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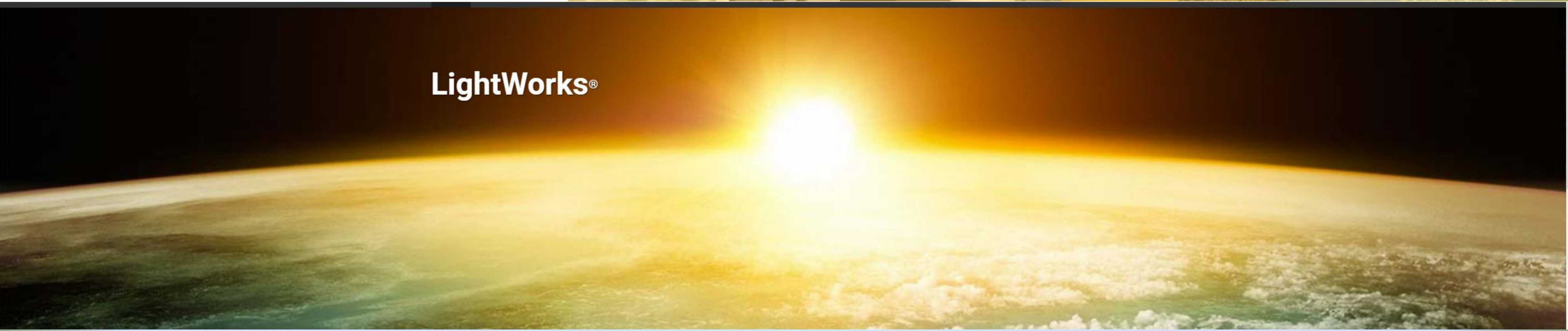

Solar-driven nitrogen separation process from air based on two-step thermochemical cycle: thermodynamic analysis

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Solar thermochemical ammonia production

Ammonia synthesis:

$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$

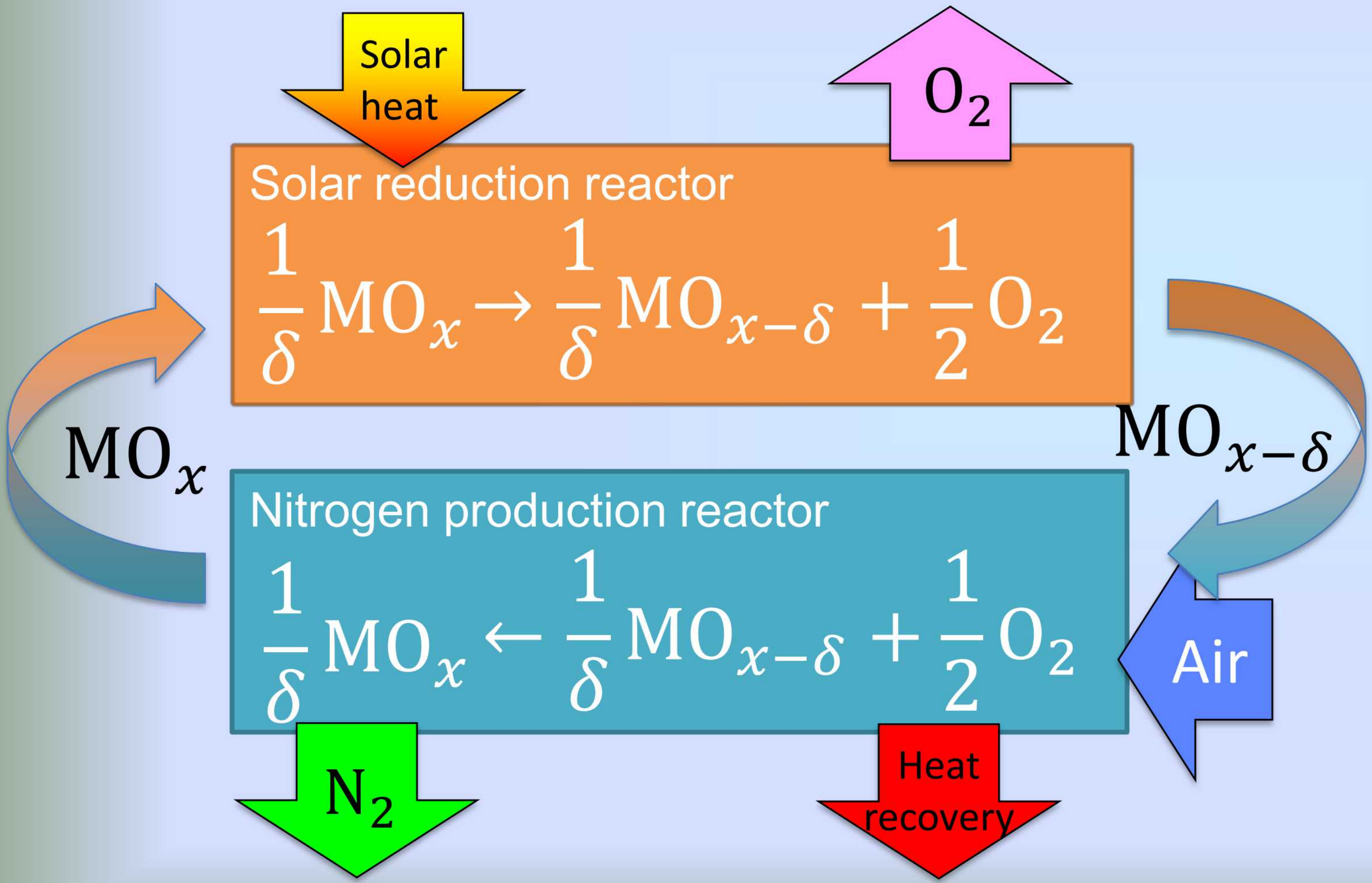
Air ≈ 79% N_2 + 21% O_2

- Ammonia is the second most produced industrial chemical
- It is industrially produced via the Haber–Bosch process
- It is responsible for over **1.4%** of global CO_2 emissions

CO_2-neutral ammonia is possible!

- N_2 separation from air typically consumes natural gas producing a lot of CO_2
- Work here focuses on N_2 separation from air, based on a solar driven two-step thermochemical metal oxide (MO_x) cycle.

Two-step thermochemical cycle



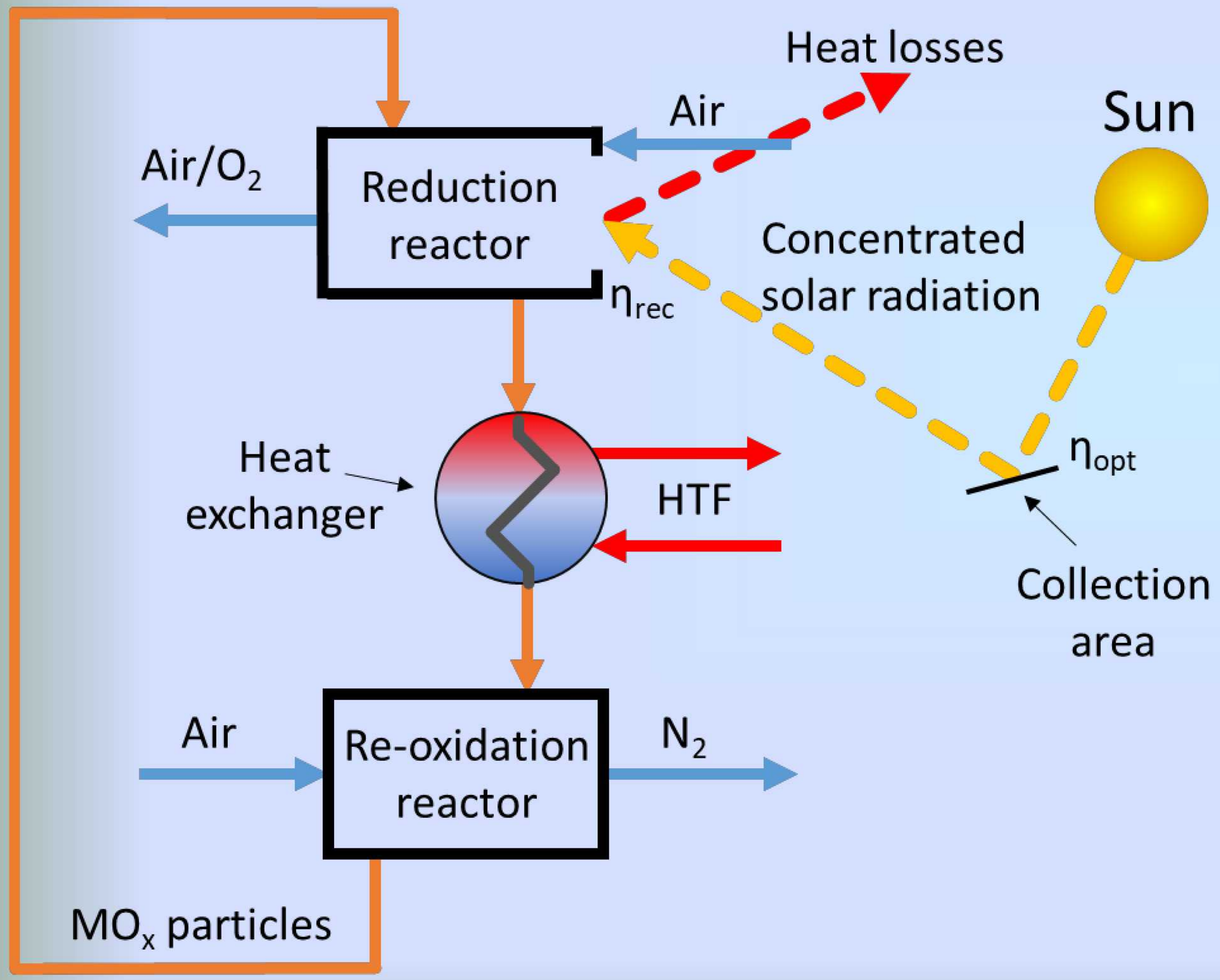
Reduction:

- $T_R = 600 - 1000\ °C$
- $p_{O_2} = 21\ kPa$

Re-oxidation:

- $T_{OX} = 400 - 600\ °C$
- $p_{O_2,out} = 10\ Pa$

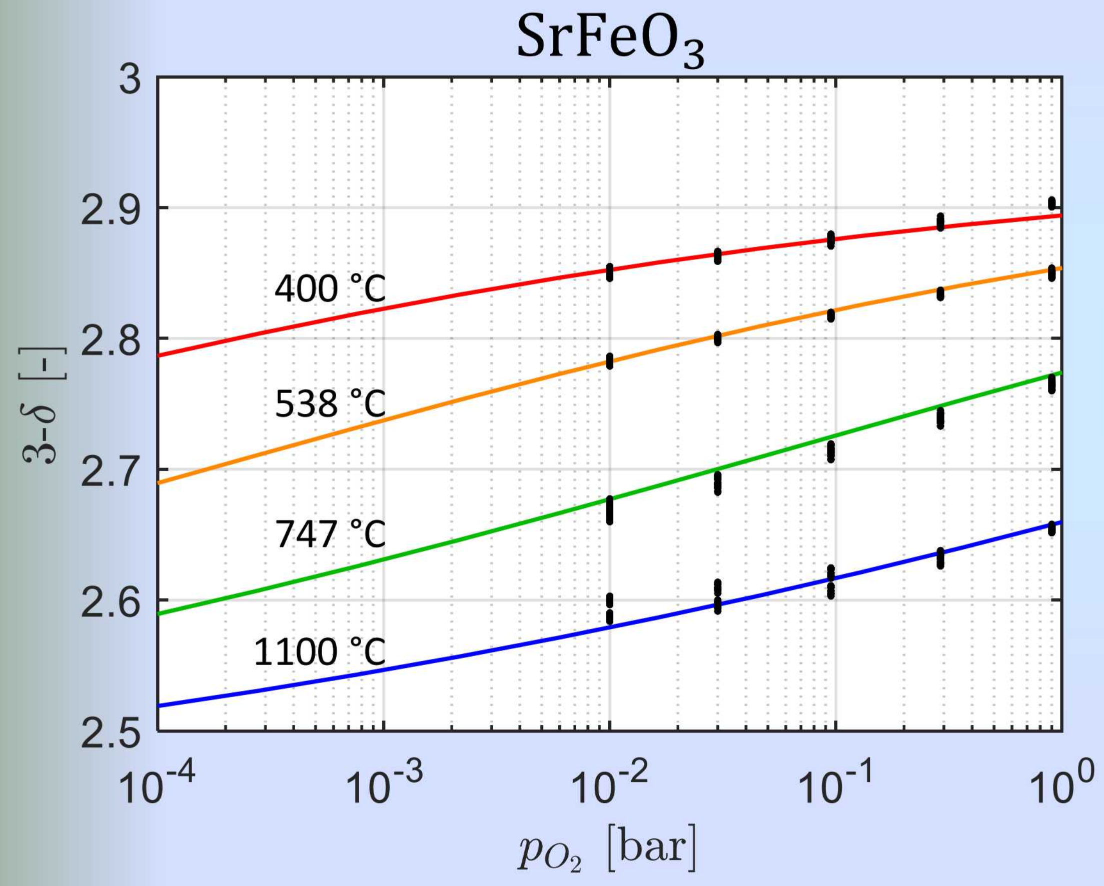
System description



Main features:

- Moving-particles
- Windowless receiver
- Countercurrent reactors
- Air sweeping (both reactors)
- Heat recovery (to be used in other sub-processes)

Material analysis



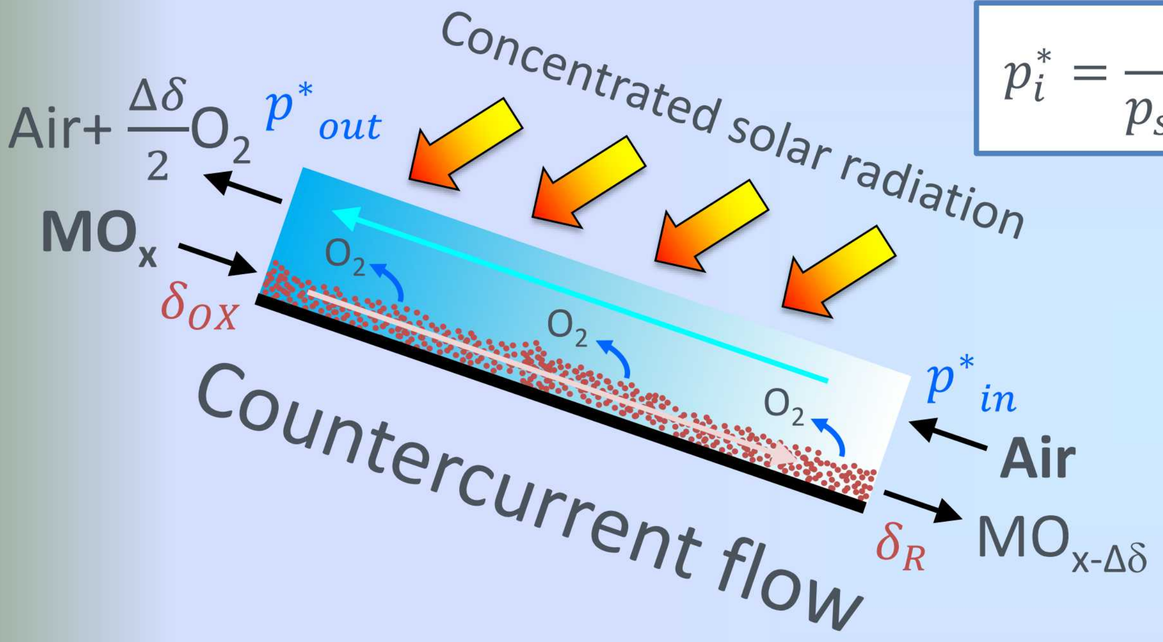
Metal oxide candidates:

- $SrFeO_3$
- $Ba_xSr_{1-x}FeO_3$
- $La_xSr_{1-x}FeO_3$

- Ba and La substitutions: 5%, 10%, 15% and 20%
- Compound energy formalism used to describe the chemical equilibrium, good agreement with experimental data
- This analysis is explained in detail by **H. Evan Bush** in "*Substituted $SrFeO_{3-\delta}$ Thermodynamics for Solar Air Separation*" at SolarPACES 2020

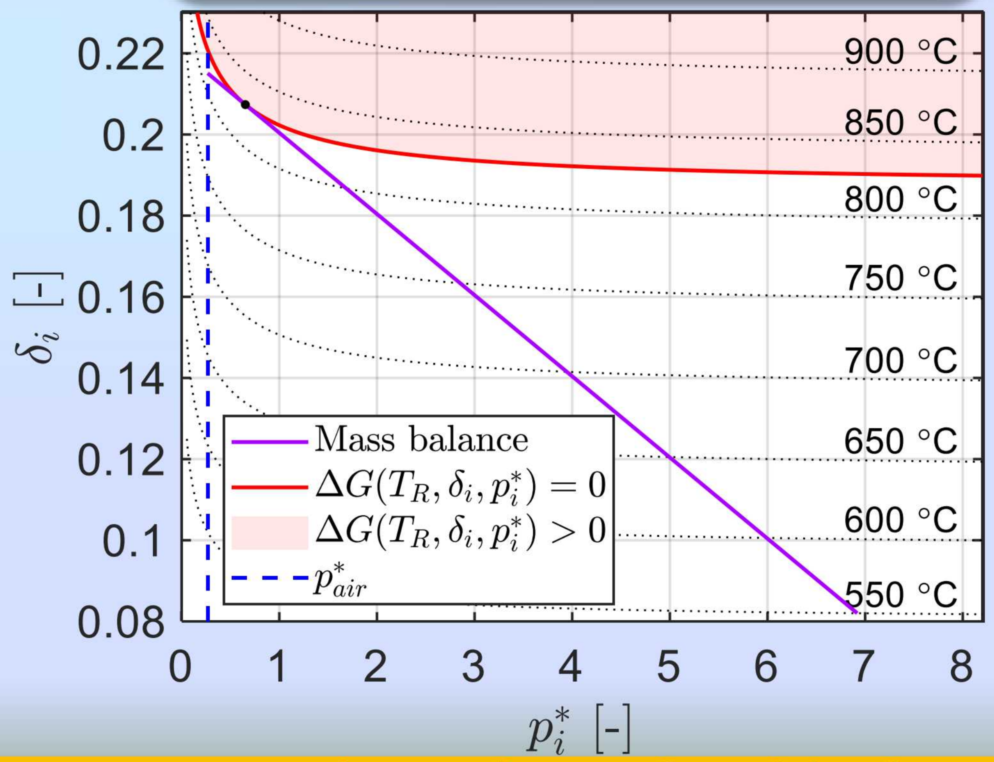
Particle reactor analysis: reduction

$$p_i^* = \frac{p_{O_2,i}}{p_{sys} - p_{O_2,i}}$$



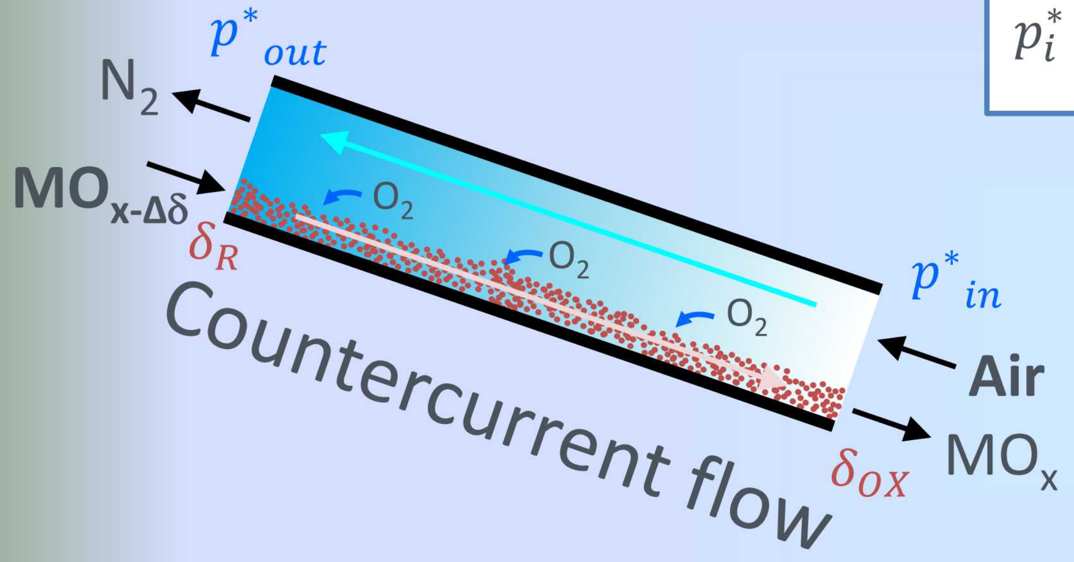
$\delta - p^*$ coordinates:

- Mass conservation: depicted by straight lines
- Gibbs criterion: $\Delta G \leq 0$



- The line slope is determined by n_{N_2}/n_{MO_x}
- Isothermal operation: $T_R = \max T_i\,(\delta_i, p_i^*)$
- Equilibrium at one single point

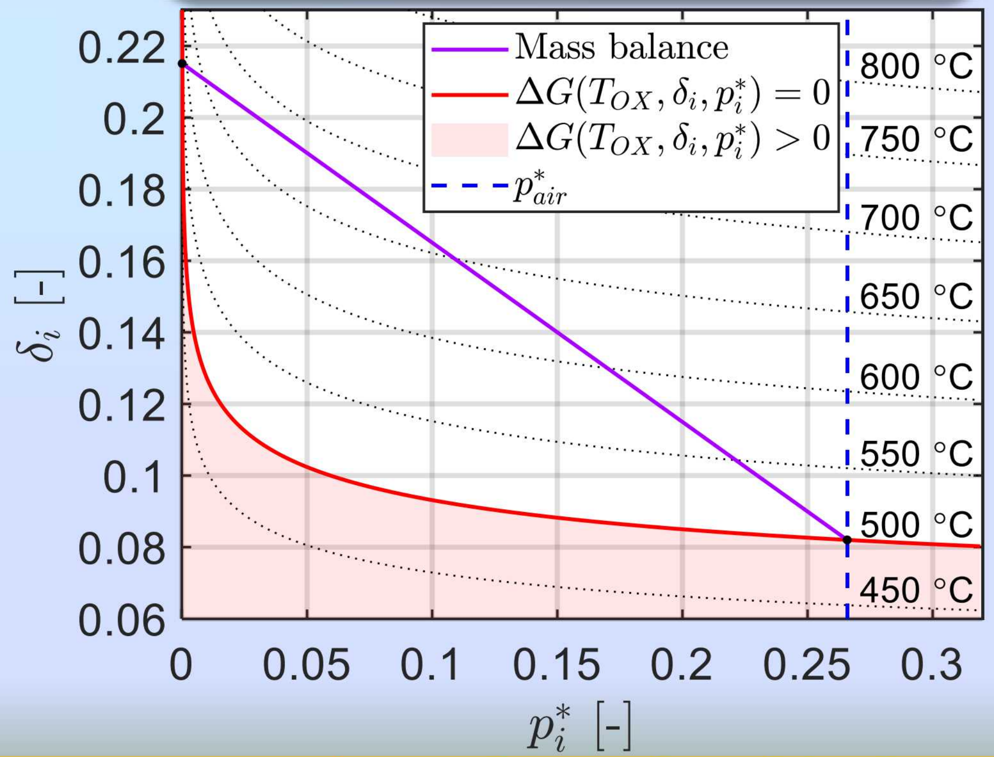
Particle reactor analysis: re-oxidation



$$p_i^* = \frac{p_{O_2,i}}{p_{sys} - p_{O_2,i}}$$

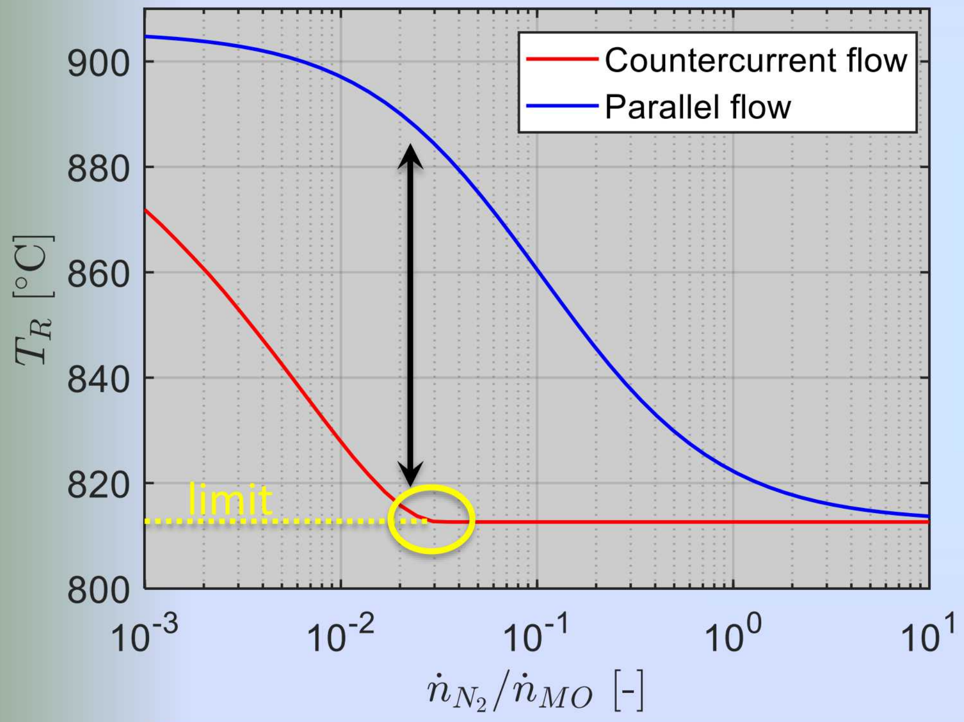
$\delta - p^*$ coordinates:

- Mass conservation: depicted by straight lines
- Gibbs criterion: ΔG ≤ 0



- The line slope is determined by n_{N_2}/n_{MO_x}
- Isothermal operation: $T_{OX} = \min T_i\,(\delta_i, p_i^*)$
- Equilibrium at both ends

System modeling: impact of sweeping ratio



Operating conditions:

Material: $SrFeO_3$

$T_{OX} = 500°C$

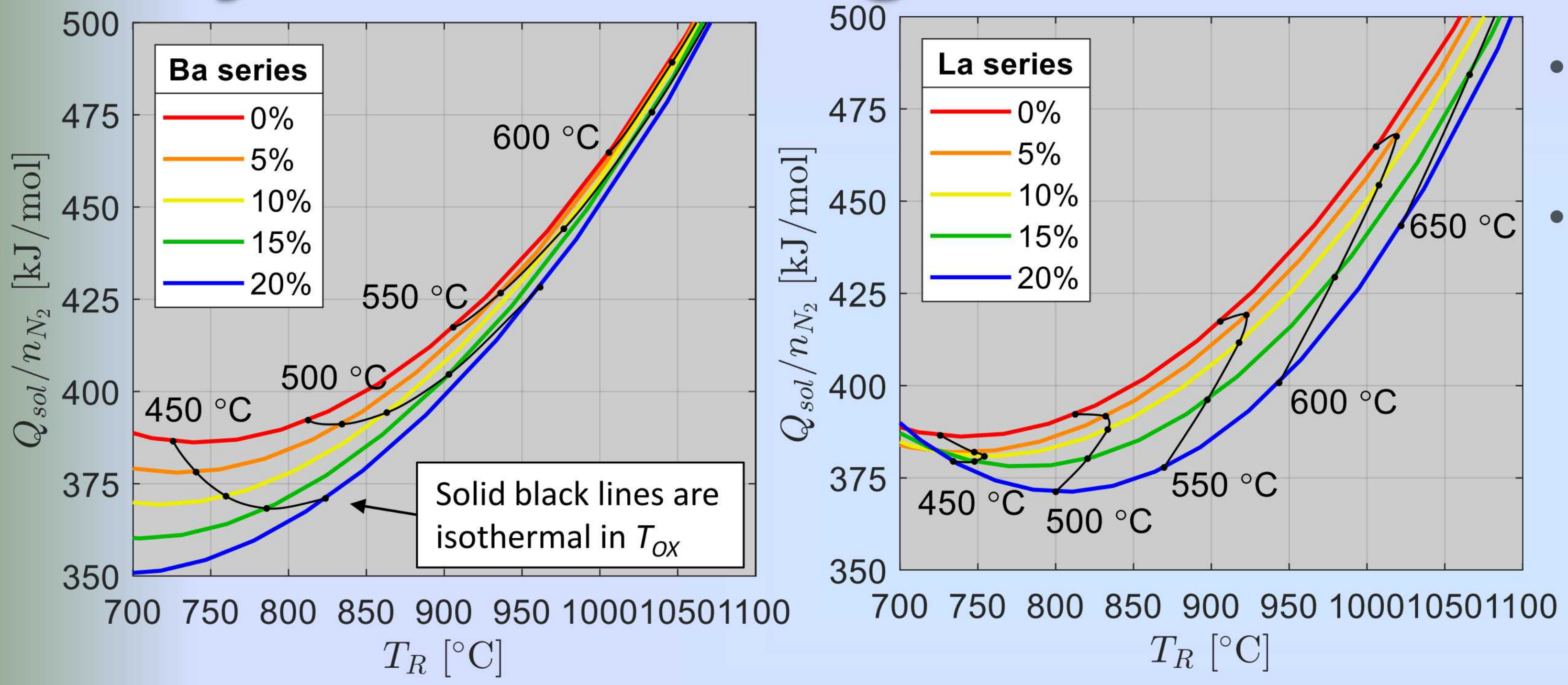
$p_{O_2,in} = 21\ kPa$ ← Air

$p_{O_2,out} = 10\ Pa$ ← N_2 produced purity

- Parallel flow leads to a large underutilized chemical potential along the reaction coordinate
- The countercurrent configuration can utilize all the chemical potential of the material

Countercurrent reactor achieves the thermodynamic limit with very low sweep flows

System modeling: material testing, impact of T_{OX}



- We examined the full measured series of Ba and La in the system model
- We have explored the full operating range fixing $p_{O_2,out} = 10$ Pa and finding all solutions such that T_R-T_{OX} meet the fixed value

- Lower T_R, lower Q_{sol}/n_{N2}
- T_{ox} is the key constraining variable to determine optimal operating conditions

The lower T_{ox}, the slower the kinetics: how low is feasible?

Ba series: appealing if the entire cycle is in **lower temperature** range (T_{OX} < 450 °C)

La series: appealing if the entire cycle is in **higher temperature** range (T_{OX} > 500 °C)

Summary

- A receiver/countercurrent reactor can utilize all the chemical potential of the material using air as the sweep gas
- Ba-substituted or La-doped $SrFeO_3$ can improve the system performance
- T_{OX} is the key constraining variable to determine the optimal operating conditions

Thank you for your attention!!

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If you like this work… there is more Solar Thermochemical Ammonia Production in SolarPACES 2020:

Substituted Strontium Ferrite Thermodynamics for Solar Air Separation
H. Evan Bush

A Low-pressure Reactor Design for Solar Thermochemical Ammonia Production
Xiang Gao

Modeling of Concentrating Solar Reduction Reactor for Oxygen Separation from Air
Matt Kury

Experimental Screening of Substituted $SrFeO_{3-\delta}$ for Solar Thermochemical Air Separation
Tyler Farr