines the oxygen chemical potential, μ

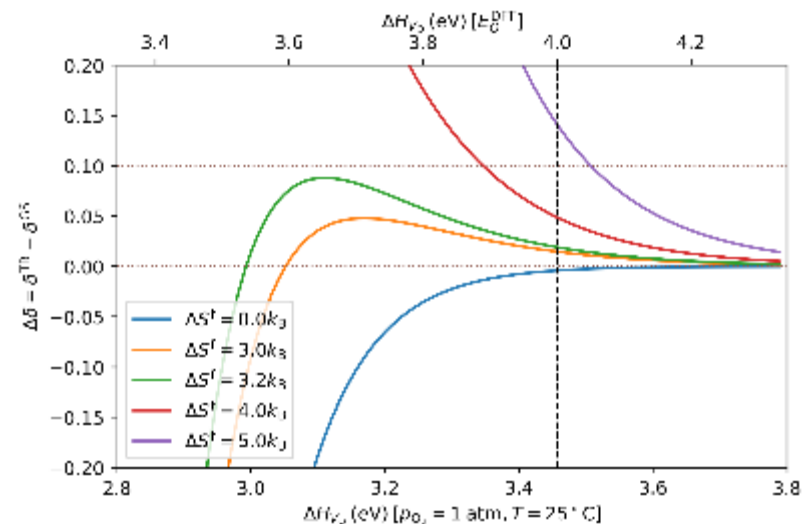
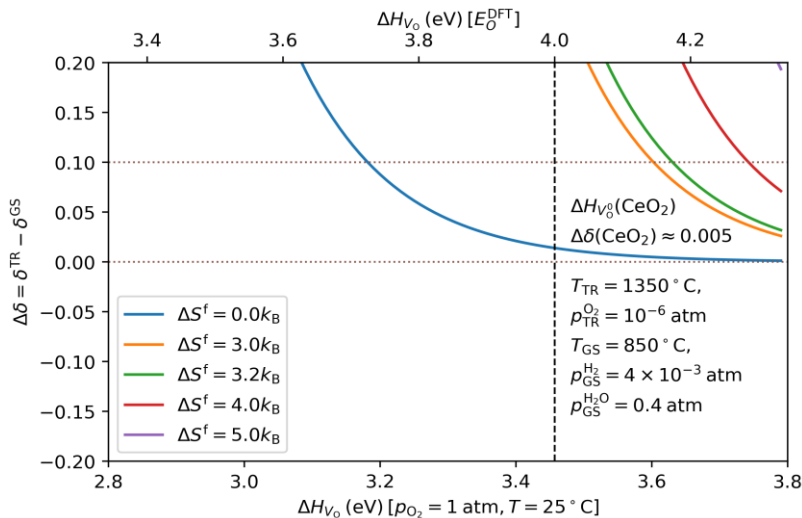
The oxygen vacancy concentration $\delta(\mu)$ is calculated

In order to split water at the GS condition, $\Delta\delta = \delta_{TR} - \delta_{GS} > 0$

Example, CeO₂:

Exp. TR: $T = 1350\text{ }^\circ\text{C}$, $p_{\text{O}_2} = 10^{-6}\text{ atm}$
 Exp. GS: $T = 850\text{ }^\circ\text{C}$, $p_{\text{H}_2} = 10^{-3}\text{ atm}$,
 $p_{\text{H}_2\text{O}} = 0.4\text{ atm}$

Target TR: $T \leq 1400\text{ }^\circ\text{C}$, $p_{\text{O}_2} = 10^{-3}\text{ atm}$
 Target GS: $T \geq 850\text{ }^\circ\text{C}$, $p_{\text{H}_2} = 10^{-1}\text{ atm}$,
 $p_{\text{H}_2\text{O}} = 1\text{ atm}$



Experimental data: *Energy Environ. Sci.* **11**(11): 3256, 2018

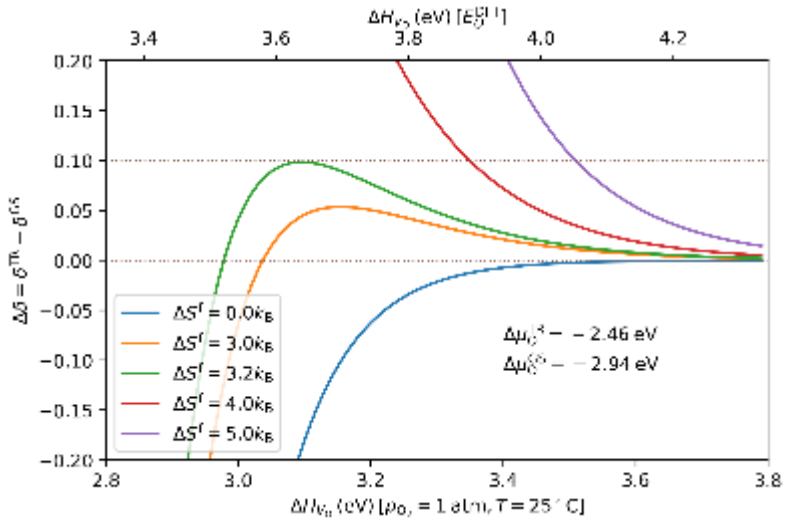


Approach- Design Oxygen Vacancies in HEPOs

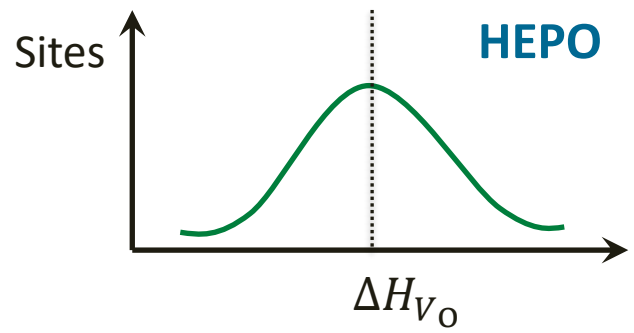
To get an ideal $\Delta\delta$ during TR and GS in HEPO, engineering oxygen vacancy formation enthalpy and entropy is critical.

$$\delta = \exp\left(\frac{\Delta S_{V_O}^f}{k_B}\right) \exp\left(-\frac{\Delta h_{V_O}^f}{k_B T}\right)$$

Target TR: $T \leq 1400$ °C, $p_{O_2} = 10^{-3}$ atm
Target GS: $T \geq 850$ °C, $p_{H_2} = 10^{-1}$ atm, $p_{H_2O} = 1$ atm



- A range of V_O formation enthalpy



- Increase oxygen vacancy formation entropy
 - Vibrational, *e.g.*,
 - Increased soft vibrational modes
 - Larger defect volume
 - Electronic and magnetic, *e.g.*,
 - Fe^{4+}/Fe^{3+} configuration
 - Long-range electron transfer
- Modulate oxygen transport



Innovation - Benefits of Mixing in HEPOs

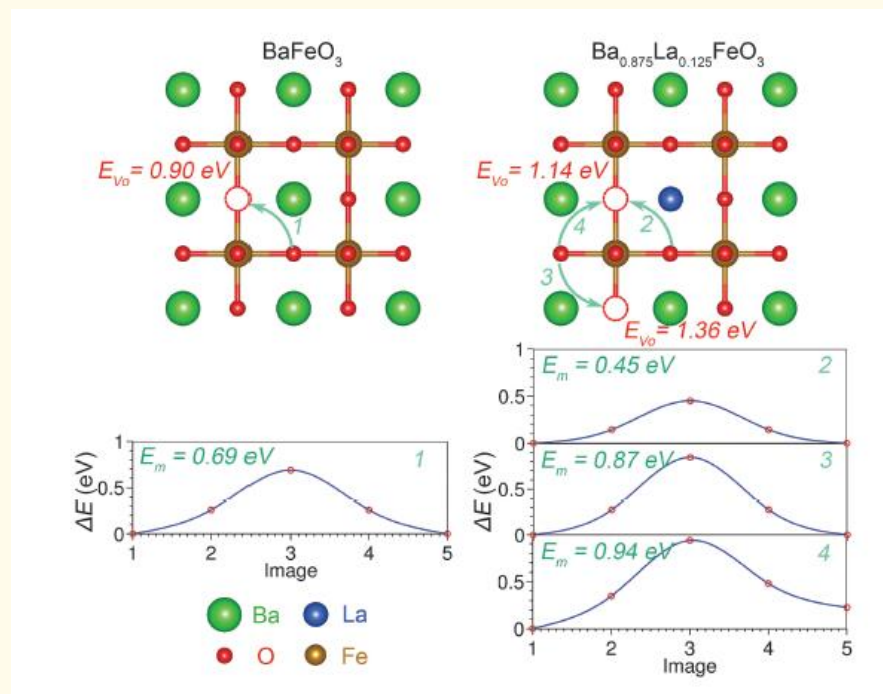
- Increase phase stability through entropy stabilization
- Modulate oxygen reduction enthalpy
- Increase oxygen reduction entropy
 - Vibrational: increased soft vibrational modes, larger defect volume
 - Electronic and magnetic: $\text{Fe}^{3+}/\text{Fe}^{3+}$ configuration, long-range electron transfer
- Modulate oxygen diffusion barrier

Mixing can increase 'defect volume' and increase reduction entropy: *Phys. Rev. B* 28(2): 759-777 (1983)

A detailed thermodynamic and kinetic analysis will be performed to optimize the hydrogen production rate.

MICHIGAN STATE
UNIVERSITY

Diffusion barrier with A-site mixing:



Phys Chem Chem Phys 17(37): 24011(2015)



V_O Formation Enthalpy in A³⁺Fe³⁺O₃ (*Pbnm*)

μ_0 (eV)

-4.76

To get an ideal $\Delta\delta$ during TR and GS in HEPO, engineering oxygen vacancy formation enthalpy and entropy is critical.

$$\delta = \exp\left(\frac{\Delta S_{V_O}^f}{k_B}\right) \exp\left(-\frac{\Delta h_{V_O}^f}{k_B T}\right)$$

We firstly investigated V_O formation enthalpy in each perovskite phase which provides insights about V_O formation tunability:

- Magnetic configurations control the formation enthalpy (1st order approximation) in A³⁺Fe³⁺O₃
- The formation enthalpy does not change significantly with same magnetic configuration
- +4/-4 configuration gives the lowest formation enthalpy 4.41 eV

	Wykoff	Magnetic	ΔH_{V_O} (eV)
NdFeO ₃	0	+4/0	5.71
		+4/-2	5.35
1	0/+2		6.47
		+4/+2	5.19
YFeO ₃	0	+4/-4	4.51
		+4/0	5.77
	1	+2/-2	6.04
		+4/-4	4.51

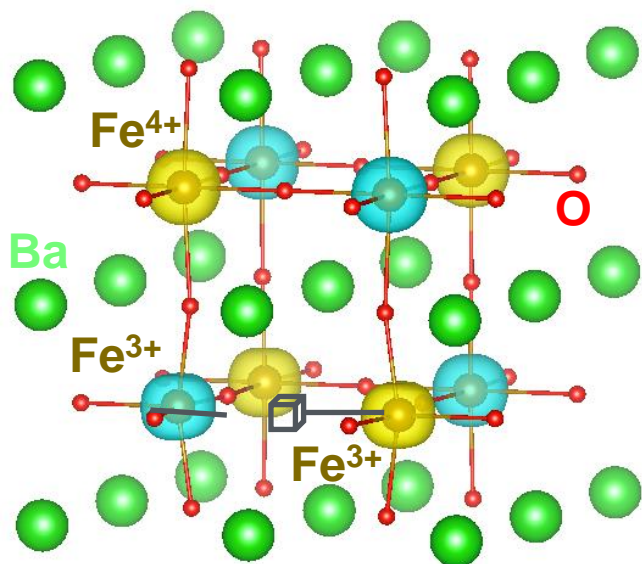
	Wykoff	Magnetic	ΔH_{V_O} (eV)
PrFeO ₃	0	4/0	5.63
		-4/+2	5.32
	1	+4/-2	5.34
SmFeO ₃	0	-4/-4	4.68
		+4/0	5.73
	1	+4/+4	4.73
		+2/+2	6.18
		-4/0	5.71

	Wykoff	Magnetic	ΔH_{V_O} (eV)
GdFeO ₃	0	+4/-4	4.62
		+2/-2	6.05
1	+4/-4		4.54
		+4/+4	4.56
LaFeO ₃	0	+4/-4	4.41
		+4/+2	5.10
	1	-4/0	5.60



V_o Energetics in A²⁺Fe⁴⁺O₃ (*Pm* $\bar{3}$ *m*)

Two nearby Fe⁴⁺ (*d*⁴)
reduced to Fe³⁺ (*d*⁵)

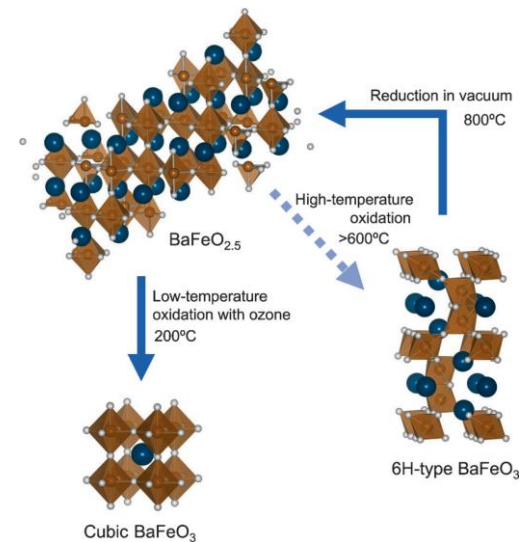
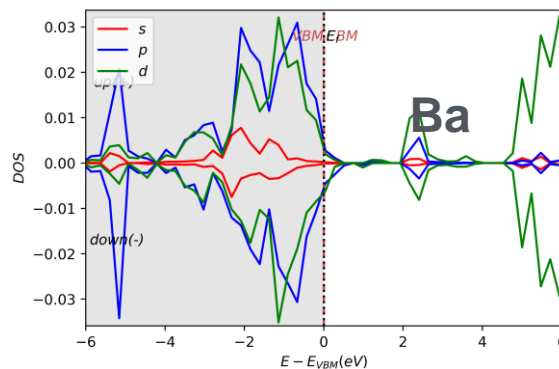


O vacancy in BaFeO₃

	Wykoff	Magnetic	ΔH_{V_0} (eV)
SrFeO ₃	0	??	0.34
BaFeO ₃	0	??	-0.24

μ_0 (eV)
-4.76

?: rather than localized in A³⁺Fe³⁺O₃, the electron has a diffusive feature in its wavefunction. It relates to the metallic nature of A²⁺Fe⁴⁺O₃.

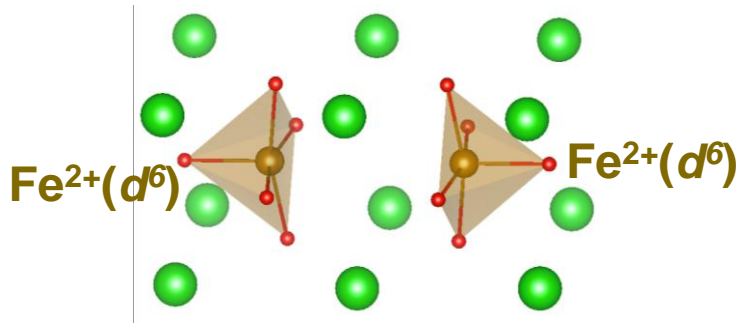


Angew. Chem. 2011, 123, 12755–12758

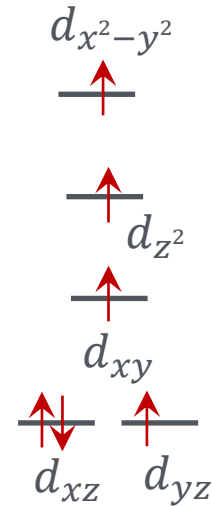


Magnetic Configurations of V_O

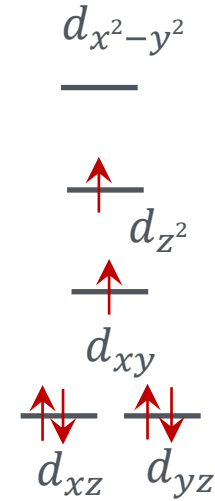
Magnetic configuration:



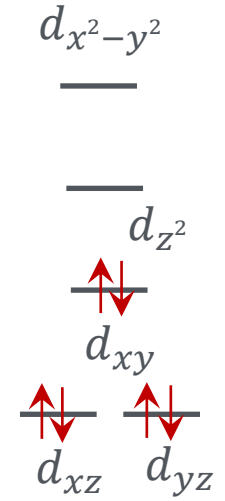
Two nearby $\text{Fe}^{3+}(d^5)$ is reduced to $\text{Fe}^{2+}(d^6)$ when a neutral oxygen vacancy is formed.



High spin
($4\mu_B$)



Low spin
($2\mu_B$)



Low spin
($0\mu_B$)

For each oxygen vacancy, there are 25 configurations if two Fe ion is not equivalent.



Potential Candidates

Goldschmidt tolerance factor

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where r_A is the radius of the A -cation, r_B is the radius of the B -cation and r_O is the radius of the anion (usually oxygen).

A^{3+}

Element	CN max	q	TF
Sc	VIII	3	0.787
Fe	VIII	3	0.755
Y	IX	3	0.860
In	VIII	3	0.805
Sb	V	3	0.762
La	XII	3	0.961
Ce	XII	3	0.953
Pr	IX	3	0.896
Nd	XII	3	0.929
Pm	IX	3	0.884
Sm	XII	3	0.918
Eu	IX	3	0.875
Gd	IX	3	0.871
Tb	IX	3	0.867
Dy	IX	3	0.862
Ho	X	3	0.875
Er	IX	3	0.855

Element	CN max	q	TF
Tm	IX	3	0.851
Yb	IX	3	0.848
Lu	IX	3	0.844
Au	VI	3	0.780
Tl	VIII	3	0.826
Bi	VIII	3	0.893
Ac	VI	3	0.875
Pa	VI	3	0.847
U	VI	3	0.842
Np	VI	3	0.836
Pu	VI	3	0.833
Am	VIII	3	0.865
Cm	VI	3	0.822
Bk	VI	3	0.819
Cf	VI	3	0.815

A^{2+}

Element	CN max	q	TF
Mg	VIII	2	0.819
Ca	XII	2	0.983
Ti	VI	2	0.808
V	VI	2	0.782
Cr	VI	2	0.786
Mn	VIII	2	0.844
Fe	VIII	2	0.830
Co	VIII	2	0.822
Zn	VIII	2	0.822
Ge	VI	2	0.760
Sr	XII	2	1.020
Pd	VI	2	0.808
Ag	VI	2	0.837
Cd	XII	2	0.972
Ba	X	2	1.049
Nd	IX	2	0.987
Sm	VIII	2	0.957

Element	CN max	q	TF
Sm	IX	2	0.976
Eu	X	2	0.987
Dy	VIII	2	0.928
Tm	VII	2	0.892
Yb	VIII	2	0.910
Pt	VI	2	0.786
Hg	VIII	2	0.910
Pb	XII	2	1.038
Ra	VIII	2	1.034
Np	VI	2	0.895
Am	IX	2	0.972
No	VI	2	0.895

Next steps:

- Perform defect calculations of the newly proposed elements
- Study whether some Lanthanide elements are redox active on A site, such as Sm and Nd
- Study the mechanism of A site mixing in solid-solution situation on oxygen vacancy formation

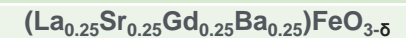
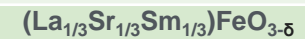


Approach- Synthesis & Fabrication

High-Throughput Solid-State Synthesis & Fabrication

- ▶ Calculate & weight materials of appropriate amounts
- ▶ High energy ball milling (HEBM) for 5 hours
- ▶ Anneal the mixed powder in tube furnace in air
- ▶ Sintering
 - 5C/min ramp up to 1300 °C
 - Isothermal sintering at 1300 ° C for 10 hours
 - Furnace cooling (~10 °C/min) to room temperature

Synthesized Sample chemical formula



**Adaptor for
up to 8 specimens!**



HEBM



Sintering



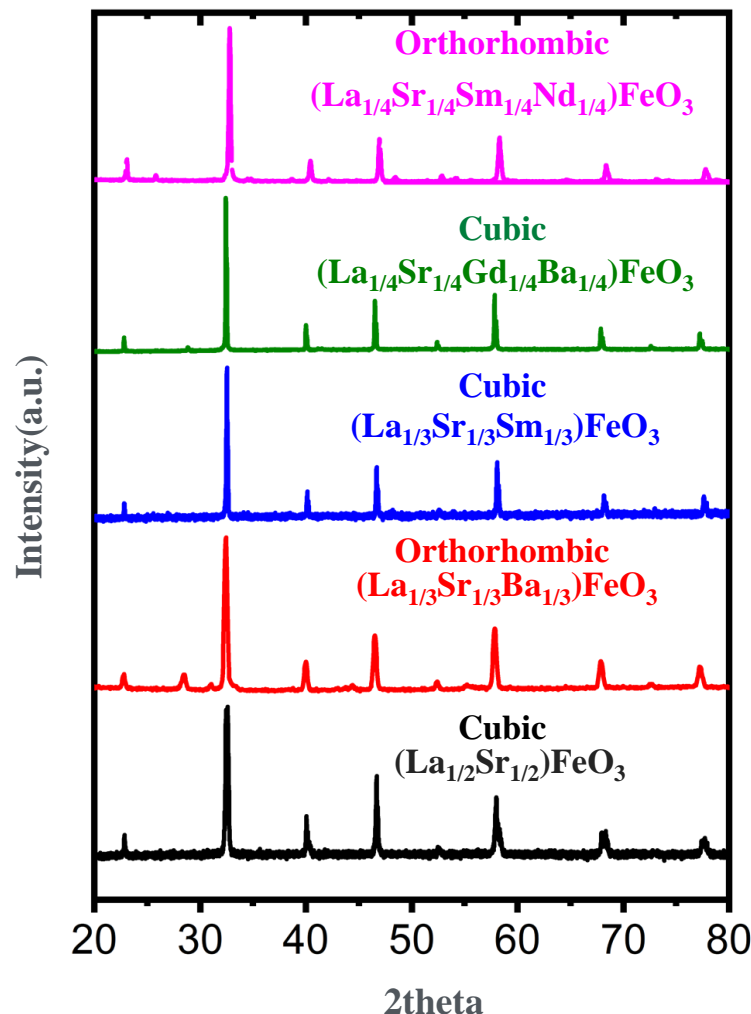


Approach- Phase Characterization

X-ray diffraction (XRD):

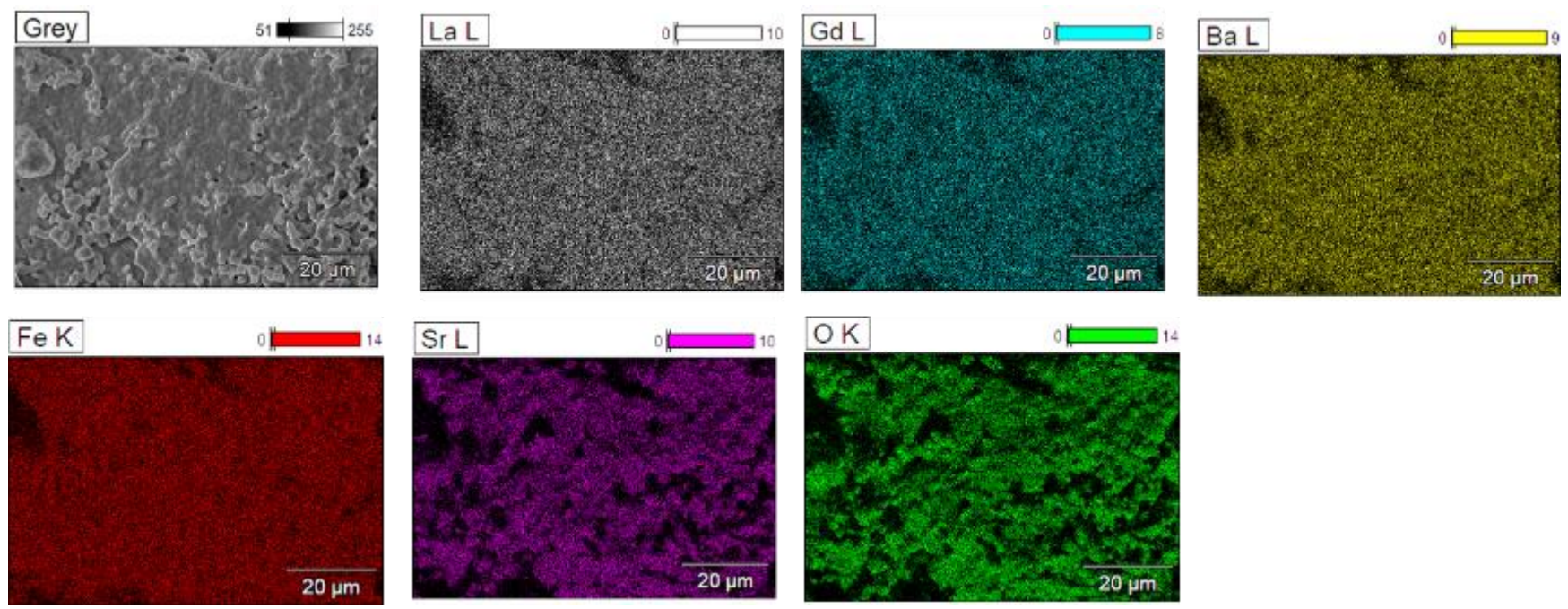
Compositions:

- $(\text{La}_{1/4}\text{Sr}_{1/4}\text{Sm}_{1/4}\text{Nd}_{1/4})\text{FeO}_3$
 - $(\text{La}_{1/4}\text{Sr}_{1/4}\text{Gd}_{1/4}\text{Ba}_{1/4})\text{FeO}_3$
 - $(\text{La}_{1/3}\text{Sr}_{1/3}\text{Sm}_{1/3})\text{FeO}_3$
 - $(\text{La}_{1/3}\text{Sr}_{1/3}\text{Ba}_{1/3})\text{FeO}_3$
 - $(\text{La}_{1/2}\text{Sr}_{1/2})\text{FeO}_3$
- All samples show single high-entropy solid solution phases of the cubic or orthorhombic perovskite structure





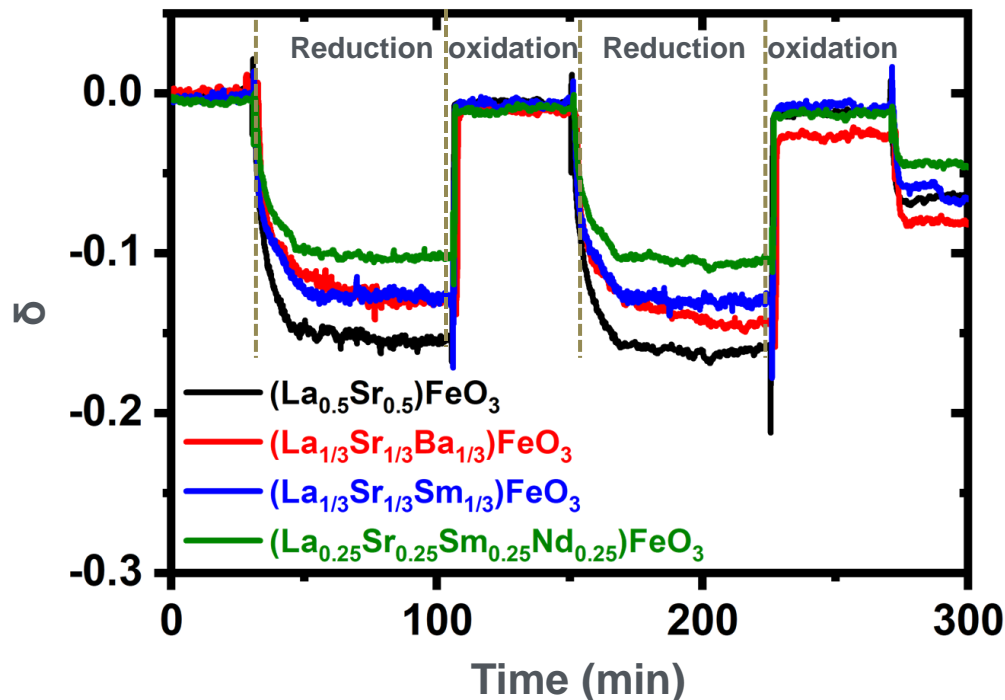
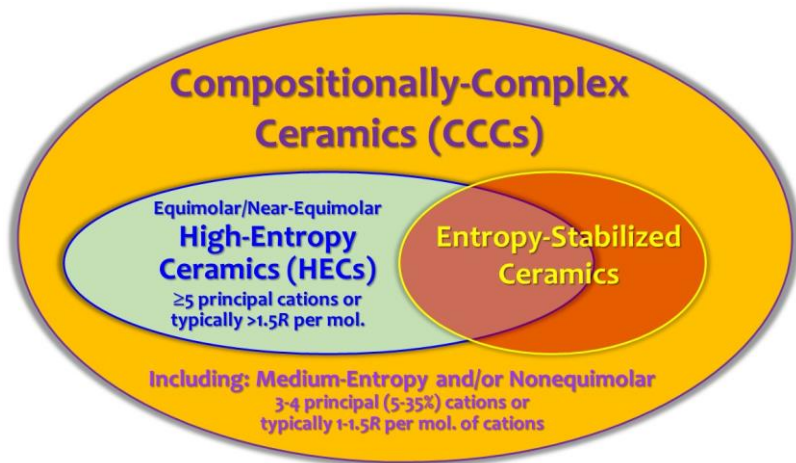
Approach- Elemental Distribution





Approach- TGA Cycling

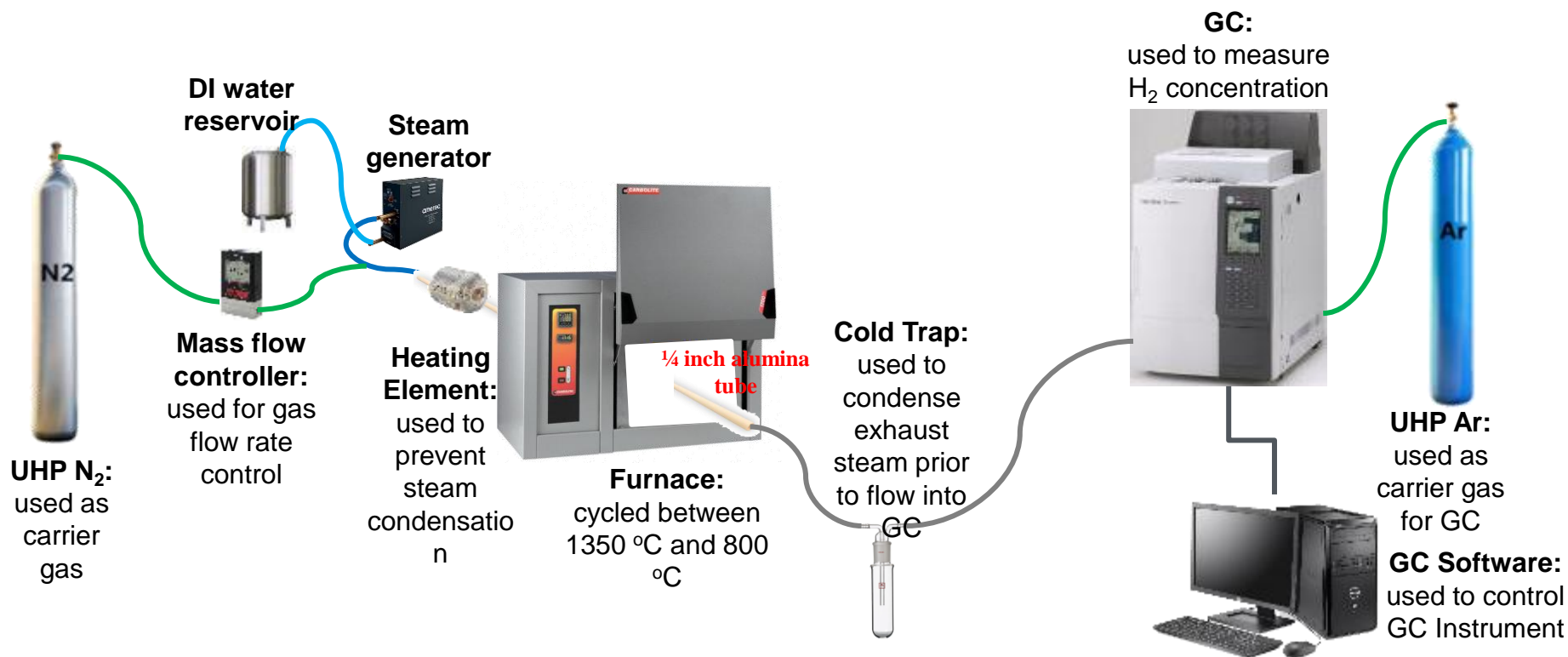
- $\Delta\delta = 0.09$
- $\Delta\delta = 0.12$
- $\Delta\delta = 0.11$
- $\Delta\delta = 0.14$



It is important to expand to **non-equimolar compositions** to achieve high $\Delta\delta$ at the DOE required water splitting conditions

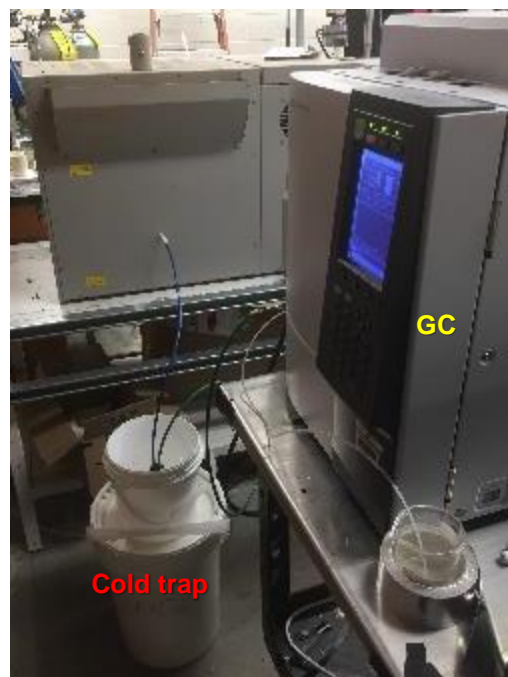
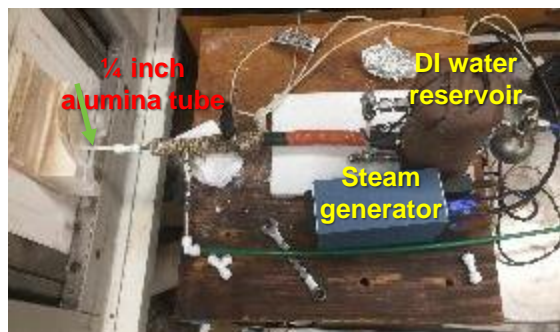
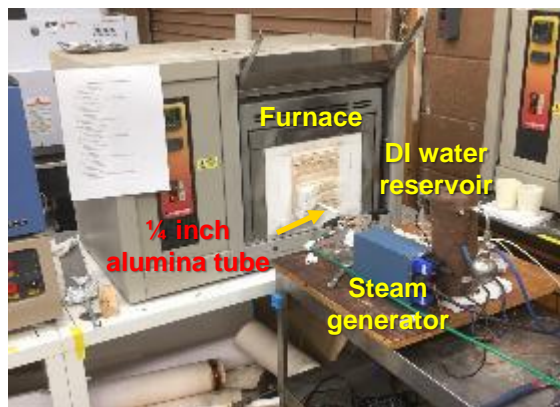


Approach- Thermochemical Water Splitting Set-Up





Approach- Thermochemical Water Splitting Set-Up





Milestone Progress (2020 Q1)

Milestone Schedule							
#	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Originally Planned	Revised Plan	Actual	Percent Completed	
1.1	Identify at least three promising candidate composites (meeting the two quantitative criteria defined on p. 2) of A-site HEPOs for further experimental investigations	Milestone	4/30/2020			~70%	Subcontract delay due to transfer from MSU to Brown and COVID-19
2.1	Synthesize at least 15 different A-site mixing compositions, including both the targeted and benchmark compositions, to validate and provide feedbacks to the models and probe the underlying mechanisms.	Milestone	7/31/2020			~50%	On schedule for 2020 Q1, but we may expect a delay next quarter due to COVID-19 closing
3.1	Determine the conditions to achieve the total “active” (reduction + oxidation) time (excluding ramping and cooling) per cycle to be less than 1 hour and 2 hours, respectively, with $T_{red} < 1400C$ and at least 80% oxidation and reduction.	Milestone	9/30/2020			~25%	On schedule for 2020 Q1
3.2	Identification of oxygen surface exchange coefficients (k) and bulk diffusion coefficients (D) for A-site mixing HEPOs. Demonstration of the cycle time for the best performer. Development of A-site mixing HEPO with $k \geq 7.5 \times 10^{-4}$ cm/s. Achieve significant progress towards meeting the budget period 1 milestones.	Go/No-Go	1/31/2021			~15%	On schedule for 2020 Q1



Remaining Barrier and Challenge

Technical:

- ▶ To develop effective strategies to search in the vast non-equimolar medium- and high-entropy composition space
- ▶ To examine whether trace O₂ impurity (1 ppm) in commercial UHP N₂ gas can partly fill the oxygen vacancy in low-loading perovskite samples during the oxidation stage.
- ▶ To revise/improve the design of testing set: One valve in the stream gas line cannot completely inhibit steam leakage into the reactor during cooling towards the oxidation stage, as seen in CeO₂.



Remaining Barrier and Challenge

Contracting and Project Managing Issues:

- ▶ There is a delay in the revised subcontract from MSU and Brown University (because of the move of a co-PI's group)
- ▶ Due to the impact of Covid-19, we expect delays in experimentation at both UCSD and WVU, as well as our node collaboration at SNL



Proposed Future Work

- ▶ Seeking more element candidates and strategies for designing compositions:
 - Enable V_O formation enthalpy tunability from A^{3+} mixing
 - Seeking promising A^{2+} candidates to allow equal molar mixing (rather than the fixed Sr^{2+} stoichiometry on 1/3 of the A site)?
 - New strategies for designing non-equimolar compositions
- ▶ Synthesis and characterization
 - Synthesize 15 HEPOs in total to explore the A-site mixing effect
 - High temperature XRD to realize the phase stability during STCH environment
- ▶ Thermochemical water splitting (WVU)
 - Install double sealed valves for the STCH setup to prevent steam leakage.
 - TGA analysis of HEPOs.
 - Investigate the kinetic properties (oxygen surface exchange coefficient k and bulk diffusion coefficient D) of HEPO samples with the ECR technique



Summary

- ▶ Insights Learnt from DFT Calculations:
 - Crystal structure matters in V_O formation enthalpy in ABO_3 .
 - Collective distortion when forming V_O in $LaFeO_3$ (cubic, $Pm\bar{3}m$) helps reduce the formation enthalpy.
 - Defect magnetic structure matters and has a large configurational space.
 - High spin state gives the lowest formation enthalpy Long-range effect was observed in $LaFeO_3$.
 - A^{3+} alloying does not affect much in the V_O formation enthalpy Sr^{2+}/Ba^{2+} helps to reduce the oxygen formation enthalpy.
- ▶ Several single phase A-site mixing HEPOs has been successfully synthesized, showing either cubic or orthorhombic structure
- ▶ TGA measurements show the theoretical reversible $\Delta\delta$ around 0.1-0.13 for some initial promising compositions
- ▶ Testing:
 - Constructed the thermochemical water splitting setup and examine the performance of CeO_2 for validating the feasibility of the setup.
 - Built the ECR instruments ready for analyzing HEPOs.