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Ammonia Production with Concentrated Sunlight

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National Solar Thermal Test Facility
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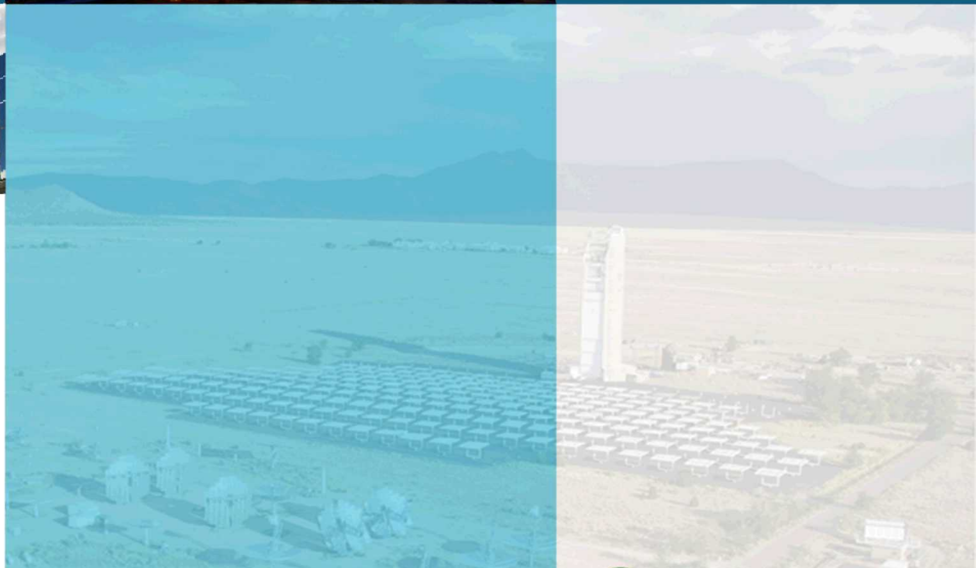

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Introduction

Motivations for Solar Ammonia Production

Ammonia (NH_3)

Production: ~10^8 metric tons per year

Fertilizer: 88% worldwide NH_3 consumption

Haber-Bosch Process

- Standard for NH_3 production
- Developed early 1900s
- NH_3 from $N_2 + H_2$ with aid of catalyst
- **Conditions**
  - High temperatures, ≥ 400°C
  - High pressures, ≥ 200 bar
- **Inputs**
  - H_2 source: steam methane reforming
  - N_2 source: cryogenic air separation

Steps:

1. **Steam methane reforming**

   $$CH_4 + H_2O \rightarrow 3H_2 + CO$$

2. **Cryogenic air separation**

   $$\text{Air} \rightarrow 0.8N_2 + 0.2O_2$$

3. **Ammonia synthesis**

   $$3H_2 + N_2 \xrightarrow{\text{cat}} 2NH_3$$

Impacts:

- ~10^9 increased population
- $2.6 \frac{\text{kg } CO_2 \text{ eq.}}{\text{kg } NH_3}$
- Constitutes >1% global GHG emissions

aiche.org/resources/publications/cep/2016/september/introduction-ammonia-production

Sustainable Haber-Bosch Alternative

Challenge: Sustainable production of NH_3

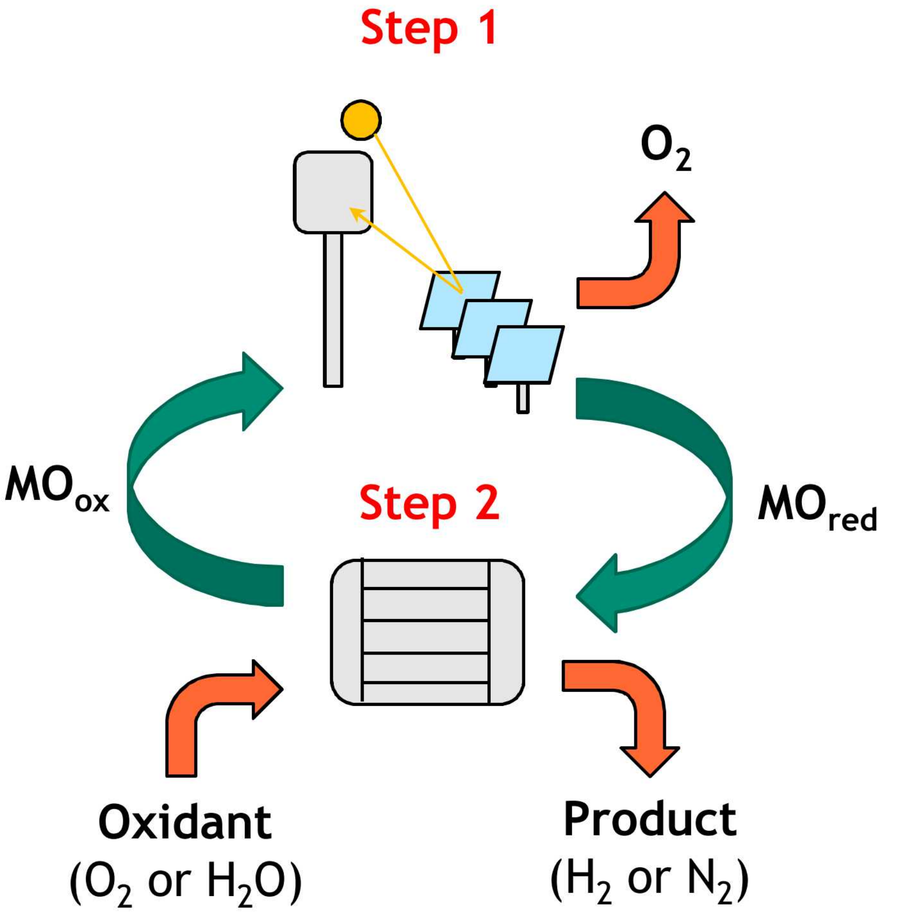
- Reduce/eliminate CO_2 emissions
- Use concentrated solar energy to drive chemical processes

Two Step Reduction-Oxidation (Redox) Cycles

- Vehicle for numerous solar thermochemistry processes

1. **Steam methane reforming**
   $CH_4 + H_2O \rightarrow 3H_2 + CO$
2. **Cryogenic air separation**
   $Air \rightarrow 0.8N_2 + 0.2O_2$
3. **Ammonia synthesis**
   $3H_2 + N_2 \rightarrow 2NH_3$

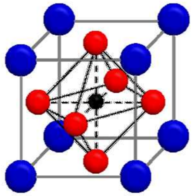
1. **Solar water splitting** ~~Steam methane reforming~~
   $MO_{ox} + \text{solar heat} \rightarrow MO_{red} + xO_{2(g)}$
   $MO_{red} + 2xH_2O_{(g)} \rightarrow MO_{ox} + 2xH_{2(g)}$
2. **Solar air separation** ~~Cryogenic air separation~~
   $MO_{ox} + \text{solar heat} \rightarrow MO_{red} + xO_{2(g)}$
   $MO_{red} + 5x[0.8N_{2(g)} + 0.2O_{2(g)}] \rightarrow 4xN_{2(g)}$
3. **Solar ammonia synthesis** ~~Ammonia synthesis~~
   $3H_2 + N_2 \rightarrow 2NH_3$



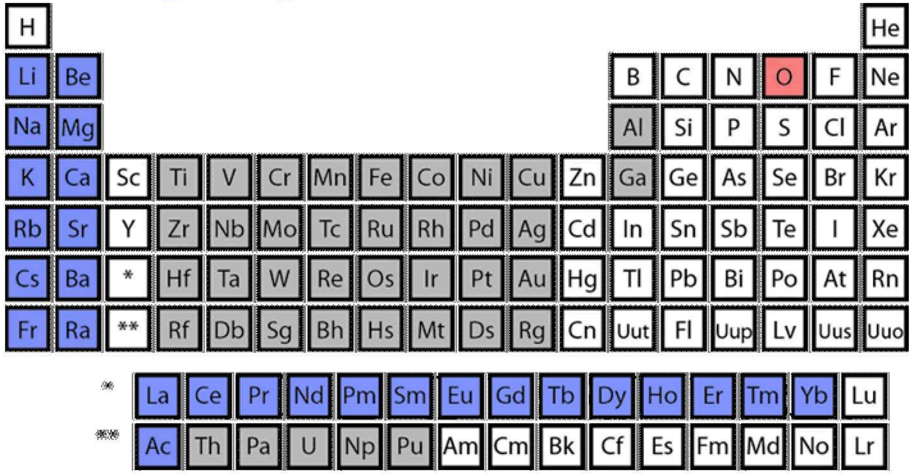
Perovskite Air Separation Materials

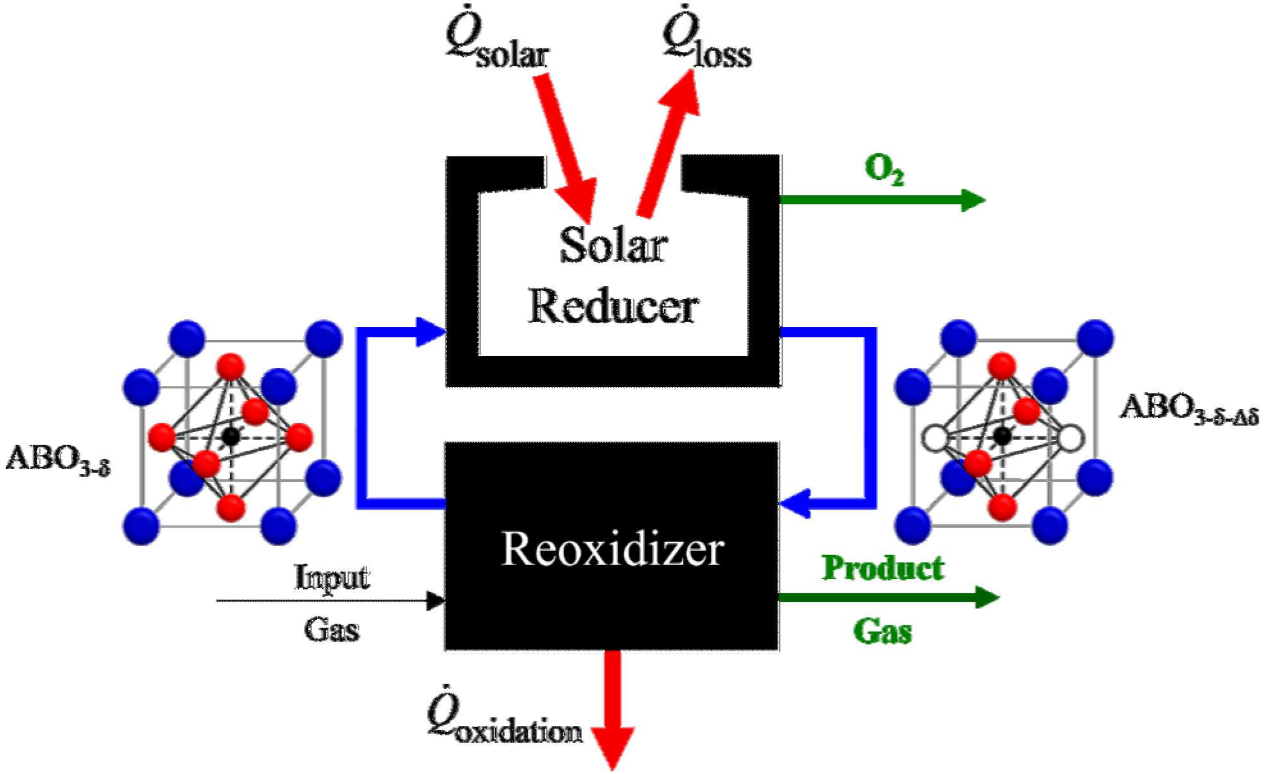
Perovskite oxides (ABO_3):

- Many combinations
- Maintain structure (nonstoichiometric redox)
- MIEC: rapid kinetics
- A/B site doping/substitution
- Can tune properties to desired reactor conditions



$A_{1-x}A'_x\ B_{1-y}\ B'_yO_3$





Cycle Design

Selecting Materials and Operating Conditions for Solar Air Separation

Considerations

Perovskite Material

- Amount of N_2 purified per lb/mol/day
- Temperatures of reactions
- Reaction rate
- Long-term stability
- Cost of metals, synthesis

Reactors and Cycle Conditions

- Temperatures and efficiencies
- Compatibility with solar infrastructure
- Transport of working materials
- Materials compatibility and cost

Things We Need To Measure/ Predict

- Equilibrium reaction extents of perovskite at cycle conditions (thermodynamics)
- Rates of reaction of perovskite within solar reactor and reoxidizer (kinetics)
- Cycle efficiency and economics, accounting for (coupled to) chemistry of the perovskite

Accomplishing the Goal

- Material synthesis
- Experiments
- Modeling (commercial and home-made)

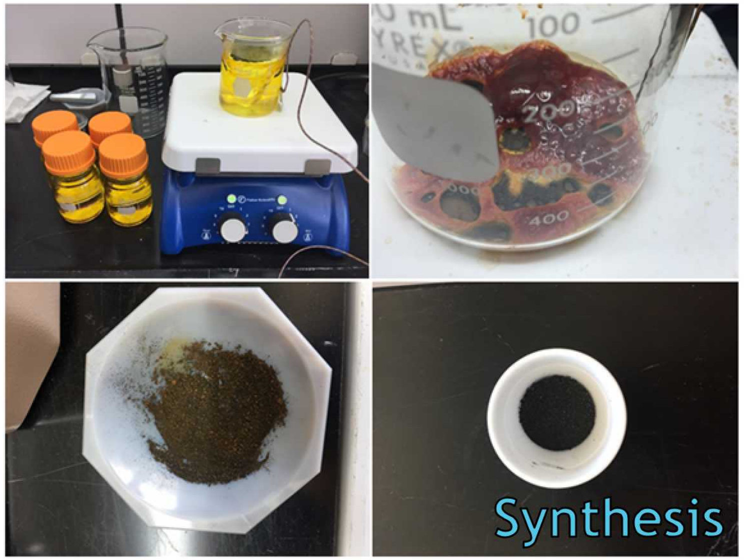
Synthesis and Characterization

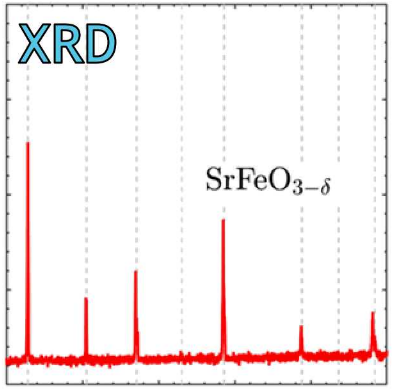
Lab scale, batch synthesis methods

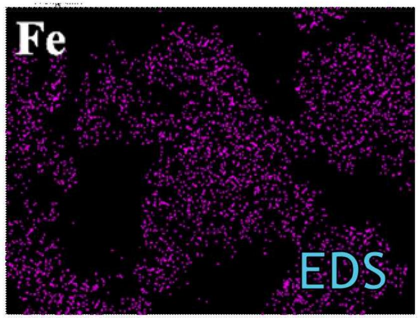
- Pure, single phase samples
- Controlled dopant concentrations

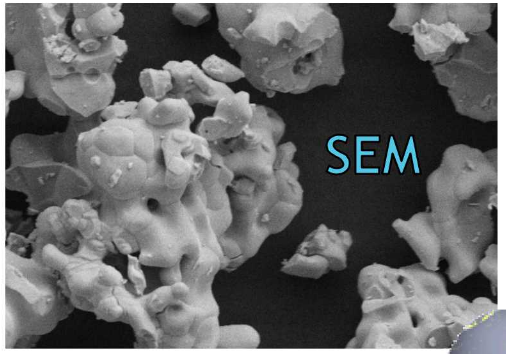
Characterization techniques

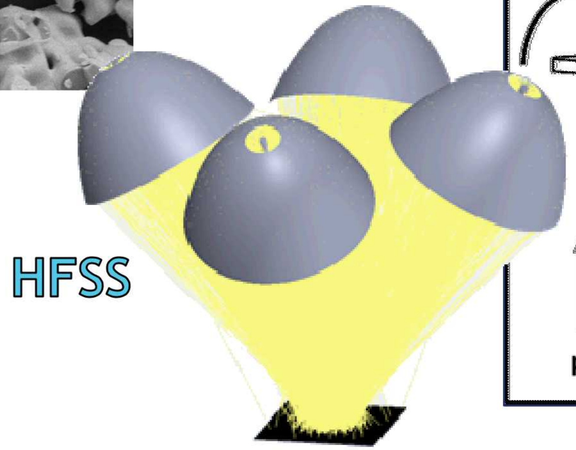
- **X-ray diffraction (XRD):** provides crystalline structure; can be matched to known materials to confirm sample composition
- **Scanning Electron Microscopy (SEM):** provides sample morphology, particle size, porosity
- **Electron-dispersive X-ray spectroscopy (EDS):** provides spatial elemental distribution, can be used to ensure samples are homogenous
- **Thermogravimetric Analysis (TGA):** Measures weight change; equipped with furnace, gas controls; can study thermodynamics and kinetics
- **High Flux Solar Simulator (HFSS):** Measures reactions under on-sun conditions

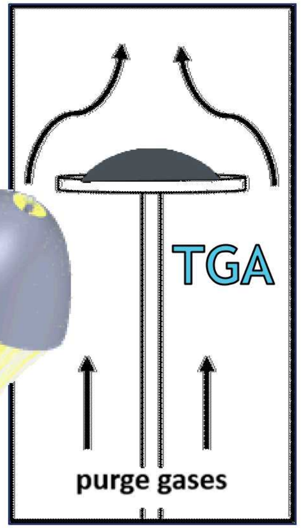










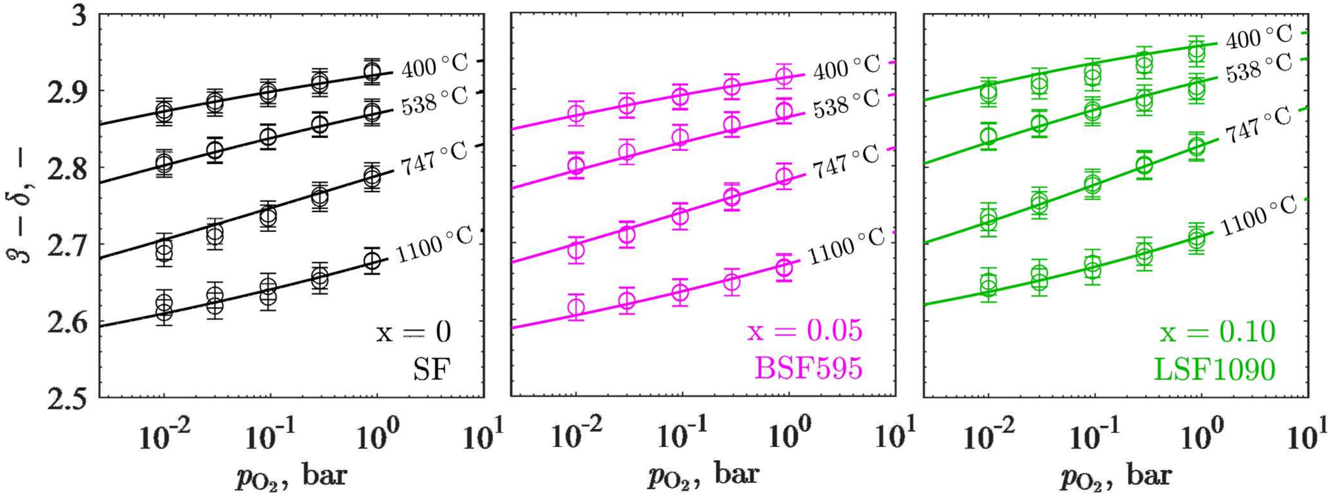


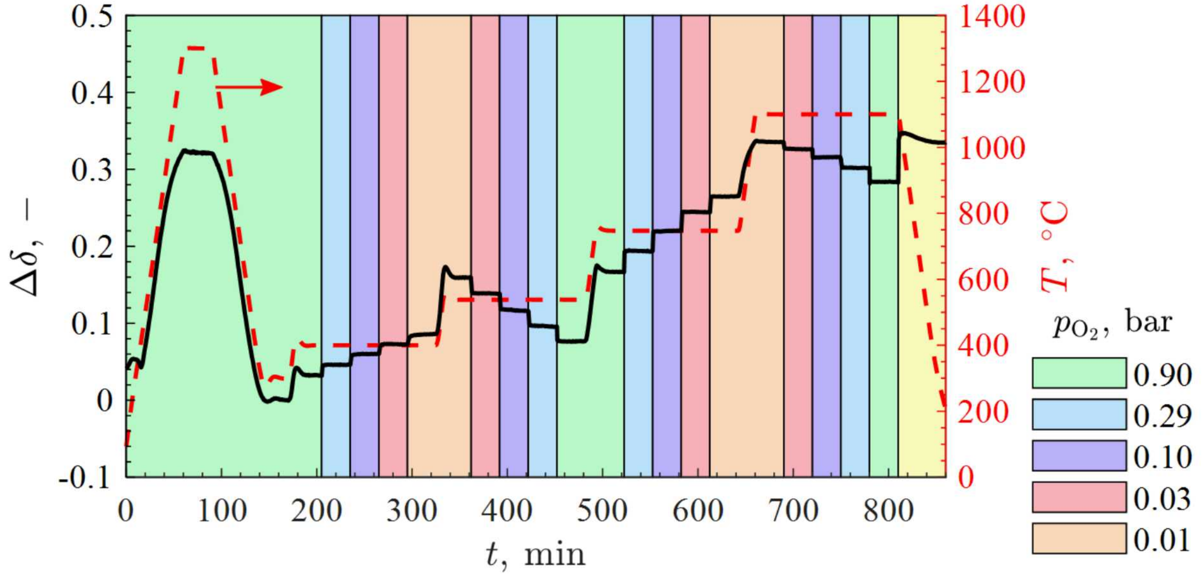
Redox Characterization and Modeling

TGA screening study identified substituted $SrFeO_3$ materials for air separation

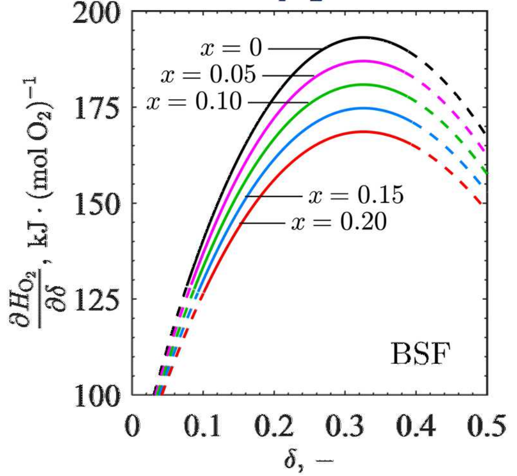
TGA equilibrium experiments used to model reaction extents, temperatures, and input energy requirements (enthalpy and entropy)

Reaction Extent

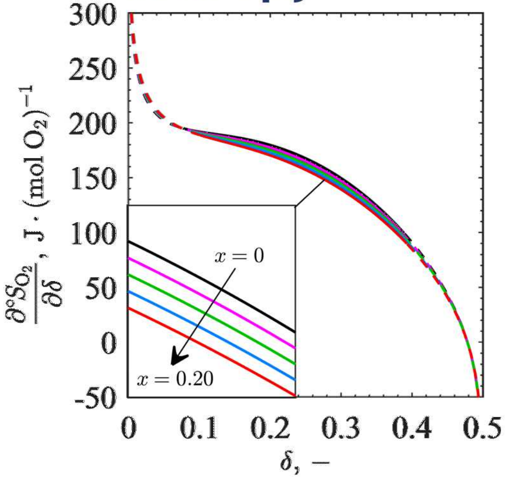




Enthalpy



Entropy



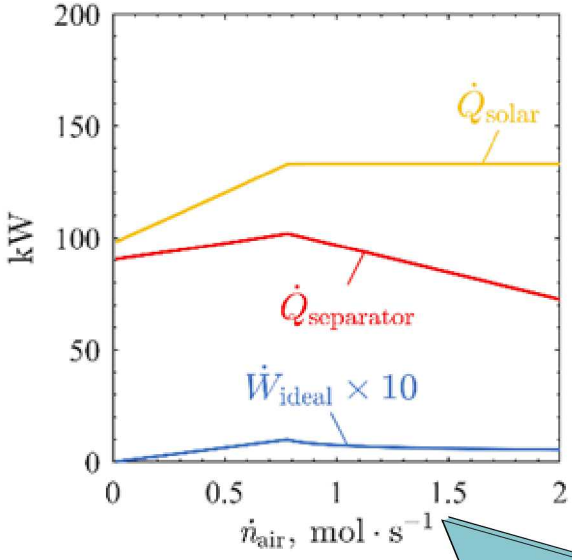
Redox Characterization and Modeling

Data were plugged into thermodynamic cycle model to predict air separation efficiency

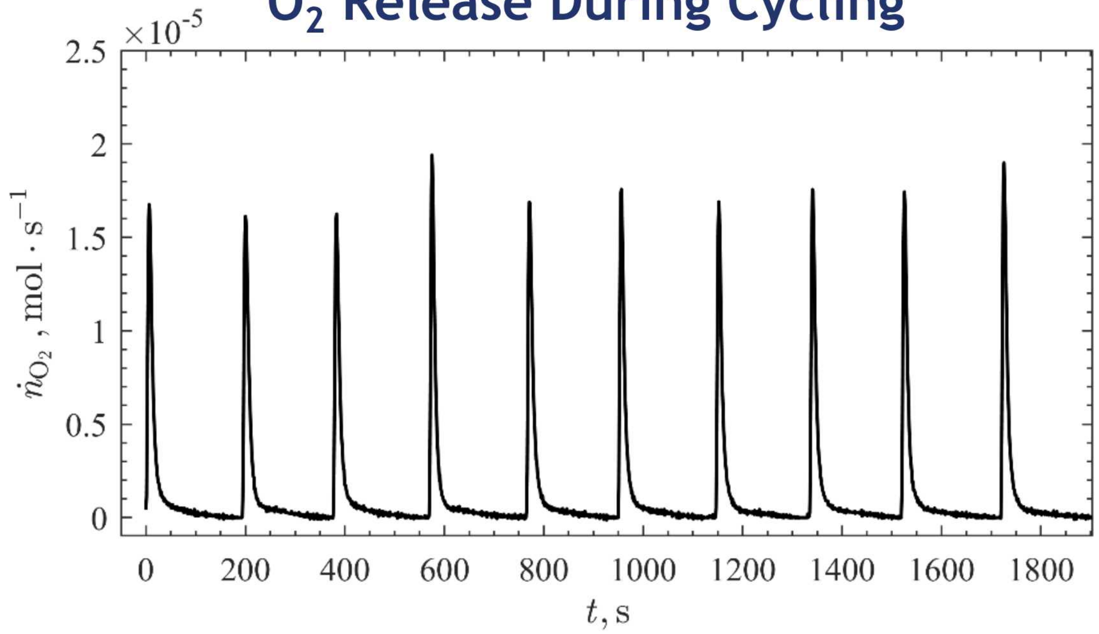
HFSS experiments were performed to study reduction kinetics, and TGA for oxidation kinetics

Cycling studies in HFSS and TGA showed that reaction was reversible and repeatable in the short-term

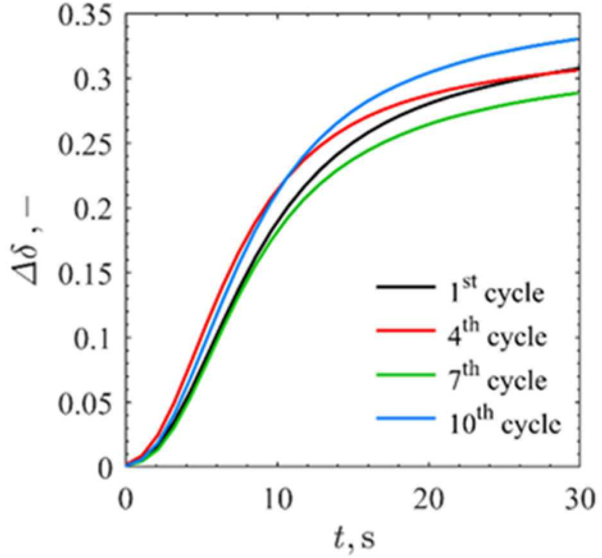
Cycle Inputs



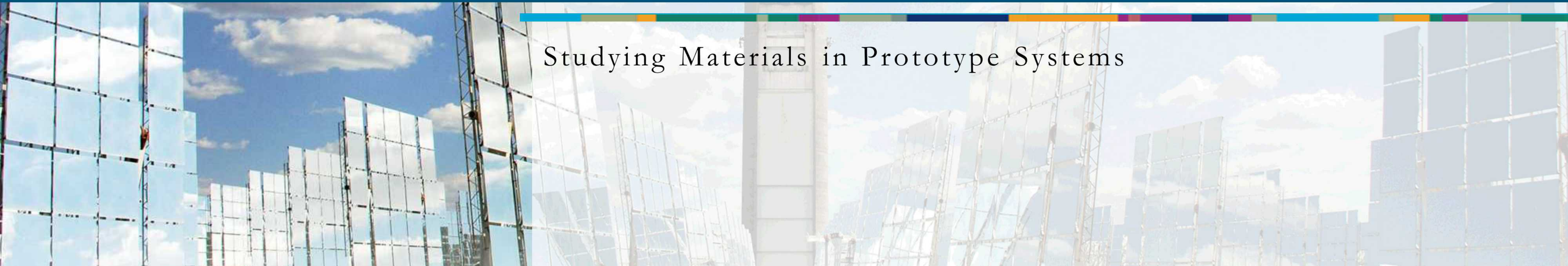
O_2 Release During Cycling



Reaction Time



Future Work



Studying Materials in Prototype Systems

Next Steps

Build prototype reactors to study air separation process on-sun

Study longer-term material stability with TGA experiments

Pair thermodynamic models with cost studies to predict process technoeconomics

Design process for producing NH_3 from the N_2 and H_2

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