



Energy Materials Network
U.S. Department of Energy



HydroGEN
Advanced Water Splitting Materials

Reduced-Temperature Thermochemical Redox Reactions

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Stanford Linear Accelerator Center/Stanford University

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Project ID: SLAC

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Project Overview

Project Vision

To reduce temperature requirement of thermochemical redox reactions by using polycation oxides that can lower phase transition temperature.

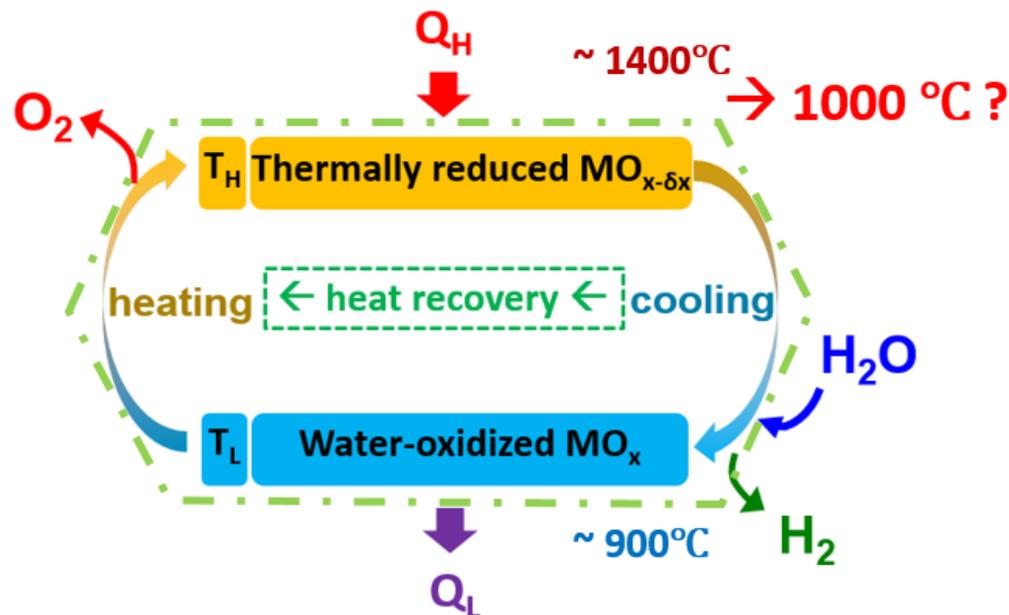
Project Impact

To develop oxides for two-step thermochemical water splitting (TWS) cycle $\leq 1000\text{ }^\circ\text{C}$, which is relevant for large scale hydrogen production.

Project Partner

Michael Toney, SLAC

Start/End Date	09/01/2016-06/30/2018
Total Funding	\$150,000





Relevance

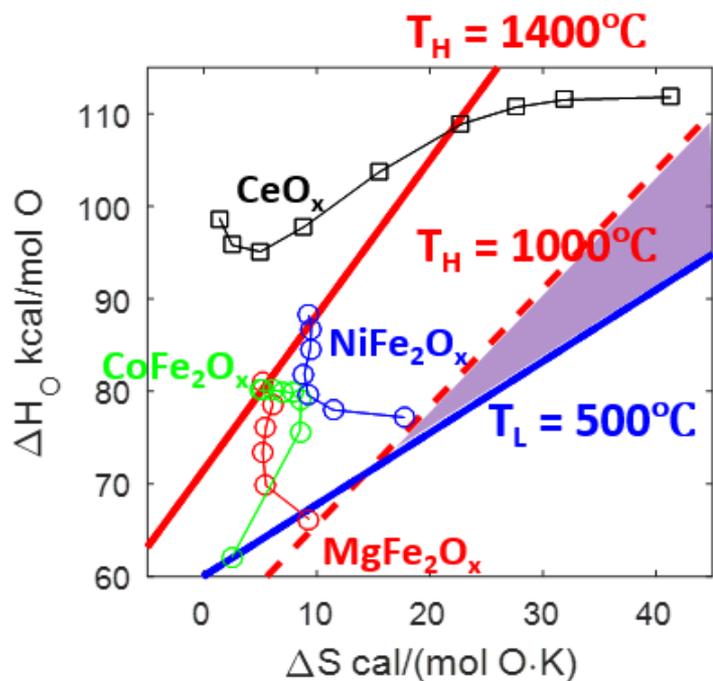
- **Project goal:** Developing novel metal oxides to produce large scale hydrogen at <\$2/kg, specifically by reducing thermochemical reaction temperature.
- *This reporting period:*
 - *Studied entropy stabilization effect on two-step TWS performance at reduced temperature*
 - *Identified redox active element in the poly-cation oxide $(\text{MgFeCoNi})\text{O}_x$*
 - *Specified phase swing during the TWS cycle*
 - *Stable ten-cycle performance*



Approach- Summary

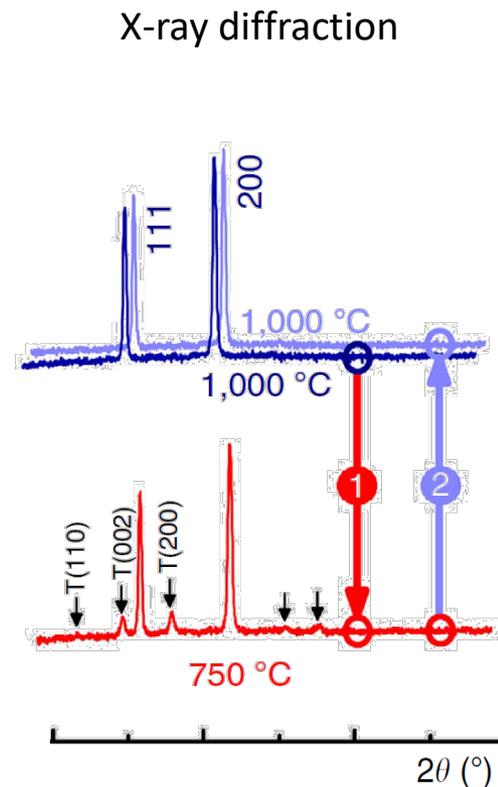
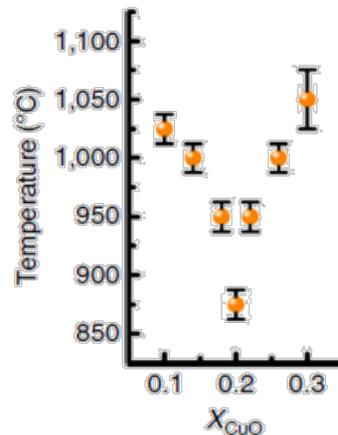
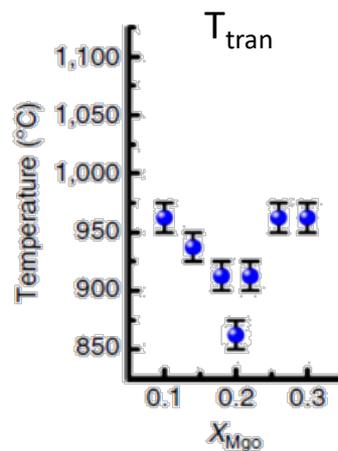
Barriers

Narrow thermodynamic window to do two-step TWS within 1000 °C.



Project Motivation

Entropy-stabilization was found to lower phase transition temperature.

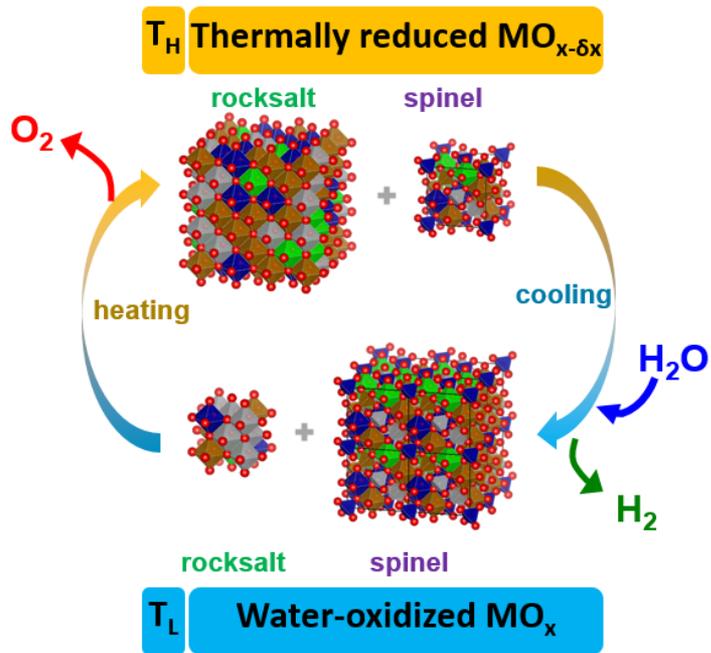


Rost, Nat. Commun., 2015

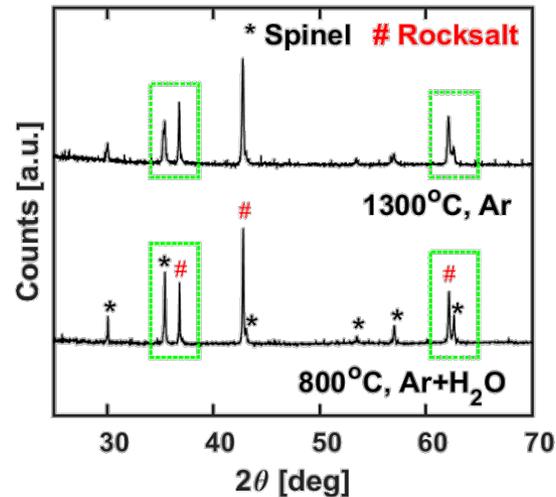


Approach- Innovation

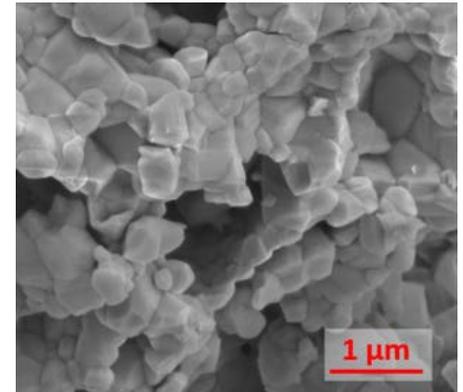
- Poly-cation oxide $(\text{FeMgCoNi})\text{O}_x$ undergoes phase swing in two-step TWS cycle.



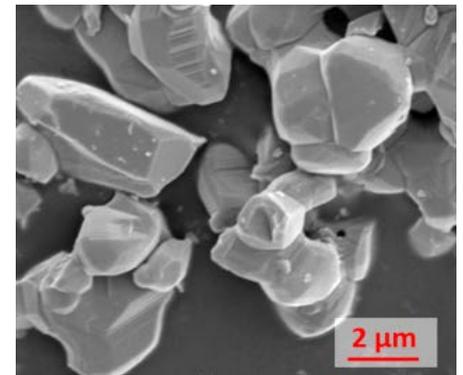
X-ray Diffraction



As synthesized



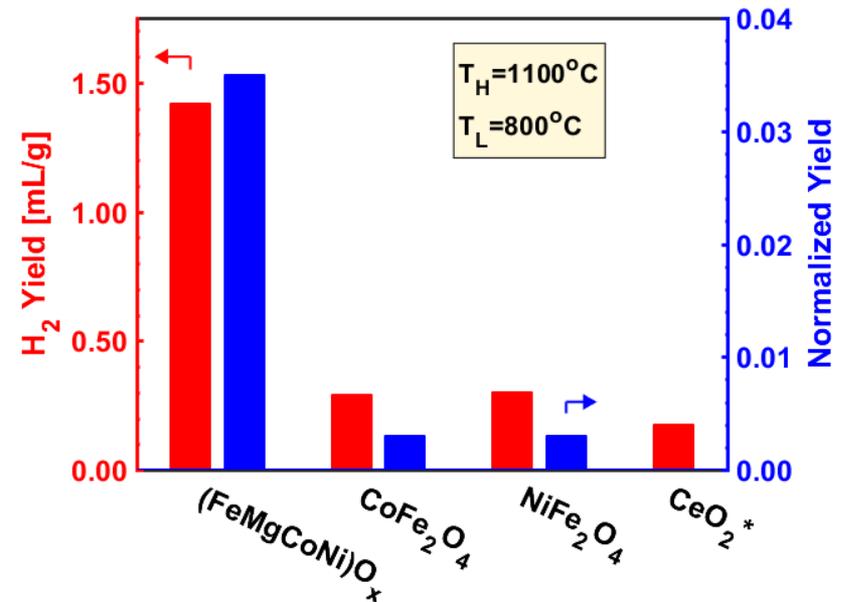
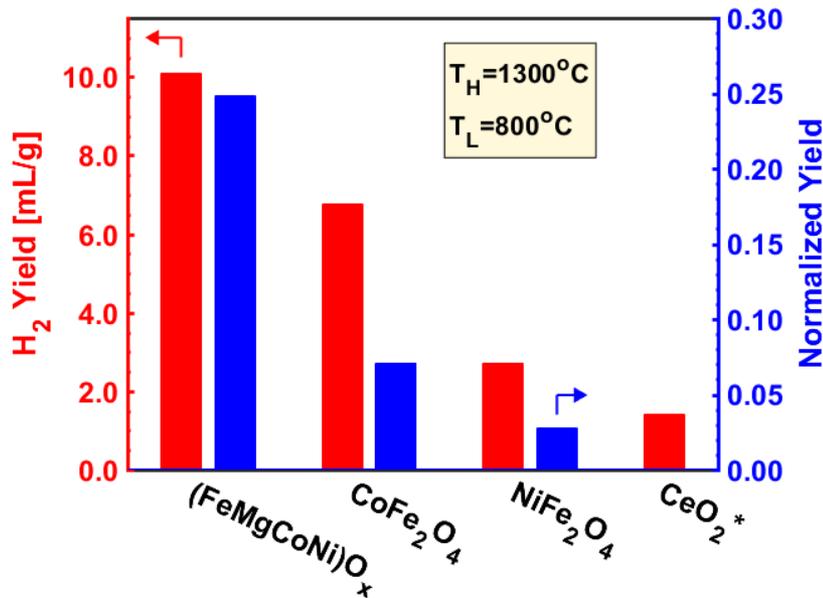
After 10 cycles at 1300-800 °C





Accomplishments

- Poly-cation oxide $(\text{FeMgCoNi})\text{O}_x$ outperforms state-of-the-art two-step TWS materials.



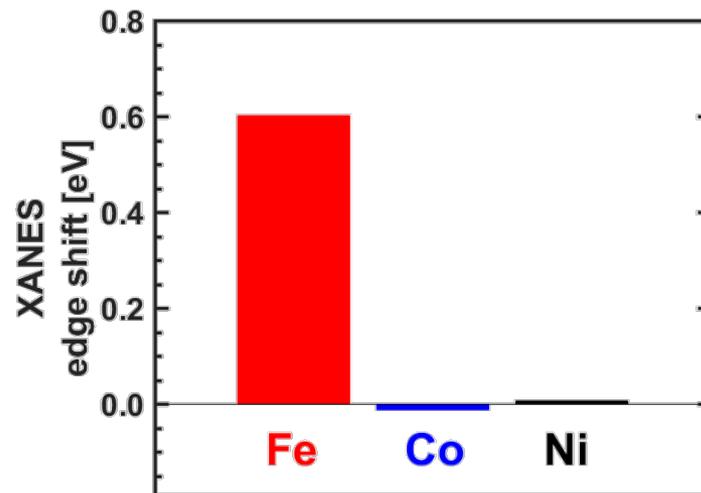
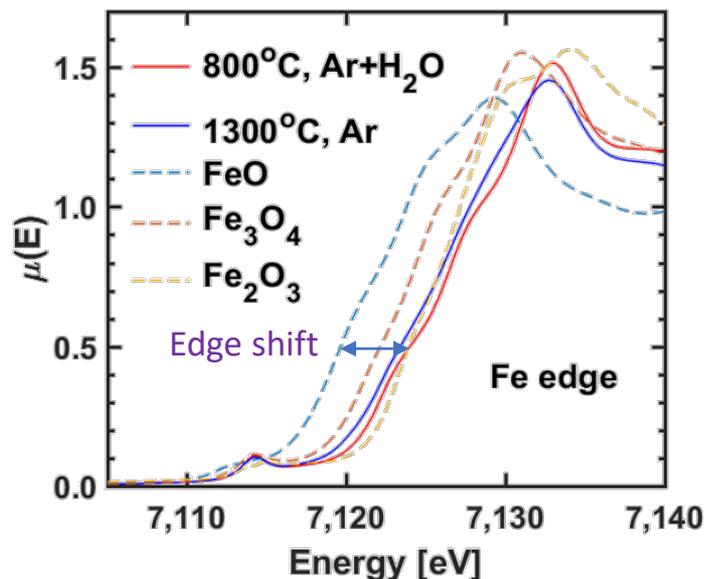
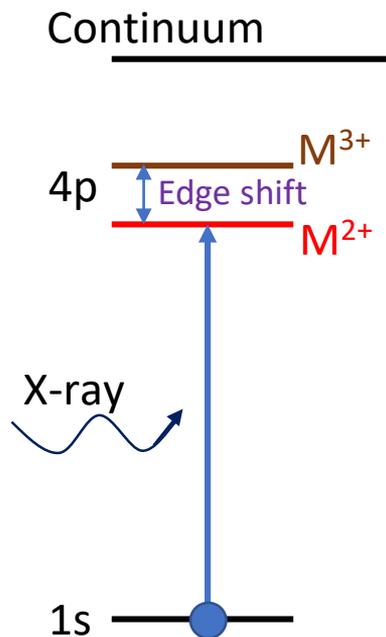
Normalized yield: measured H_2 yield normalized by the yield if Fe goes through complete $\text{Fe}^{2+}/\text{Fe}^{3+}$ transition during the TWS cycle.



Accomplishments

- Fe is the redox active element relevant for two-step TWS of $(\text{FeMgCoNi})\text{O}_x$

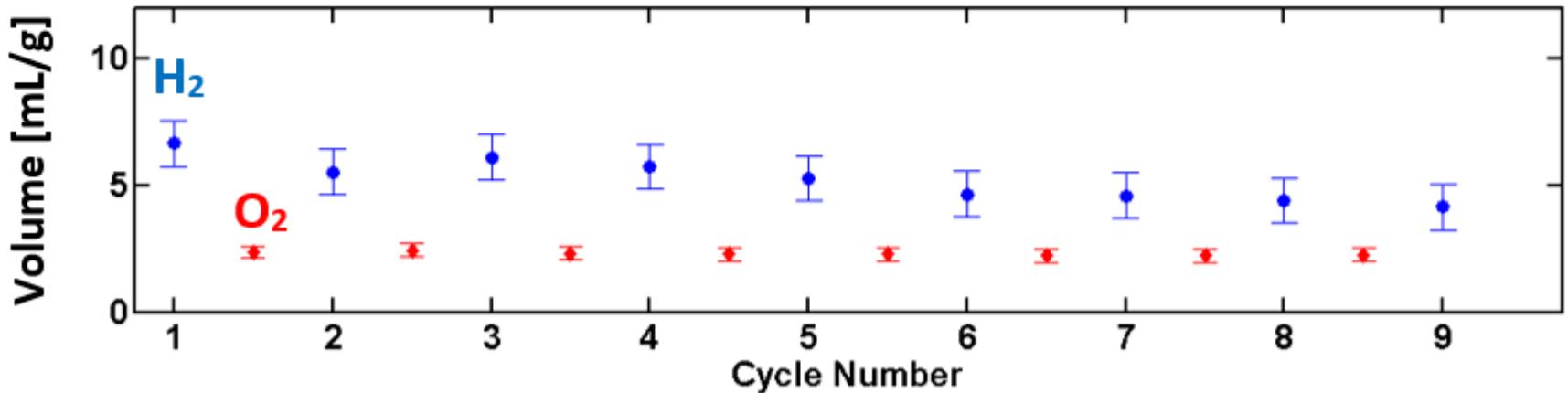
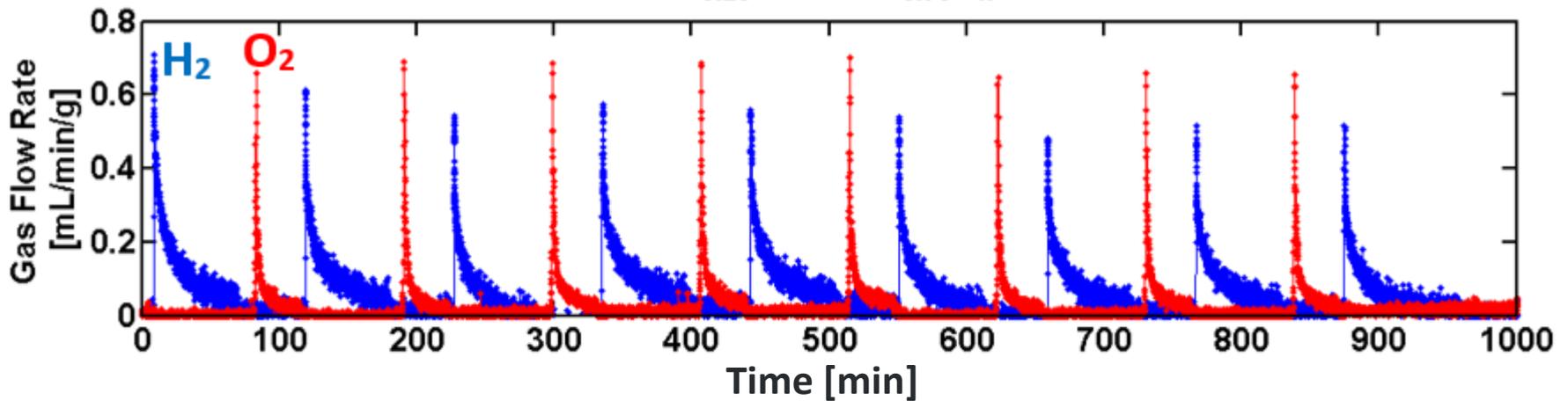
X-ray absorption near-edge structure





Accomplishments

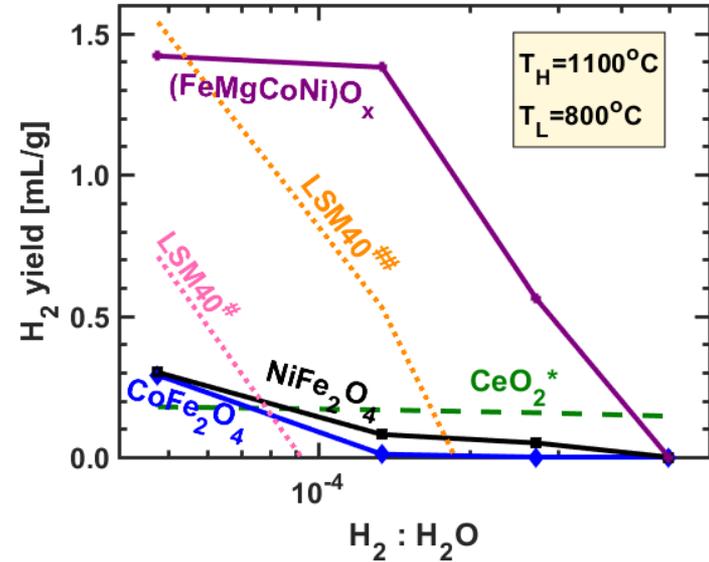
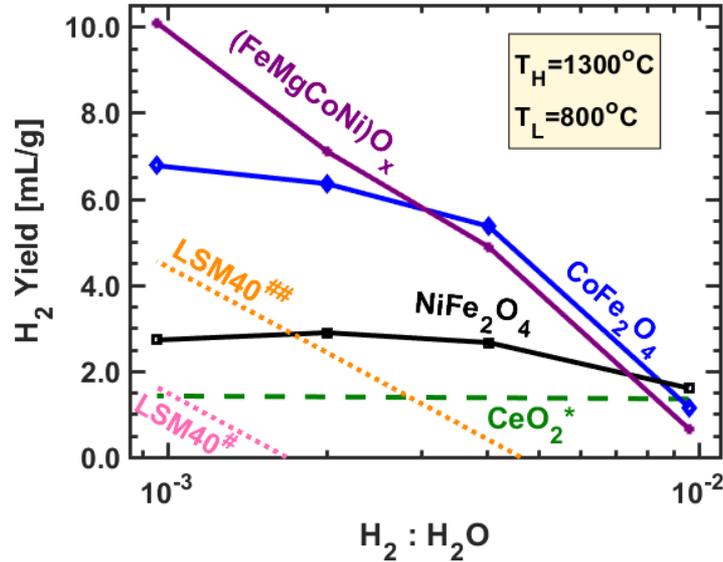
- Kinetics study of poly-cation oxide $(\text{FeMgCoNi})\text{O}_x$ at $T_H = 1300\text{ }^\circ\text{C}$ and $T_L = 800\text{ }^\circ\text{C}$.





Accomplishments

- Poly-cation oxide $(\text{FeMgCoNi})\text{O}_x$ has good H_2O to H_2 conversion.



- Outlook and projected outcomes for the remainder of the project's budget period 1 scope of work:
- Optimizing compositions of poly-cation oxides to further improve its TWS performance.



Collaboration

Collaborator	Project Role
Majumdar Group	Material synthesis; Thermochemical performance characterization; X-ray diffraction
Chueh Group	
Toney Group	Synchrotron x-ray absorption spectroscopy



Proposed Future Work

- To develop new materials that can be used for two-step TWS **below 1000 °C**.
- Mechanism study: what are the role of **redox inactive** Mg, Co and Ni in the thermochemical redox reactions?
- **Thermodynamic** hydrogen production **limit** of specific poly-cation oxide(s).
- To identify reaction **rate-determining step(s)**.



Project Summary

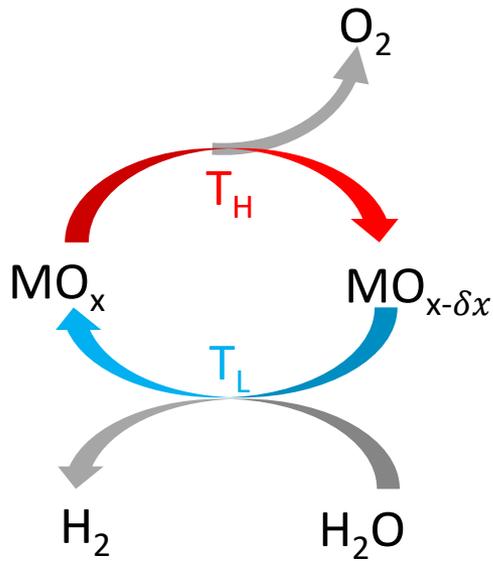
- **Approach**
 - Tuning entropy-stabilization in poly-cation oxide to lower thermochemical redox reaction temperature
- **Performance of $(\text{FeMgCoNi})\text{O}_x$**
 - Two-step TWS within 1100 °C
 - High hydrogen yield and good H_2O to H_2 conversion
 - Phase swing identified: coexistence of rocksalt/spinel phases
 - Fe is the redox active element for two-step TWS
 - Large portion of Fe is active in redox reactions



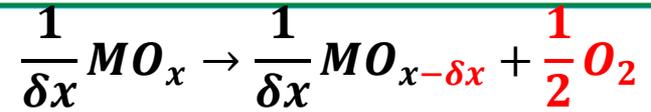
Technical Back-Up Slides



Spontaneous reaction conditions



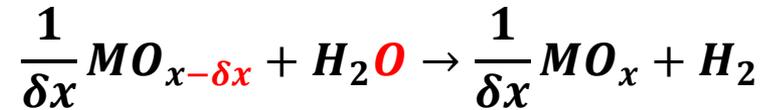
Thermal Reduction (@ T_H)



$$\Delta G_1 = \frac{\Delta H_{f1}^0(MO_{x-\delta x}) - \Delta H_{f1}^0(MO_x)}{\delta x} - T_H \left[\frac{S_1^0(MO_{x-\delta x}) - S_1^0(MO_x)}{\delta x} + \frac{S_1^0(O_2) - R \ln \frac{p_{O_2}}{p^0}}{2} \right] < 0$$

$$p_{O_2} = 10^{-5} \text{ bar}$$

Water Splitting (@ T_L)



$$\Delta G_2 = \frac{\Delta H_{f2}^0(MO_x) - \Delta H_{f2}^0(MO_{x-\delta x})}{\delta x} - \Delta H_{f2}^0(H_2O) - T_L \left[\frac{S_2^0(MO_x) - S_2^0(MO_{x-\delta x})}{\delta x} + S_2^0(H_2) - R \ln \frac{p_{H_2}}{p^0} - S_2^0(H_2O) + R \ln \frac{p_{H_2O}}{p^0} \right] < 0$$

$$p_{H_2} = 10^{-4} \text{ bar}$$

$$p_{H_2O} = 10^{-1} \text{ bar}$$

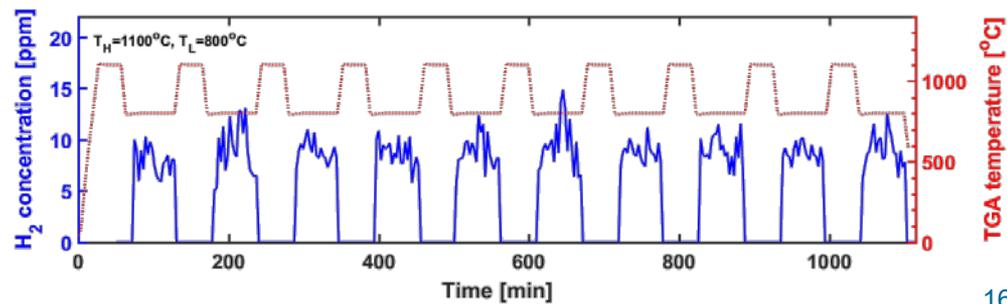
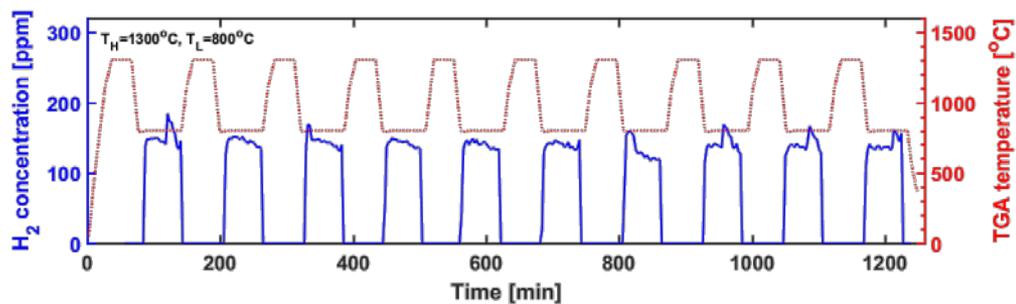
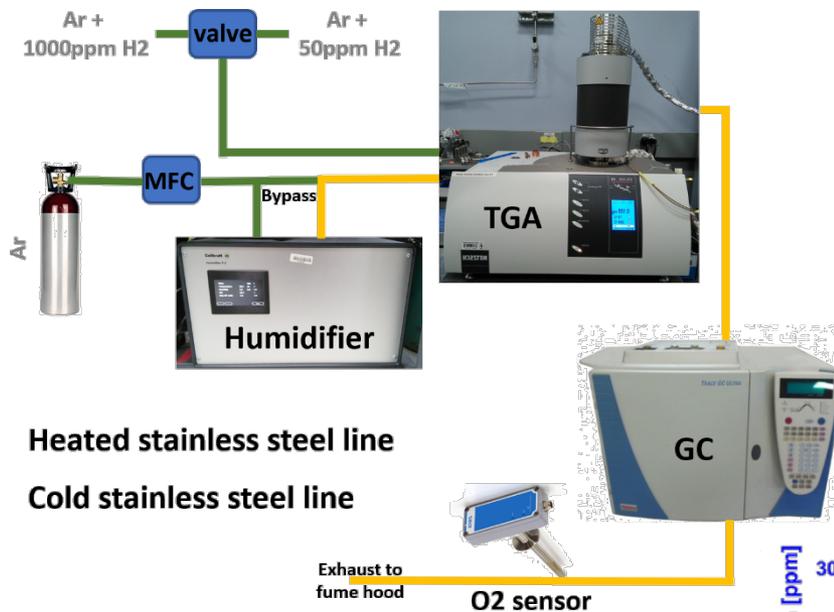
$$\Delta H_f(x) = \lim_{\delta x \rightarrow 0} \frac{\Delta H_f^0(MO_{x-\delta x}) - \Delta H_f^0(MO_x)}{\delta x}$$

$$\Delta S(x) = \lim_{\delta x \rightarrow 0} \frac{S^0(MO_{x-\delta x}) - S^0(MO_x)}{\delta x}$$

- Functions of x
- Temperature dependence neglected



TGA system





Stagnation flow reactor system

