U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP Program Summit 2019

Solar-Thermal Ammonia Production (STAP)

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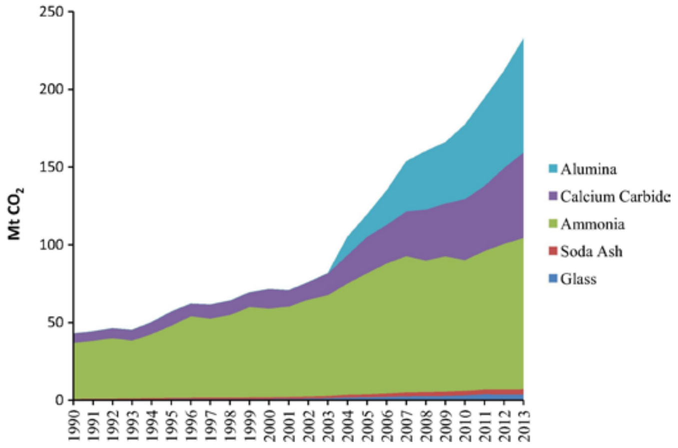
The Challenge

- 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 ^oC)
    - Capital and carbon intensive; practical in large facilities
  - Consumes > 1% of global energy use[1]
  - 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 gas[3]
- The US imported almost 4 million metric tons of ammonia (28% of its total use) in 2016[4]



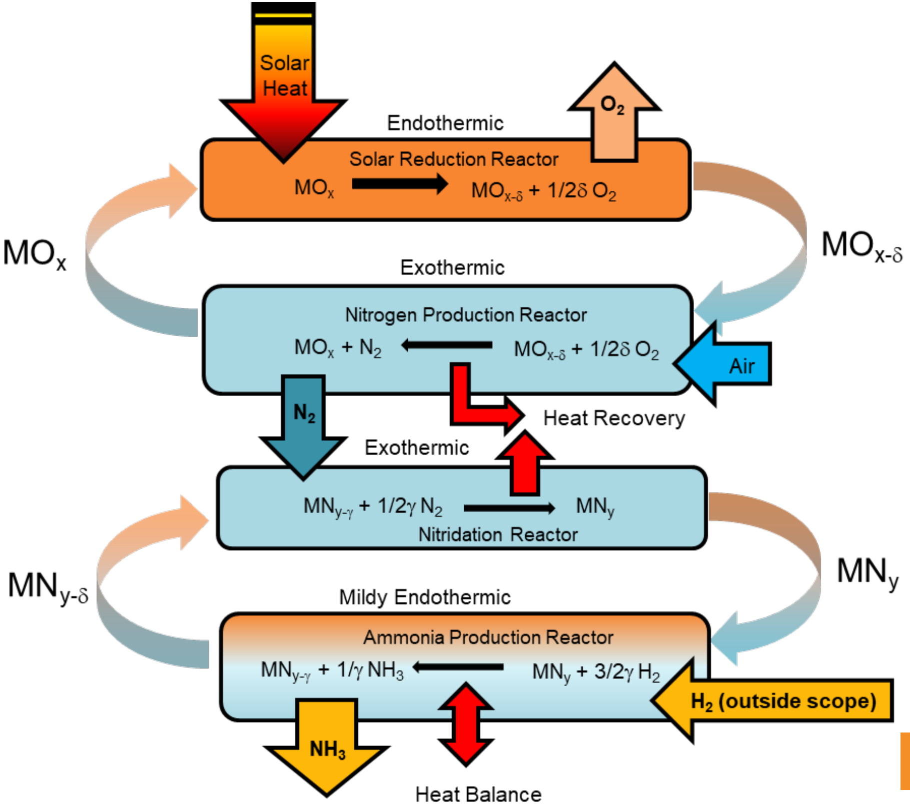
CO_2 industrial emissions from China, 2005[2]

[1]Erisman, et al. Nat. Geosci. 2008, 1, 636−639. [2]Rafiqul et al, Energy, 2005; 30(13), 2487. [3]Ritter, Chem Eng News. 2008; 86(33),53. [4]U.S. Geological Survey, Mineral Commodity Summaries, January 2017.

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 H_2
- 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 N_2 recovery from air	Synthesis and characterization of nitrides for NH_3 production	Process and reactor design, development, and demonstration	Full system and techno-economic analyses
• Maximize oxygen capacity and minimize reduction endotherm • Measure redox capacity as a function of T & pO_2, reaction kinetics, reaction endotherm, heat capacity, and cyclability	• Systematic investigation of complex nitrides that promote nitrogen vacancies • Measure rates of nitridation and reduction and NH_3 yield	• Robust heat and mass transfer models enable parametric studies of operating conditions • Receiver and reactor design based on models • Fabrication and lab-scale testing	• 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 N_2 Purification

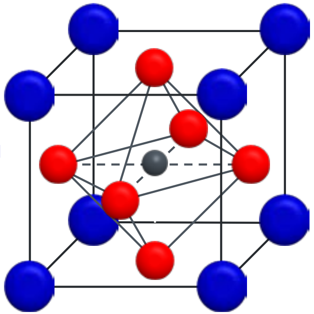
- Mixed Ionic-Electronic Conductors (MIECs) allow for fast redox kinetics, large and tunable oxygen non-stoichiometries
- The optimized material will balance kinetics, temperature, and enthalpy to maximize δ, minimize ΔT, maximize kinetics
  - Match to temperature/pO_2 regimes

$SrFeO_3$

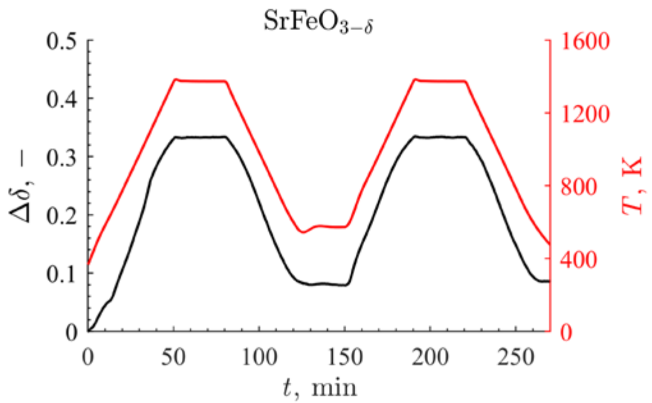
Blue — Strontium

Gray — Iron

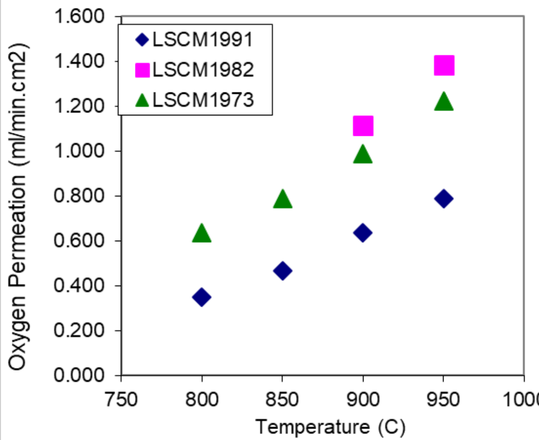
Red — Oxygen



$SrFeO_{3-\delta}$ perovskite structure



$SrFeO_{3-\delta}$ TGA under air

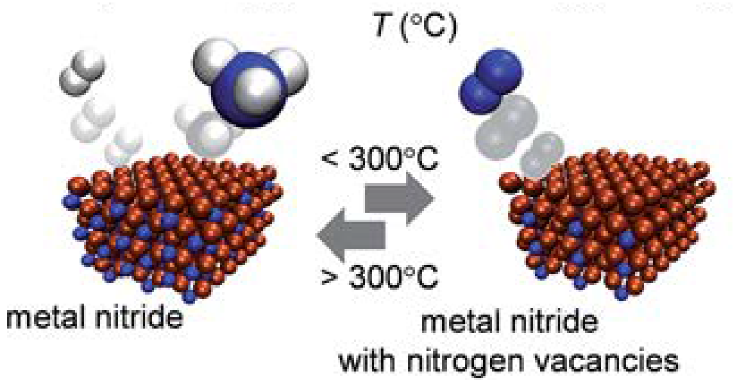


Oxygen permeation vs T through pressed disk across pO_2 gradient (air and He)

Metal Nitrides (MN) for NH_3 Production

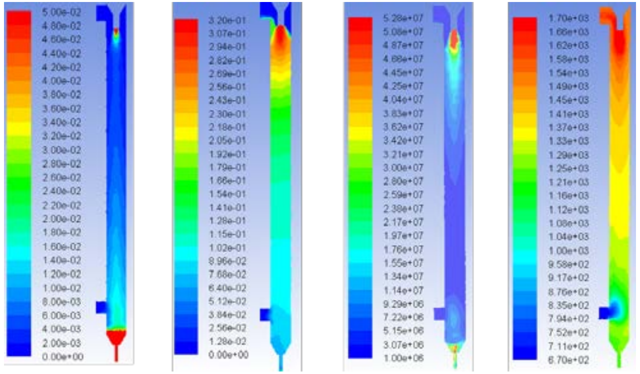
Identification of suitable MN is highest risk/highest reward aspect of STAP

- 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

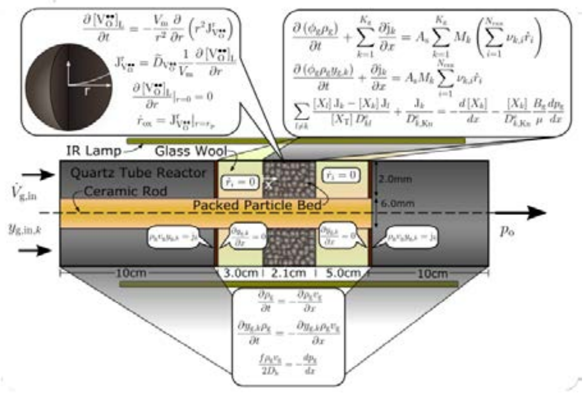
Detailed CFD Modeling of Multiphase Reactors



Particle volume fraction | Particle oxygen nonstoichiometry (δ) | Exotherm (W/m²) | Fluid Temperature (K)

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

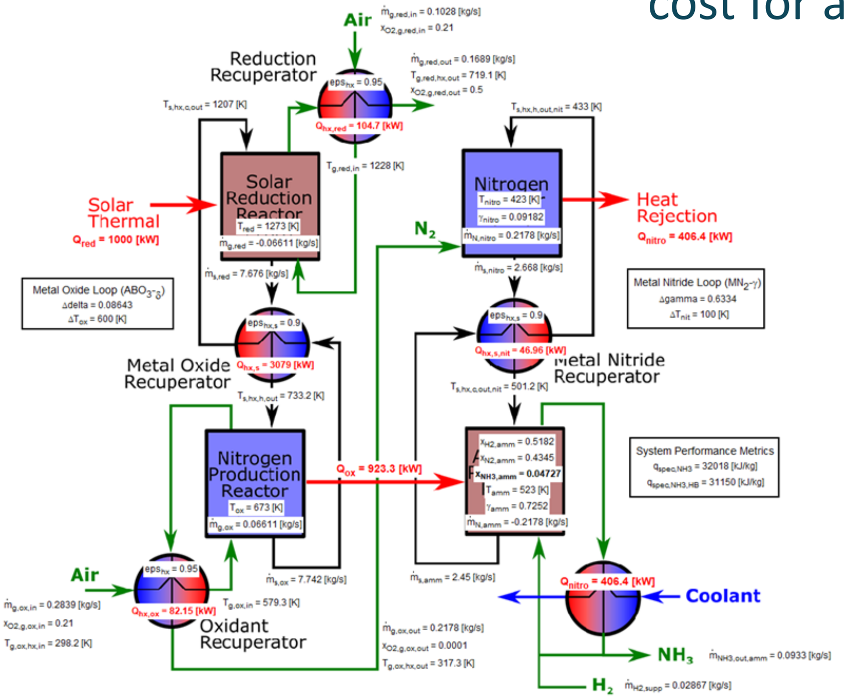


Albrecht, "Multiscale modeling and experimental interpretation of perovskite materials in thermochemical energy storage and conversion for application in concentrating solar power," *PhD Thesis*, 2016.

- 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

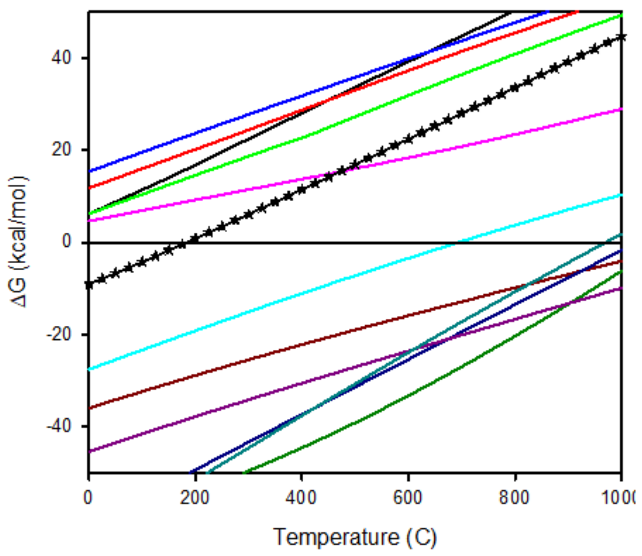
- Demonstrate the feasibility of a solar thermochemical looping technology to produce and store nitrogen (N_2) from air for the subsequent production of ammonia (NH_3) via an advanced two-stage process
- Greatly reduce, or eliminate altogether, the large carbon footprint created by the Haber-Bosch process, 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

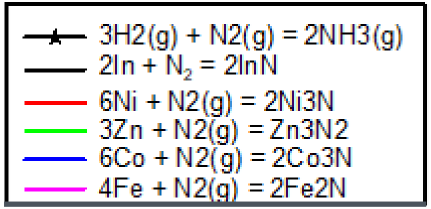
Thermodynamics: The Challenge of NH_3 Synthesis

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: NH_3 favored



Group B: Nitridation favored