Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Reduced-Temperature Thermochemical Redox Reactions

PI: Arun Majumdar, William Chueh
Presenter: Shang Zhai

Stanford Linear Accelerator Center/Stanford University

June 13, 2018

Project ID: SLAC

NREL | Berkeley Lab | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

Project Vision

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

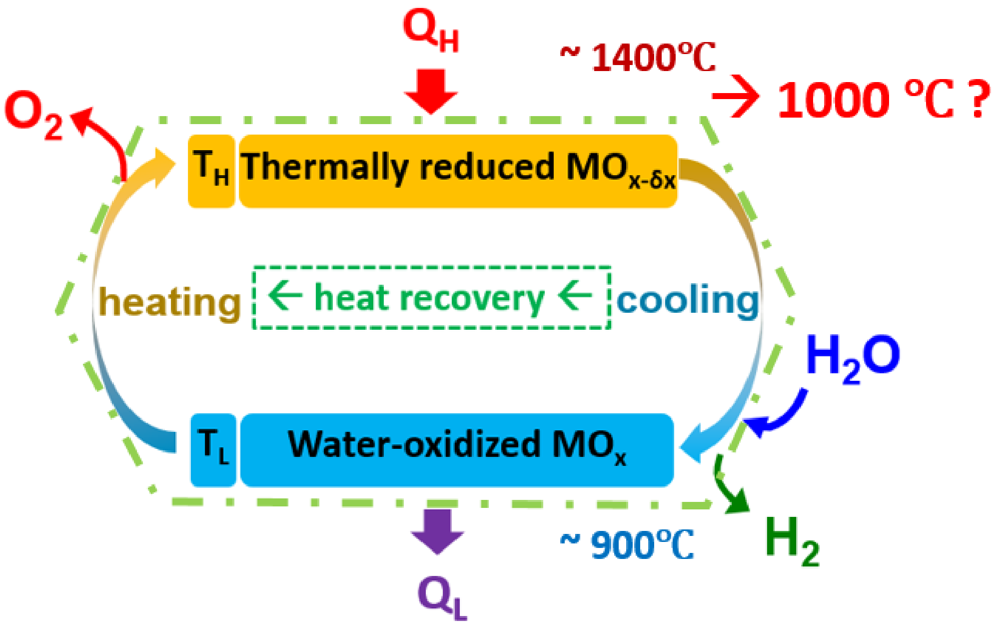
Project Partner

Michael Toney, SLAC

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

Project Impact

To develop oxides for two-step thermochemical water splitting (TWS) cycle ≤ 1000 °C, which is relevant for large scale hydrogen production.



Relevance

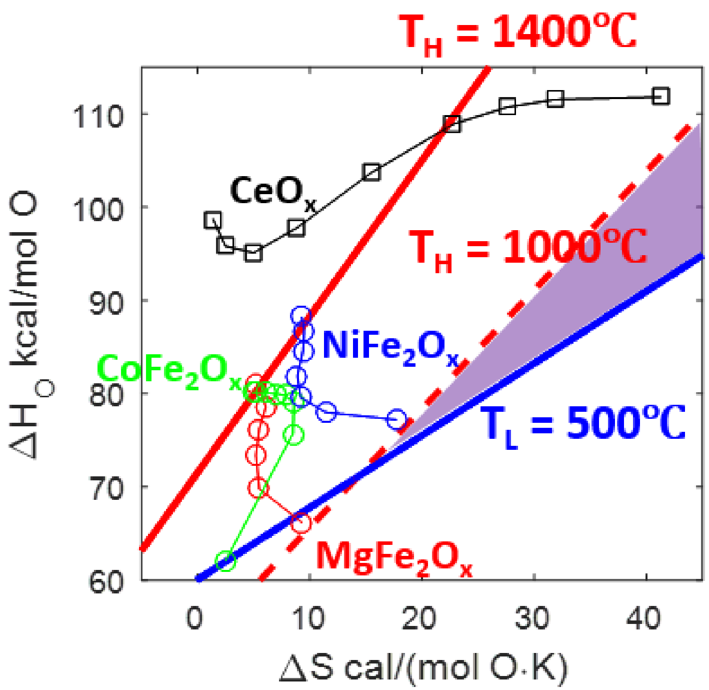
- **Project goal**: Developing novel metal oxides to produce large scale hydrogen at <$2/kg, specifically by reducing thermochemical reaction temperature.

- *This reporting period:*
  - *Studied entropy stabilization effect on two-step TWS performance at reduced temperature*
  - *Identified redox active element in the poly-cation oxide (MgFeCoNi)O_x*
  - *Specified phase swing during the TWS cycle*
  - *Stable ten-cycle performance*

Approach- Summary

Barriers

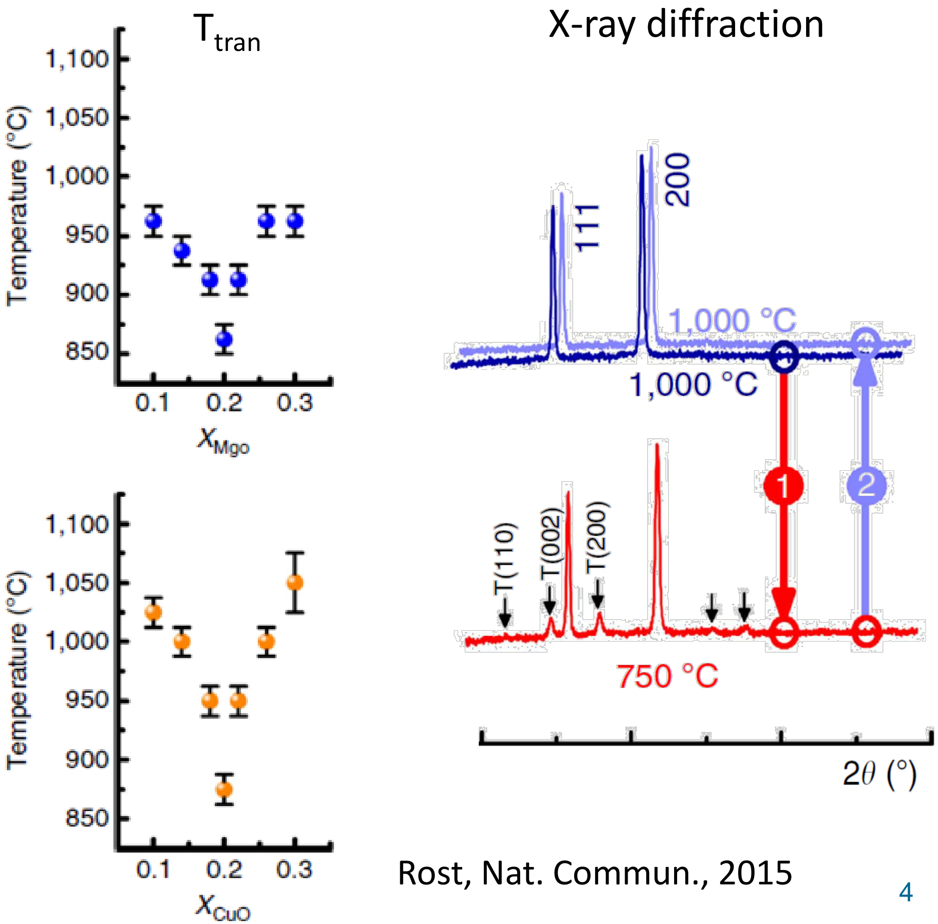
Narrow thermodynamic window to do two-step TWS within 1000 °C.



Project Motivation

Entropy-stabilization was found to lower phase transition temperature.

$(MgCoNiCuZn)O_x$

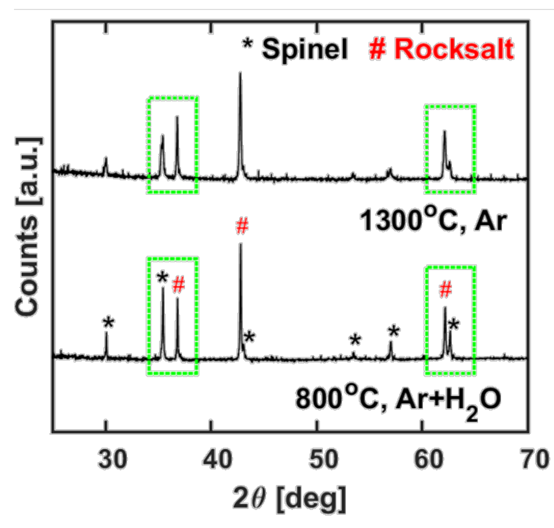


Rost, Nat. Commun., 2015

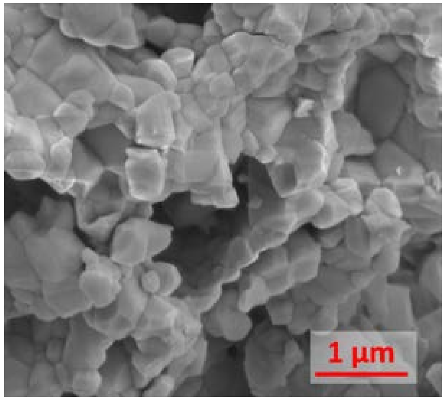
Approach- Innovation

- Poly-cation oxide (FeMgCoNi)O_x undergoes phase swing in two-step TWS cycle.

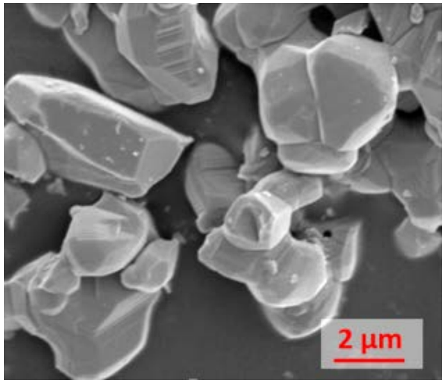
X-ray Diffraction



As synthesized

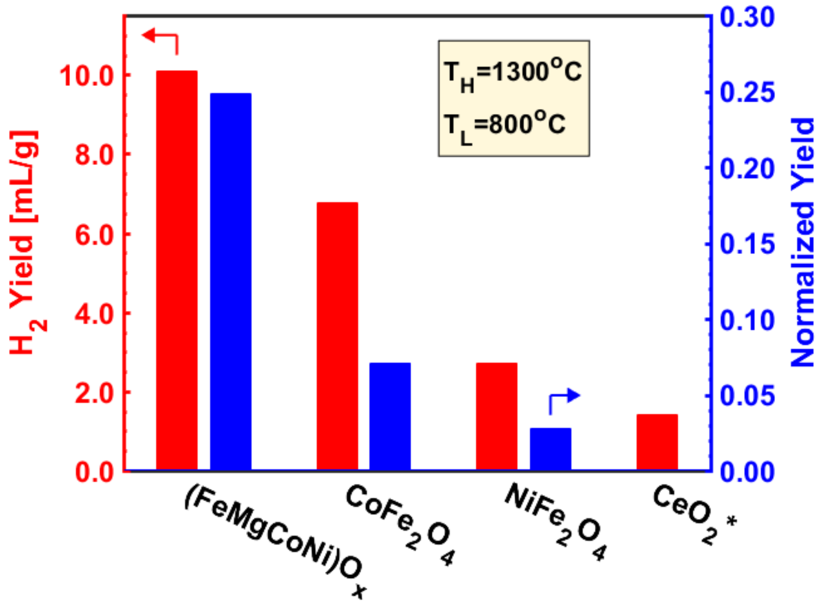


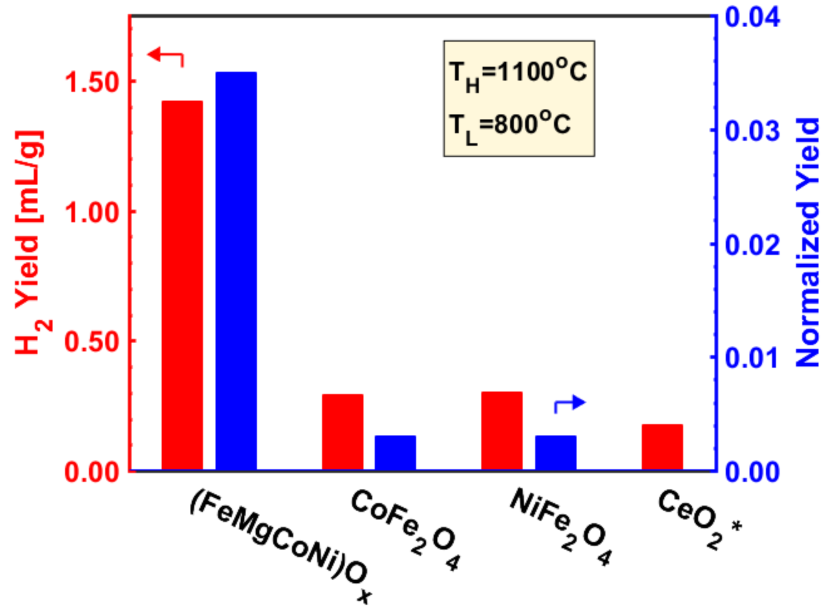
After 10 cycles at 1300-800 °C



Accomplishments

- Poly-cation oxide (FeMgCoNi)O_x outperforms state-of-the-art two-step TWS materials.

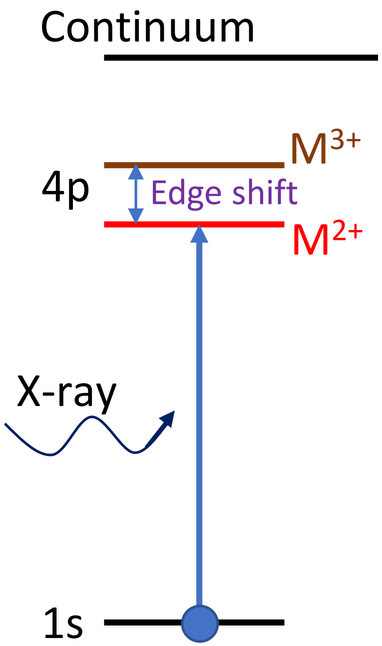




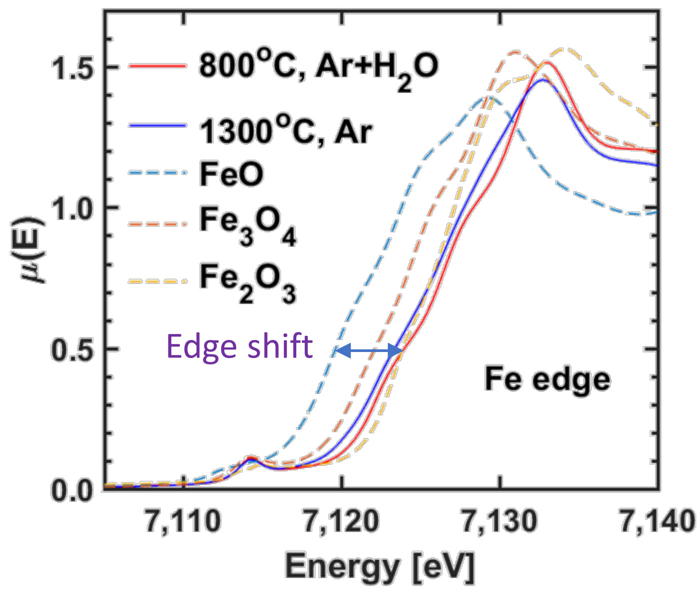
Normalized yield: measured H_2 yield normalized by the yield if Fe goes through complete Fe^{2+}/Fe^{3+} transition during the TWS cycle.

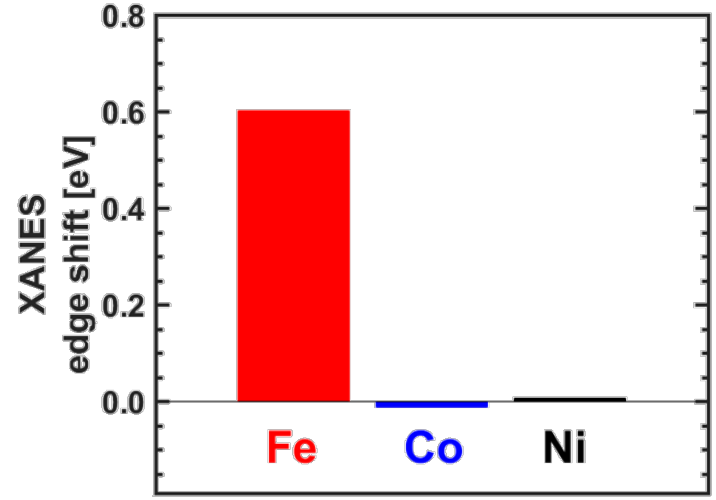
Accomplishments

- Fe is the redox active element relevant for two-step TWS of (FeMgCoNi)O_x



X-ray absorption near-edge structure

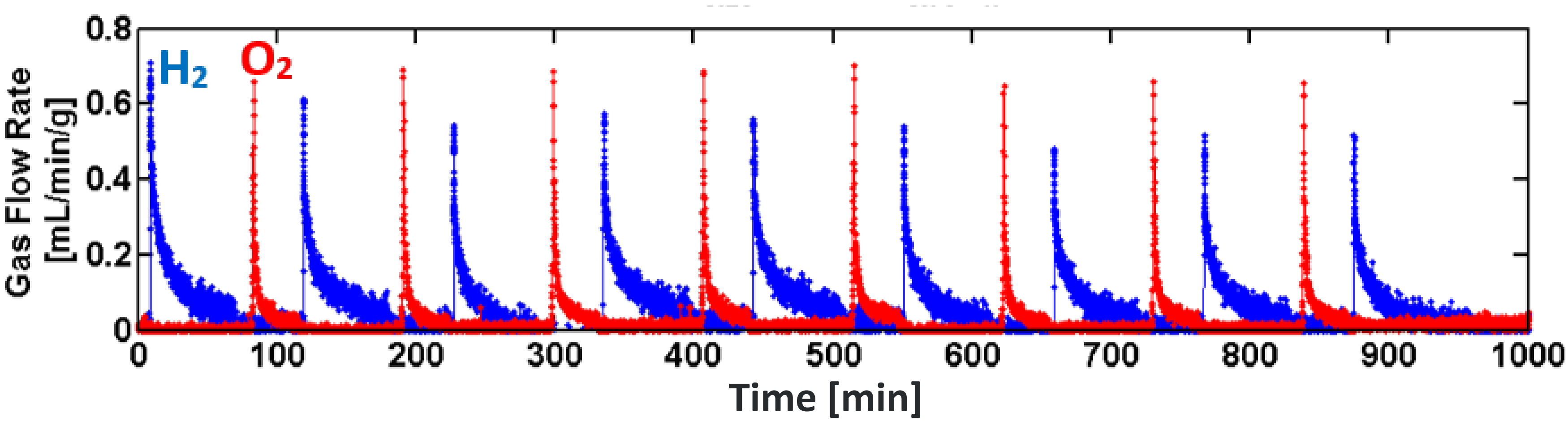


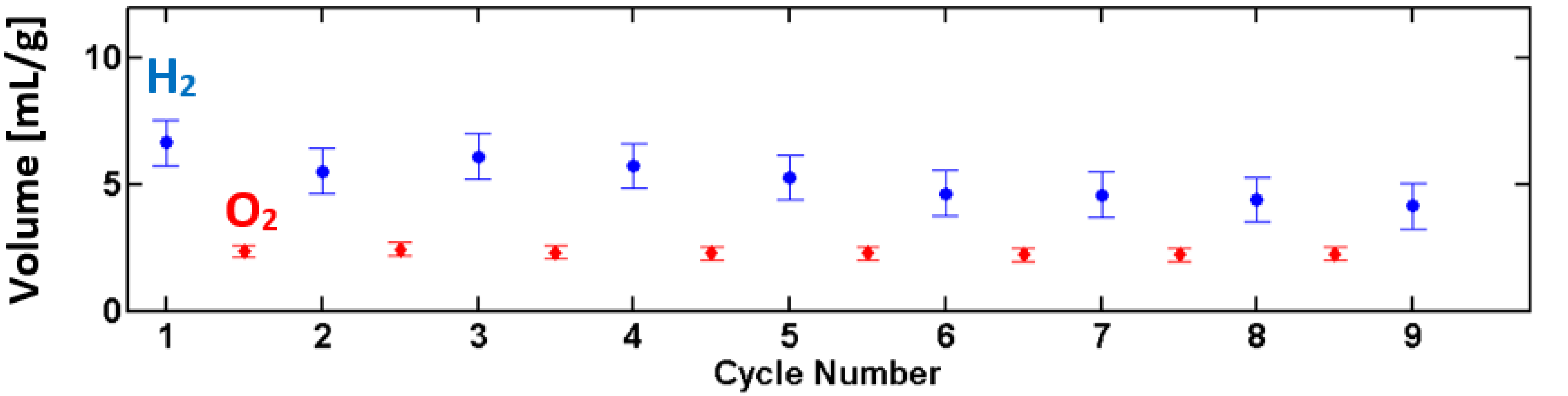


SSRL

Accomplishments

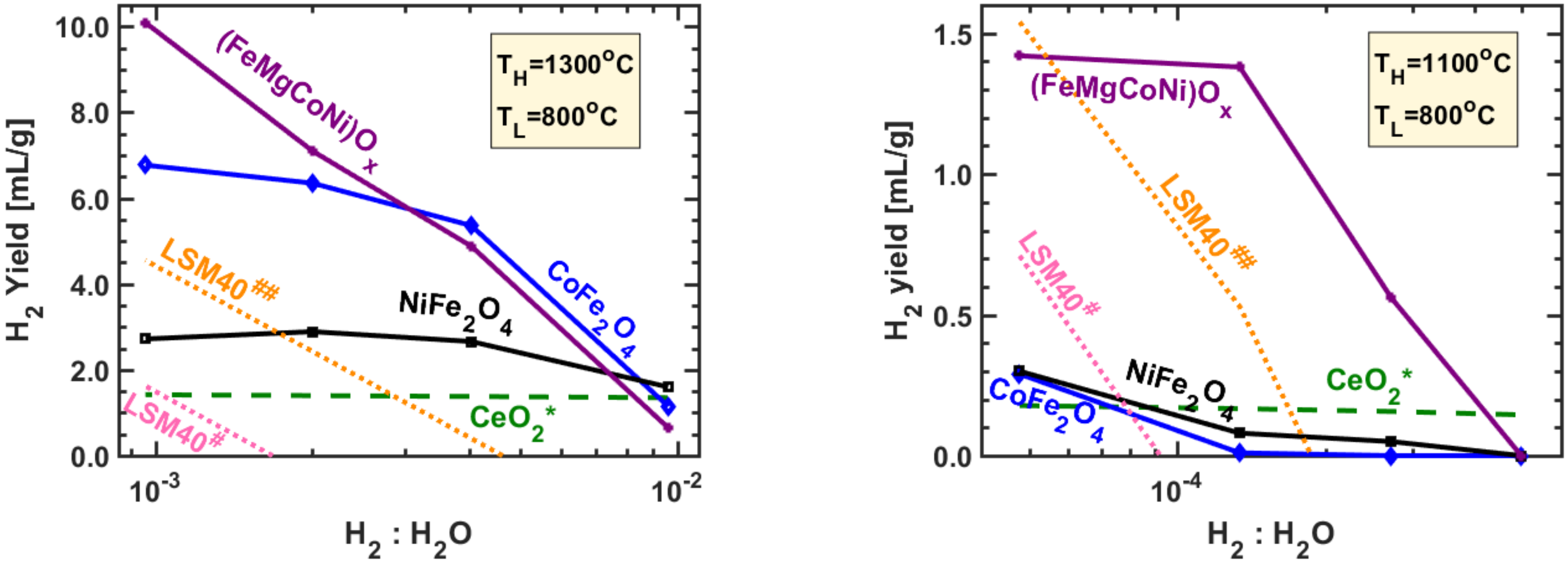
- Kinetics study of poly-cation oxide $(FeMgCoNi)O_x$ at T_H = 1300 °C and T_L = 800 °C.





Accomplishments

- Poly-cation oxide $(FeMgCoNi)O_x$ 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

<table>
<tr><th>Collaborator</th><th>Project Role</th></tr>
<tr><td>Majumdar Group</td><td rowspan="2">Material synthesis;
Thermochemical performance characterization;
X-ray diffraction</td></tr>
<tr><td>Chueh Group</td></tr>
<tr><td>Toney Group</td><td>Synchrotron x-ray absorption spectroscopy</td></tr>
</table>

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 (FeMgCoNi)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

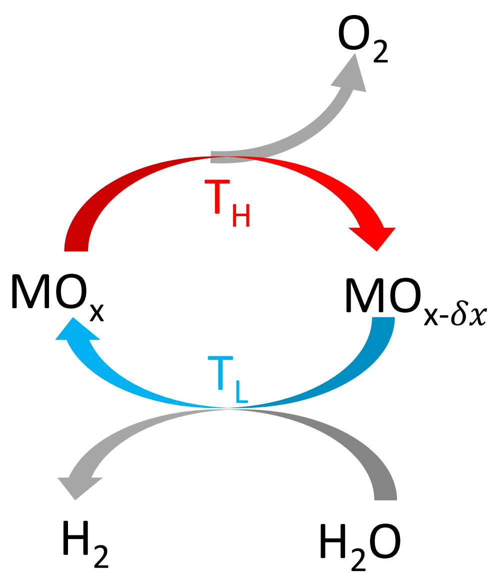
Spontaneous reaction conditions

Thermal Reduction (@T_H)

$$\frac{1}{\delta x} MO_x \rightarrow \frac{1}{\delta x} MO_{x-\delta x} + \frac{1}{2} O_2$$

$$\Delta G_1 = \frac{\Delta H^0_{f1}(MO_{x-\delta x}) - \Delta H^0_{f1}(MO_x)}{\delta x} - T_H\left[\frac{S^0_1(MO_{x-\delta x}) - S^0_1(MO_x)}{\delta x} + \frac{S^0_1(O_2) - R\ln\frac{p_{O2}}{p^0}}{2}\right] < 0$$

$p_{O2} = 10^{-5}$ **bar**



Water Splitting (@T_L)

$$\frac{1}{\delta x} MO_{x-\delta x} + H_2O \rightarrow \frac{1}{\delta x} MO_x + H_2$$

$$\Delta G_2 = \frac{\Delta H^0_{f2}(MO_x) - \Delta H^0_{f2}(MO_{x-\delta x})}{\delta x} - \Delta H^0_{f2}(H_2O) - T_L\left[\frac{S^0_2(MO_x) - S^0_2(MO_{x-\delta x})}{\delta x} + S^0_2(H_2) - R\ln\frac{p_{H_2}}{p^0} - S^0_2(H_2O) + R\ln\frac{p_{H_2O}}{p^0}\right] < 0$$

$p_{H2} = 10^{-4}$ **bar**

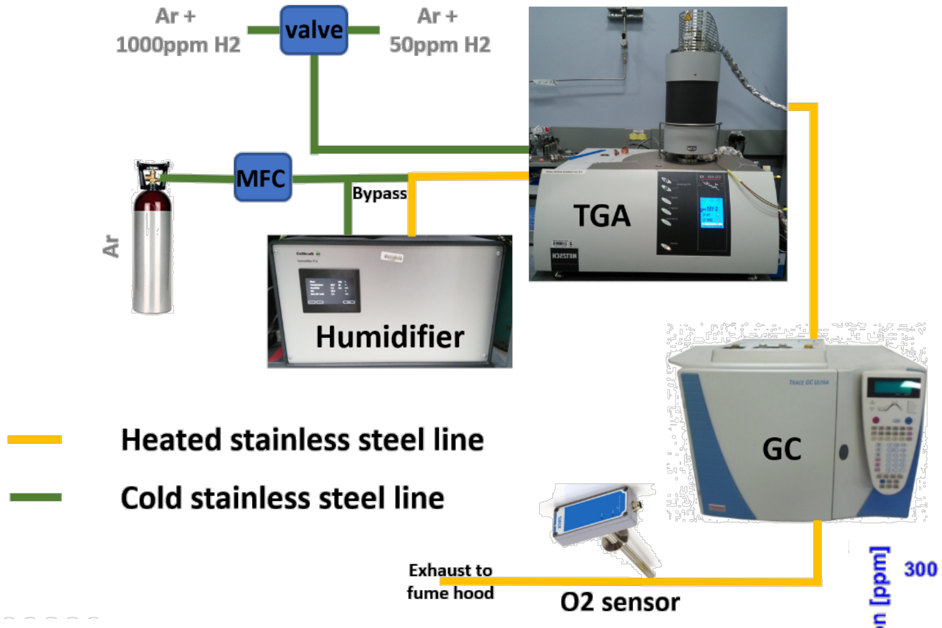
$p_{H2O} = 10^{-1}$ **bar**

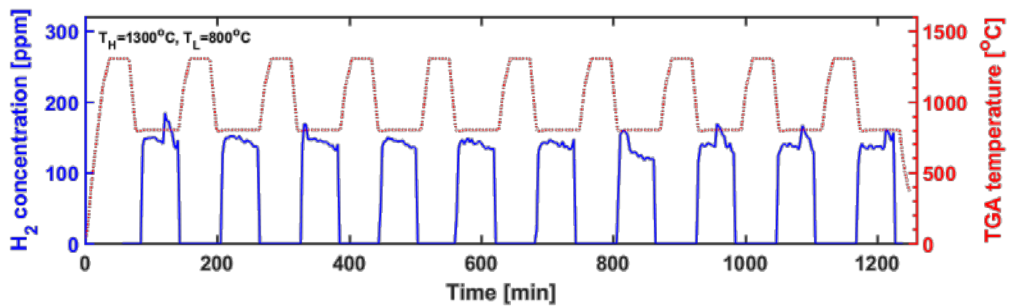
$$\Delta H_f(x) = \lim_{\delta x \to 0} \frac{\Delta H^0_f(MO_{x-\delta x}) - \Delta H^0_f(MO_x)}{\delta x}$$

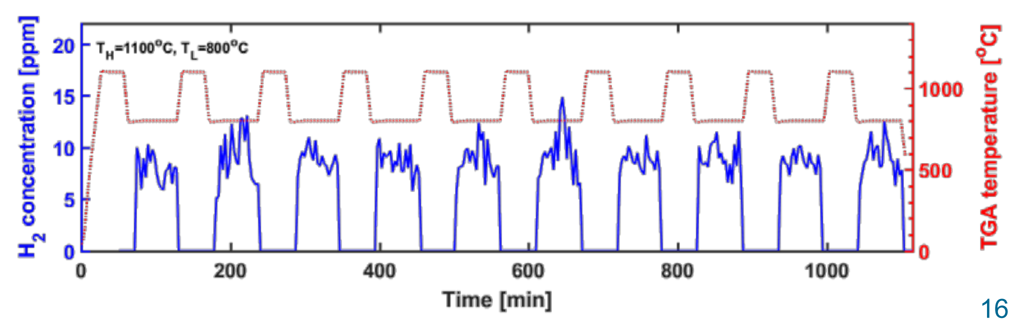
$$\Delta S(x) = \lim_{\delta x \to 0} \frac{S^0(MO_{x-\delta x}) - S^0(MO_x)}{\delta x}$$

- Functions of x
- Temperature dependence neglected

TGA system


Ar +
1000ppm H2
valve
Ar +
50ppm H2
MFC
Bypass
Ar
TGA
Humidifier
GC
Heated stainless steel line
Cold stainless steel line
Exhaust to
fume hood
O2 sensor


T_H=1300°C, T_L=800°C
H_2 concentration [ppm]
TGA temperature [°C]
Time [min]
0
100
200
300
500
1000
1500
400
600
800
1200


T_H=1100°C, T_L=800°C
H_2 concentration [ppm]
TGA temperature [°C]
Time [min]
0
5
10
15
20
500
1000
200
400
600
800

Stagnation flow reactor system