

Solar-Thermal Ammonia Production (STAP)

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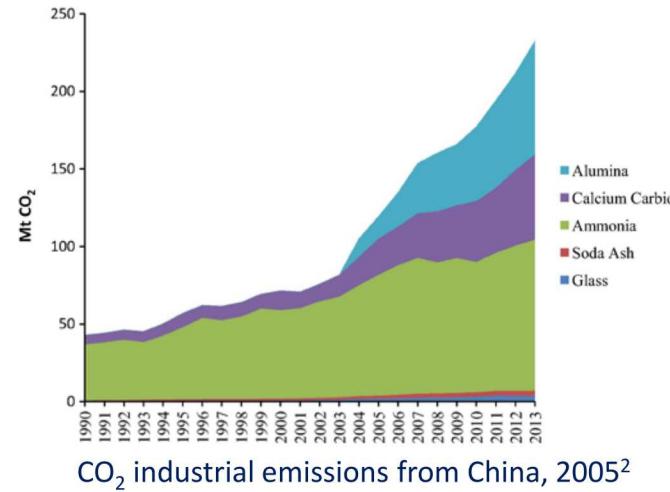
The Team

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- Georgia Institute of Technology: Peter Loutzenhiser, H. Evan Bush
- Arizona State University: Ellen Stechel, Ivan Ermanoski
- Acknowledgments: James Miller, Sasha Egan

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The Challenge

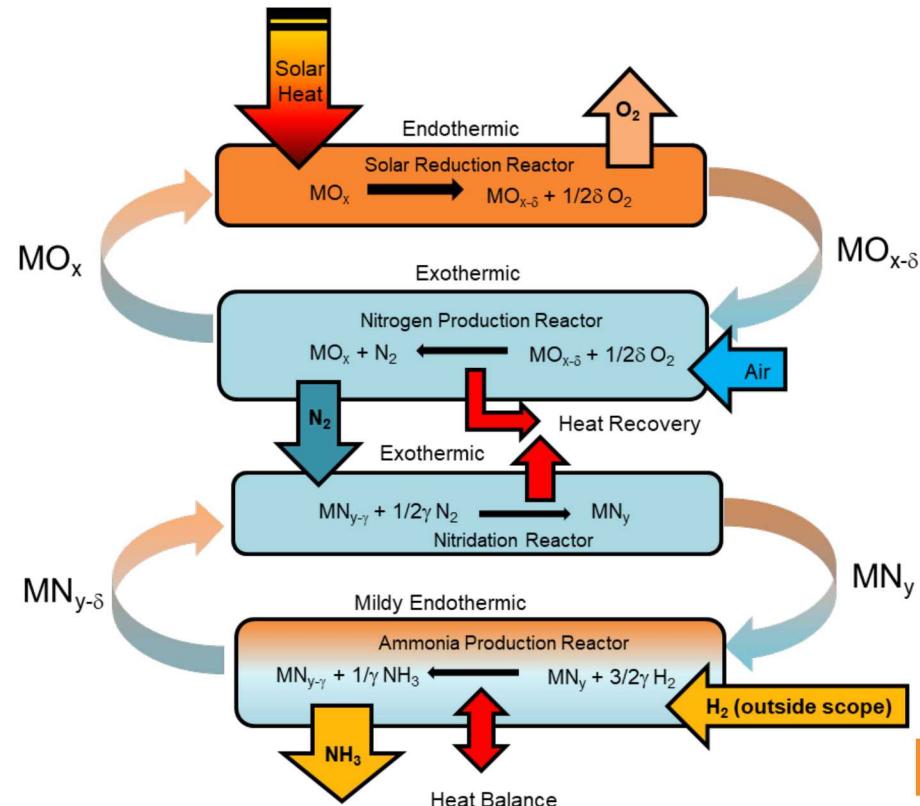
- Ammonia (NH_3) is an energy-dense chemical and a vital component of fertilizer
 - Potential to be used as an alternative fuel and/or in CSP thermochemical energy storage
- NH_3 currently synthesized via the Haber-Bosch process from natural gas
 - Requires high pressures (15-25 MPa) and moderately high temperatures (400-500 °C)
 - Capital and carbon intensive; practical in large facilities
 - Consumes > 1% of global energy use¹
 - Process including H_2 production generates about 2.3 t of fossil-derived CO_2 per t of NH_3 ,² and expends 2% of the world's energy budget from natural gas³
- The US imported almost 4 million metric tons of ammonia (28% of its total use) in 2016⁴



The Solution

A solar thermochemical looping technology to produce and store nitrogen from air for the subsequent production of ammonia via a novel synthesis pathway

- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint using renewable H₂
- The process consumes neither the oxide nor the nitride particles, which actively participate in the reactions, cyclically



Technical Approach

Synthesis and characterization of oxides for N₂ recovery from air

- Maximize oxygen capacity and minimize reduction endotherm
- Measure redox capacity as a function of T & pO₂, reaction kinetics, reaction endotherm, heat capacity, and cyclability

Synthesis and characterization of nitrides for NH₃ production

- Systematic investigation of complex nitrides that promote nitrogen vacancies
- Measure rates of nitridation and reduction and NH₃ yield

Process and reactor design, development, and demonstration

- Robust heat and mass transfer models enable parametric studies of operating conditions
- Receiver and reactor design based on models
- Fabrication and lab-scale testing

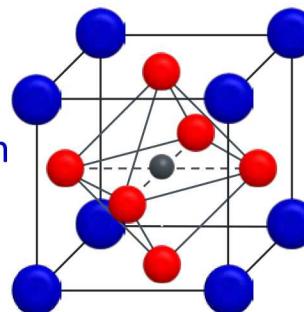
Full system and techno-economic analyses

- Underpins other thrusts
- Interrelation between component and system designs, operating conditions, mass and energy flows, and normalized costs
- Continuously update and refine based on experimental and modeling results

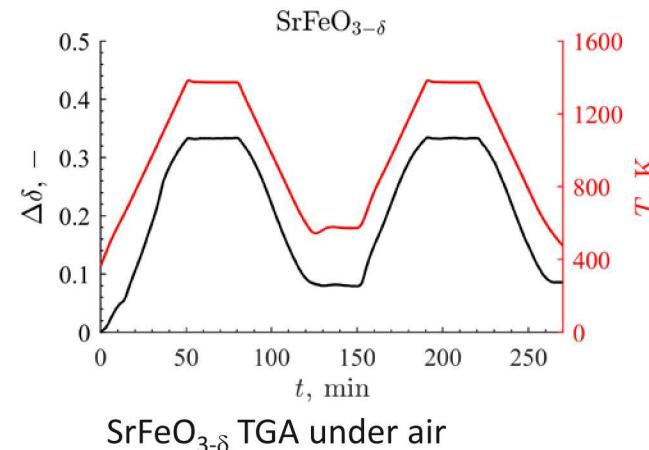
MIECs for N₂ Purification

- Mixed Ionic-Electronic Conductors (MIECs) allow for fast redox kinetics, large and tunable oxygen non-stoichiometries
- The optimized material will balance kinetics, temperature, and enthalpy to maximize δ , minimize ΔT , maximize kinetics
 - Match to temperature/pO₂ regimes

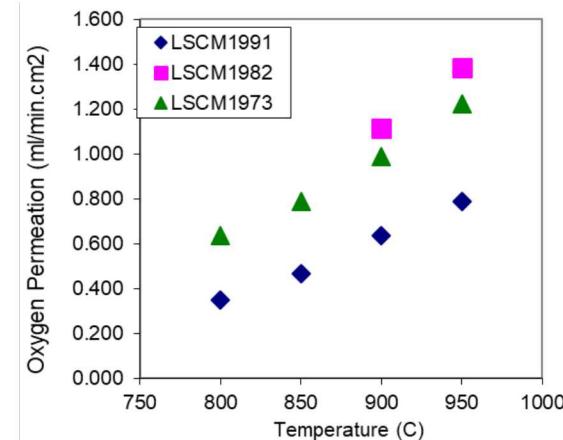
SrFeO₃
Blue — Strontium
Gray — Iron
Red — Oxygen



SrFeO_{3- δ} perovskite structure



SrFeO_{3- δ} TGA under air

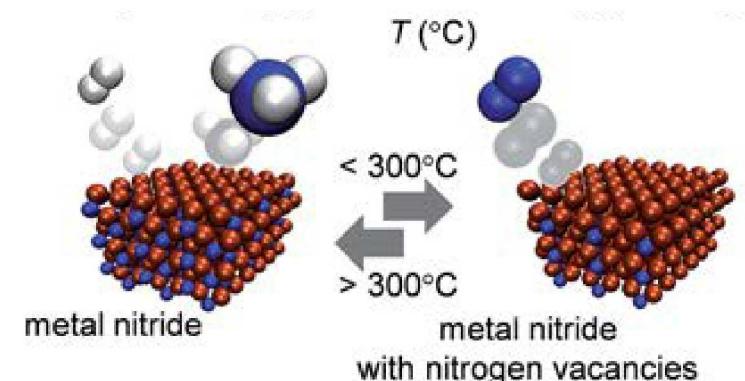


Oxygen permeation vs T through pressed disk across pO₂ gradient (air and He)

Metal Nitrides (MN) for NH_3 Production

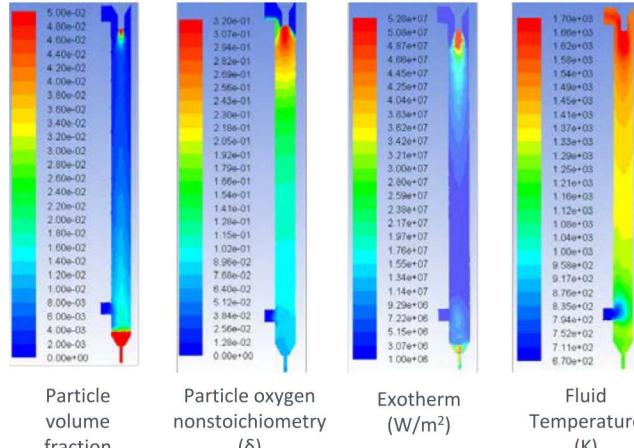
Identification of suitable MN is highest risk/highest reward aspect of STAP

- Based on thermodynamics, successful material likely to be complex nitrides
 - Induce nitrogen vacancies through doping (MIEC analogue)
 - Line compounds limited, aren't tunable
 - Beginning with promising MN compounds (Mn, Mo, Co, Cr) systematically synthesize doped compounds and measure effect on nitridation/ NH_3 production
 - Utilize thermodynamic models to predict thermodynamically-favorable reactions and guide syntheses



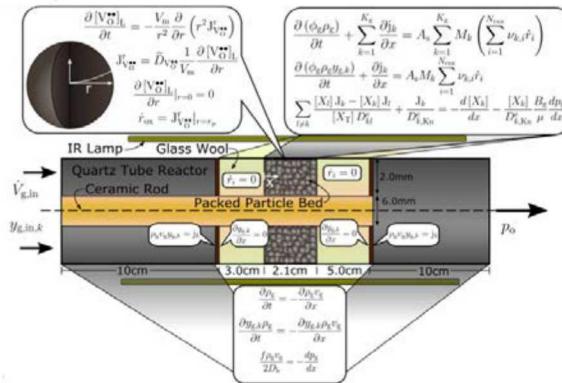
Multi-physics Model Requirements

Detailed CFD Modeling of Multiphase Reactors



Babiniec, "Considerations for the Design of a High-Temperature Particle Reoxidation Reactor for Extraction of Heat in Thermochemical Energy Storage Systems," *ASME P&E Conference*, 2016.

Transient Modeling of Packed Bed Reactors

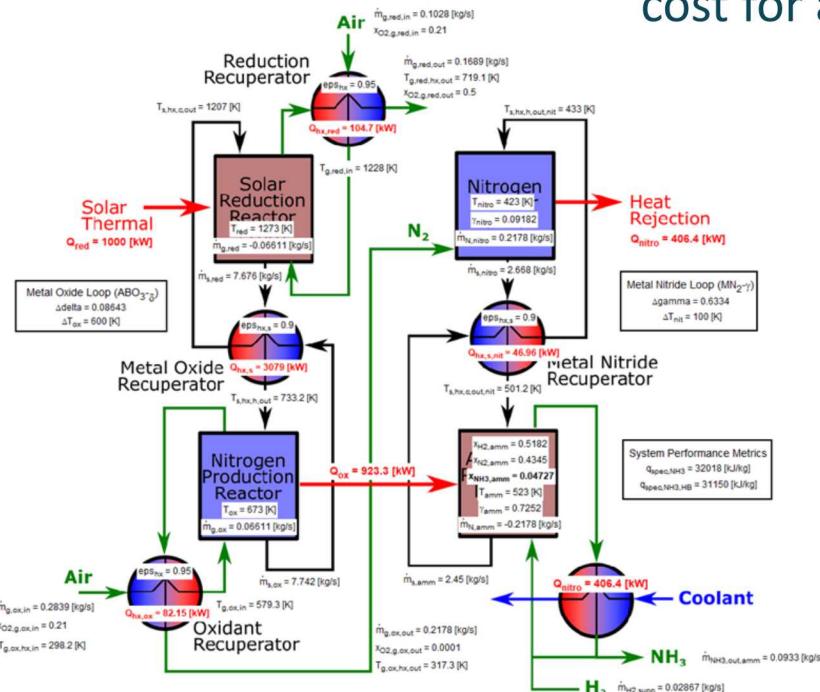


Albrecht, "Multiscale modeling and experimental interpretation of perovskite materials in thermochemical energy storage and conversion for application in concentrating solar power," *PhD Thesis*, 2016.

- System and reactors are highly coupled and thermally integrated
- Require multi-physics models that can capture:
 - Multi-phase chemically reacting flow
 - Heat transfer (particle-gas, particle-particle, particle-wall, radiation)
 - Equilibrium constrained chemical reaction

System and Techno-Economic Analyses (TEA)

Develop and refine throughout the project, systems and techno-economic models to guide materials choices, reactor design, and determine projected cost for a scaled-up system



Preliminary System Modeling

- Operating temperature and pressure of nitride reactors will be an important analysis
- Heat recuperation on oxide side important for high efficiency (similar to solar fuels)
- Thermally integrating oxide and nitride sides important for high efficiency
- Nitride material thermodynamics require more development of optimal parameters

Outcomes

- Demonstrate the feasibility of a solar thermochemical looping technology to produce and store nitrogen (N_2) from air for the subsequent production of ammonia (NH_3) via an advanced two-stage process
- Greatly reduce, or eliminate altogether, the large carbon footprint created by the Haber-Bosch process, greatly decreasing CO_2 emissions
- Demonstrate feasibility and cost benefit of coupling STAP process to a CSP plant and a path to < \$500 per metric ton of NH_3
- Impact: Feed the world with a fossil fuel-free, renewable energy pathway to ammonia synthesis

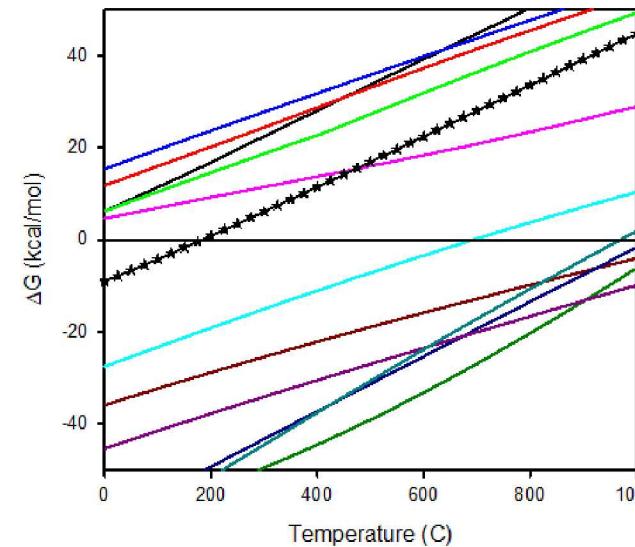
Thank You



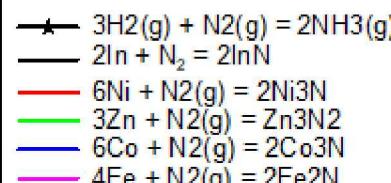
Thermodynamics: The Challenge of NH₃ Synthesis

Identification of suitable MN is highest risk/highest reward aspect of STAP

- Data for 35 different metals reviewed (subset plotted here)
- Includes metals where nitridation is favorable at all T (**Group A**) and several where formation is not favorable at any T (**Group B**)
- Tune ΔH through combinations of metals from Groups A and B, e.g. CoMo, NiMo, FeMo



Group A: NH₃ favored



Group B: Nitridation favored

