Demonstration of materials and processes for solar thermochemical air separation

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Objective

- Ammonia (NH_3) is one of the most produced chemicals in the world due to its application in fertilizer production
- NH_3 production is very energy-consuming

➔ Goal: sustainable production of ammonia using concentrated solar energy

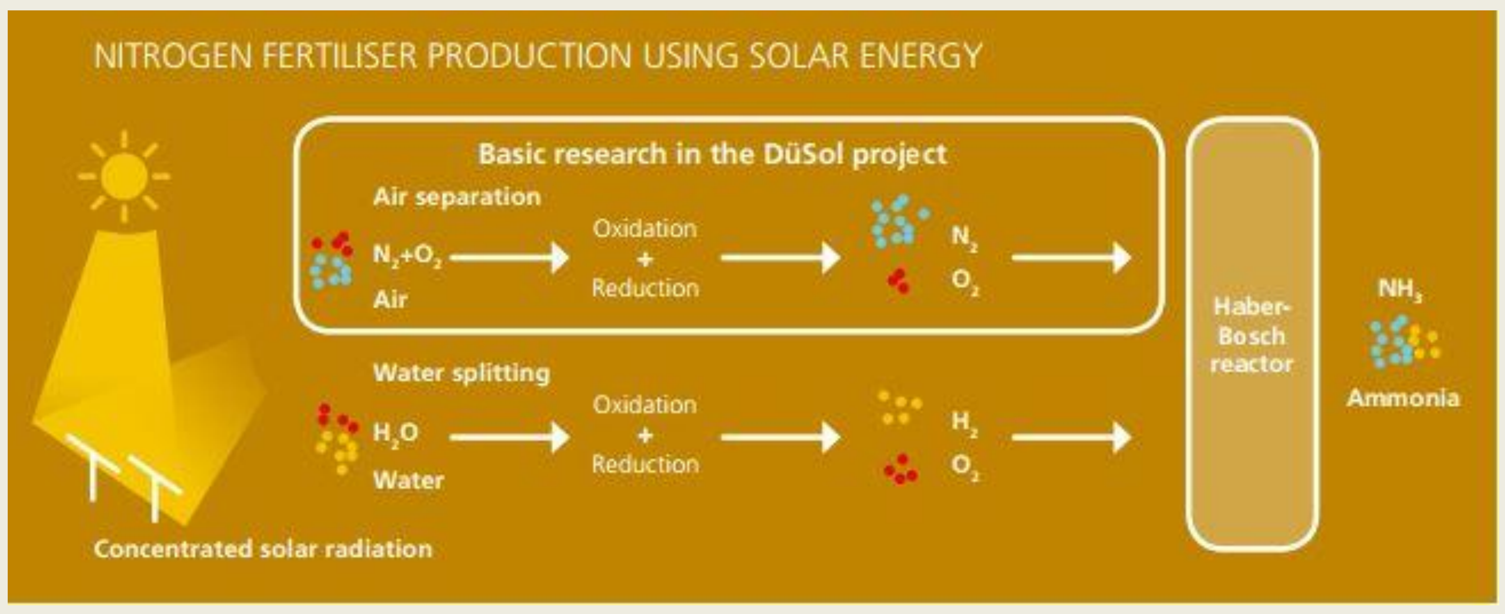
➔ Development of thermochemical air separation methods for application in industry

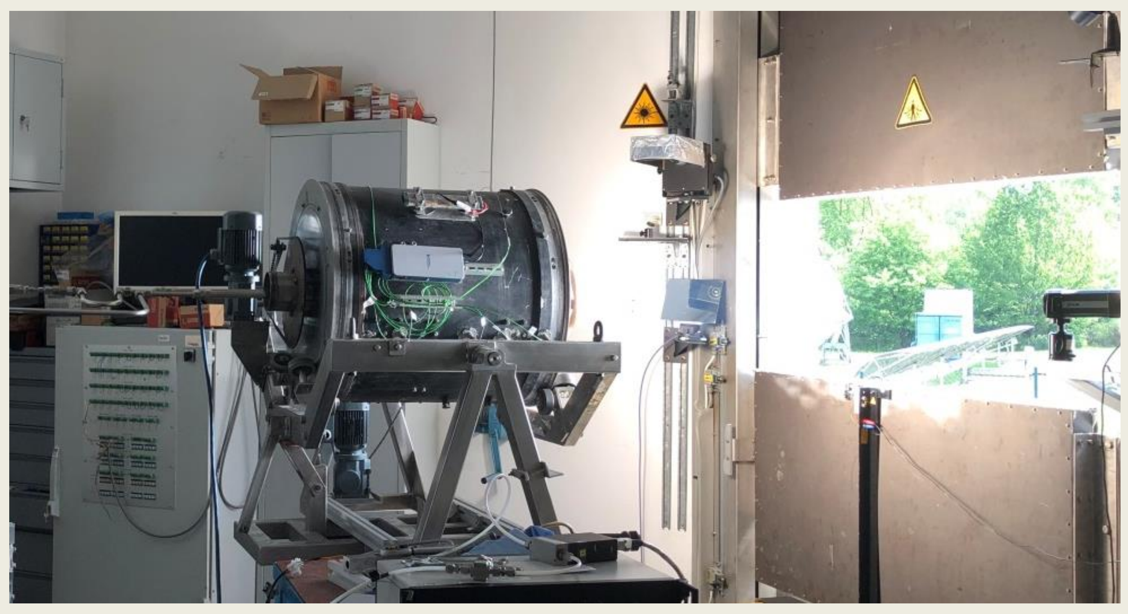
Working principle of thermochemical air separation

- Metal oxides (here: perovskite $SrFeO_3$) are reduced thermally, oxygen is released at high temperature (600-1000 °C)
  ➔ Oxygen production (side-product)
- Re-oxidation of metal oxides in air at lower temperature
  ➔ Nitrogen production (feedstock for Haber-Bosch cycle)

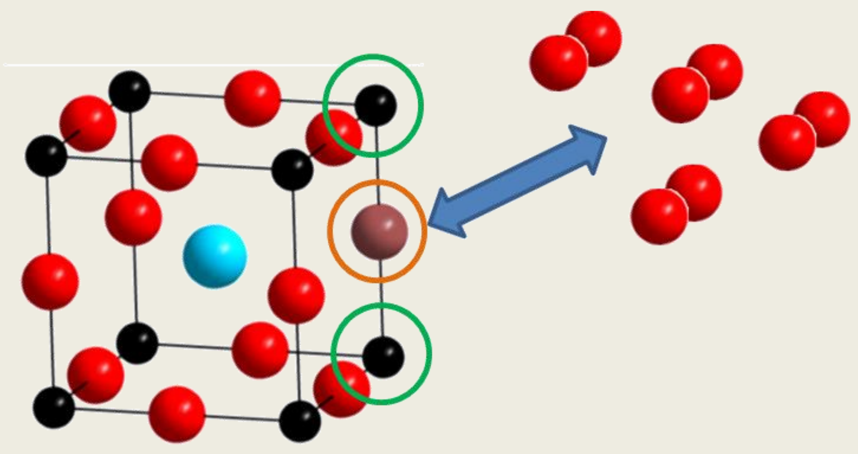
Challenges

- Development of a new process driven by concentrated solar energy
- Continuous production of a nitrogen stream with high purity (avoidance of Haber-Bosch catalyst poisoning)
- Materials development is crucial for the success of this technology as material-specific properties such as the thermodynamics govern the energy requirement and gas product purity





Methods: Materials development



$$\Delta G = \Delta H - T \cdot \Delta S + \frac{1}{2} RT \cdot \ln\left(\frac{p_{O_2}}{p_0}\right)$$

Reduction of perovskite $AMO_{3-\delta}$

Thermodynamic equilibrium, dependent on ΔH, ΔS, T, p_{O2}

Reduction: **M** is reduced under the formation of **O** vacancies

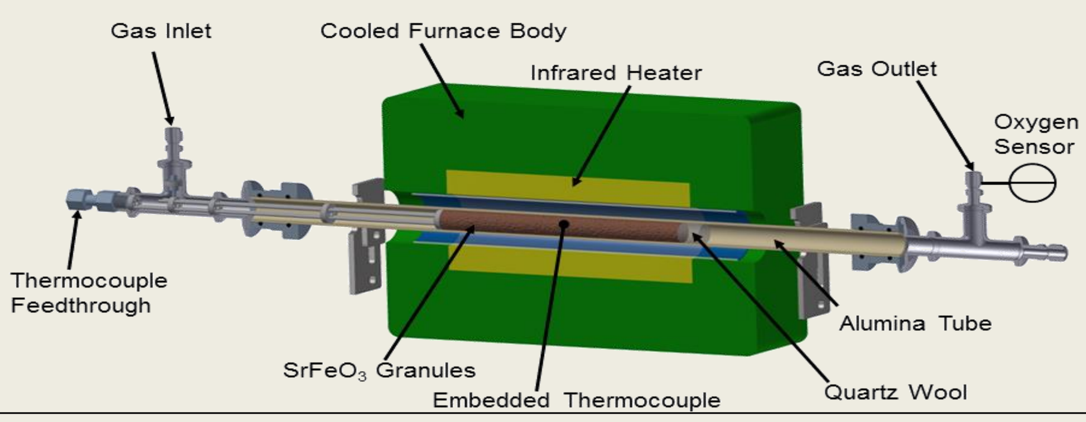
➔ Change the **M** transition metal to influence vacancy formation energy (i.e., redox enthalpy change ΔH)

Laboratory tests

$SrFeO_3$ as a reference material

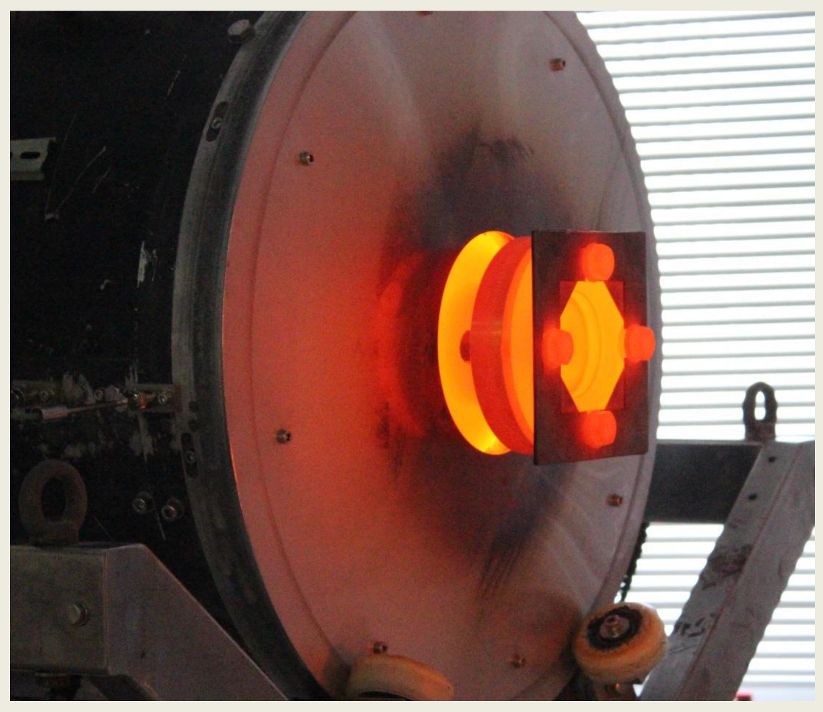
- Synthesis was performed via high temperature solid state reaction from iron oxide and strontium carbonate.

- Redox tests in an infrared furnace

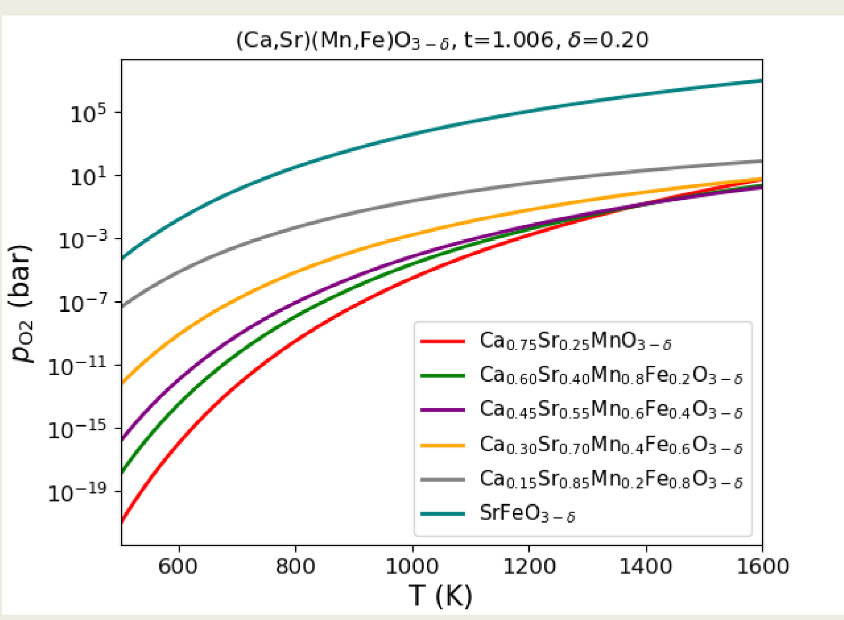


On-sun tests in rotary kiln

- Solar furnace DLR Cologne
- Demonstration using 250 g $SrFeO_3$
- 4 rpm in rotary kiln (diameter ca. 0.5 m)
- Synthetic air feedstock, 4 l/min
- Measurement of oxygen concentration at the outlet (lambda sensor)



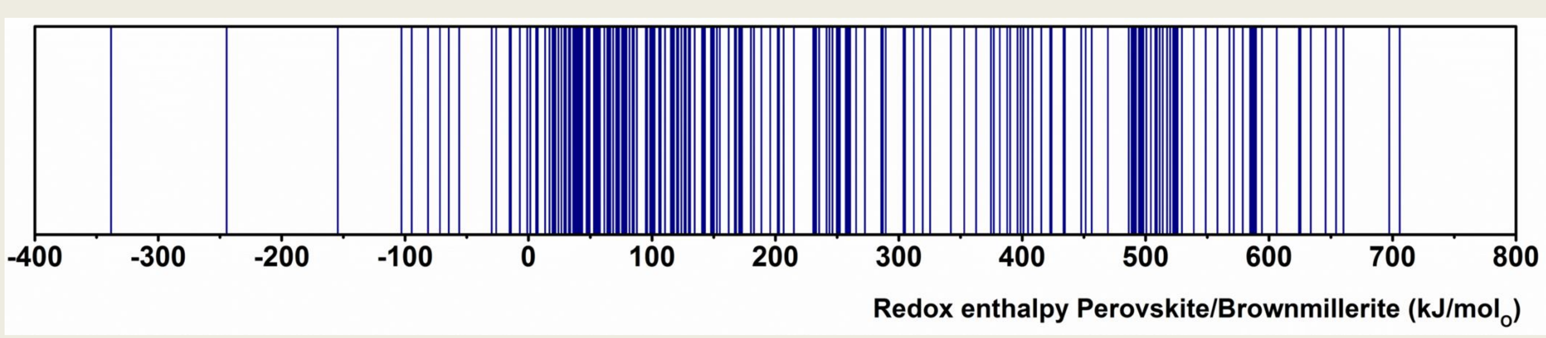
Results: Materials development



Calculated thermodynamic equilibrium based on theoretical data through density functional theory (Materials Project, Lawrence Berkeley National Lab, USA)

🡐 Target reduction temperature, and concentration of remaining oxygen in nitrogen product stream can be adjusted by control over Mn content in $SrFeO_3 – SrMnO_3$ perovskites

⇓ Wide spectrum of redox enthalpies covered in theoretical data (allows targeted Materials Design)

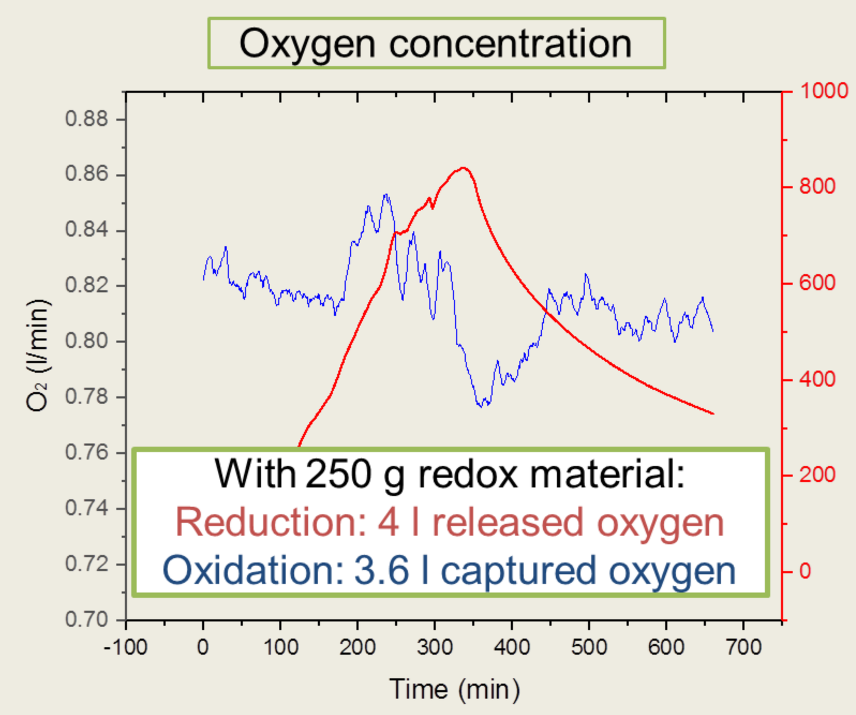


Further challenges:

- Process optimization
- Fertilizer production

➔ follow-up project planned

Demonstration of air separation



Successful demonstration of solar-thermochemical air separation

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