DLR's Contribution to the Helmholtz Virtual Institute Solar Syngas: Materials for solar-thermochemical fuels production

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International Workshop on Solar Thermochemistry
Jülich, Germany 13.09.2017

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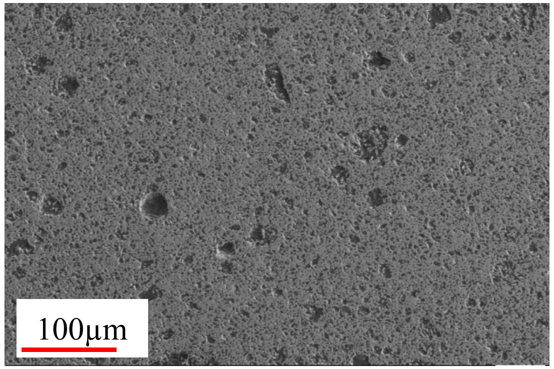
Overview

- Material characterization
  - Thermodynamic properties
  - Thermal expansion
  - Degradation
- Material development
  - Tailored perovskites
- Meso scale particle production
  - Drip casting
- Particle characterization
  - Heat transfer in particle bed at high T low p

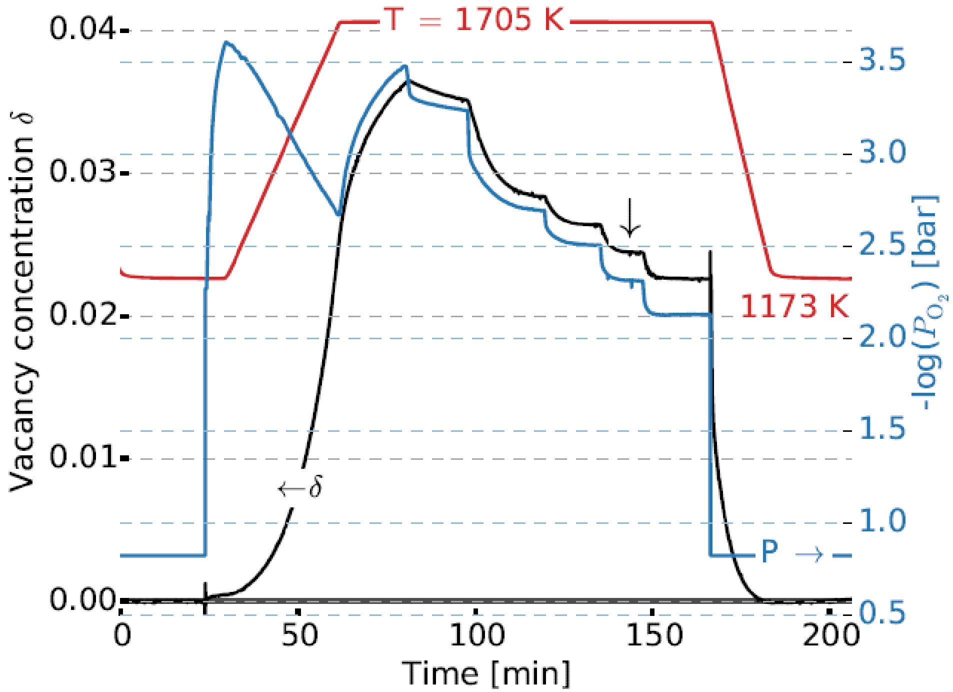
B. Bulfin

Ceria and Ceria Zirkonia: Statistical Thermodynamics

Material:
$Ce_{0.85}Zr_{0.15}O_2$
(porous granules)



Vacancy concentration δ, the oxygen partial pressure pO2 and the temperature profile for a typical TGA experiment



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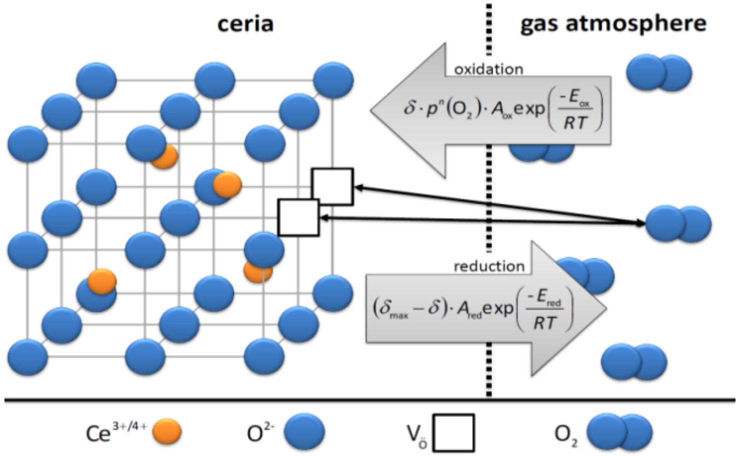
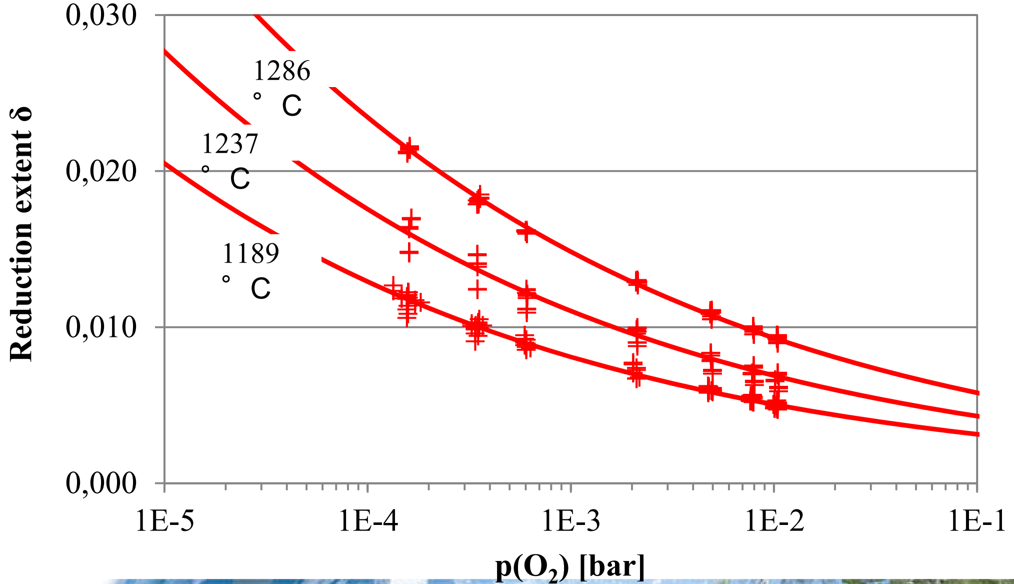
B. Bulfin

Ceria and Ceria Zirkonia: Statistical Thermodynamics – Thermodynamic Model



$$\delta(p(O_2), T) = \frac{\delta_{max} \cdot \frac{A_{Red}}{A_{Ox}} \cdot p^{-n}(O_2) \cdot \exp\left(\frac{-\Delta E}{RT}\right)}{1 + \frac{A_{Red}}{A_{Ox}} \cdot p^{-n}(O_2) \cdot \exp\left(\frac{-\Delta E}{RT}\right)}$$

	δ_{max}	A_{Red}/A_{Ox}	n	ΔE	R^2
		[bar^n]	-	[kJ/mol]	
CeO_2	0,5	12575 ± 7550	0,2320 ± 0,0079	206,7 ± 8,2	0,9754
CeZr-S16	0,425	101 ± 11	0,2084 ± 0,0019	121,6 ± 1,4	0,9893

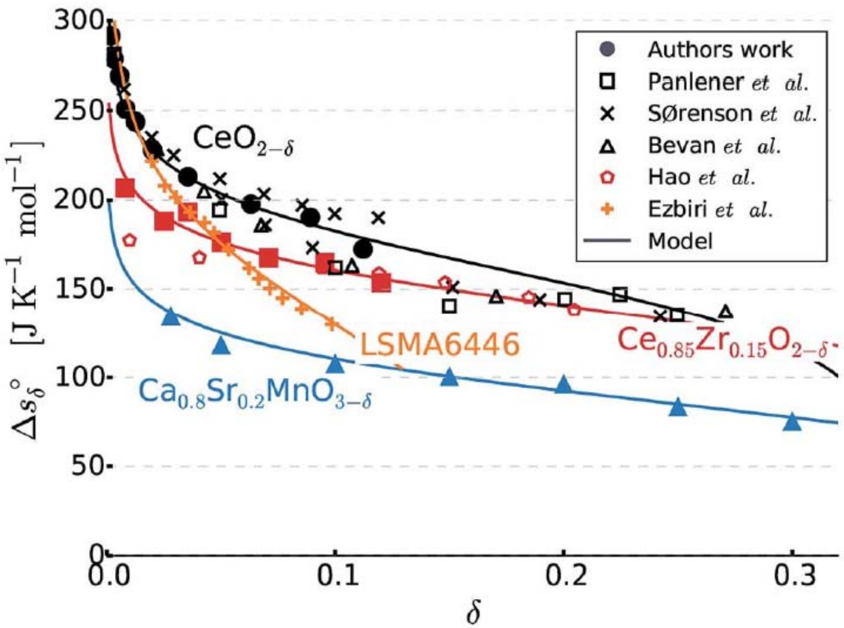


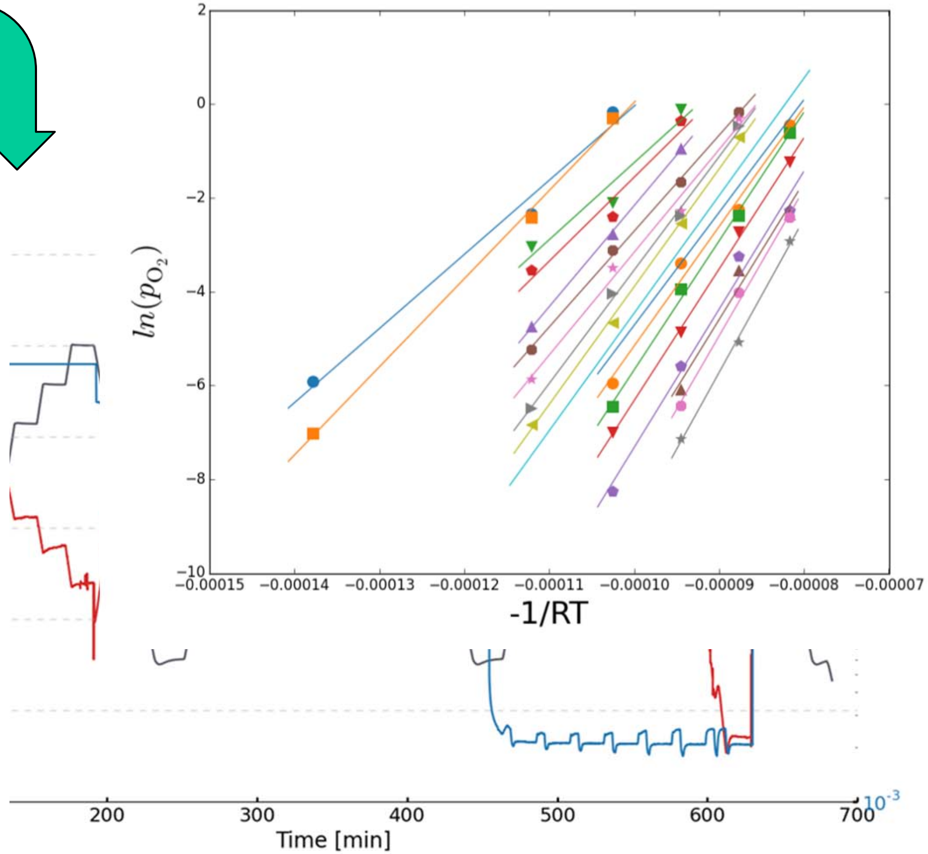
B. Bulfin et al. ***Phys. Chem. Chem. Phys.***, 2016,**18**, 23147-23154

B. Bulfin

Redox tests of $SrMn_xFe_{1-x}O_{3-\delta}$ in a thermobalance

$$\frac{1}{2} ln\left(\frac{p_{O_2}}{p^\circ}\right) = \frac{\Delta h^\circ_O(\delta)}{RT} + \frac{\Delta s^\circ_O(\delta)}{R}\bigg|_{\delta=\mathrm{const}}$$





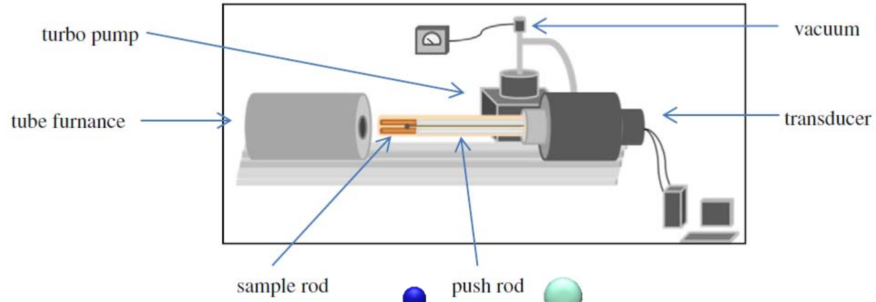
Bulfin, B. et al. (**2017**). "Applications and Limitations of Two Step Metal Oxide Thermochemical Redox Cycles; A Review." Journal of Materials Chemistry A

N. Knoblauch

Investigation of reduction by dilatometry

[Thermal expansion] → [Thermal expansion] + [$(\Delta V)\downarrow$ (oxygen vacancies) < $(\Delta V)\uparrow$ ($Ce^{4+} \rightarrow Ce^{3+}$)]

reduction temperature



Length variation:

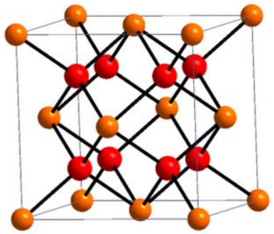
$$\left(\frac{\Delta L}{L_{CeO_2}}\right) = \frac{L_{CeO_{2-\delta}}(T) - L_{CeO_2}(T)}{L_{CeO_2}(T)}$$

Ce^{4+} 97pm

Ce^{3+} 114,3pm

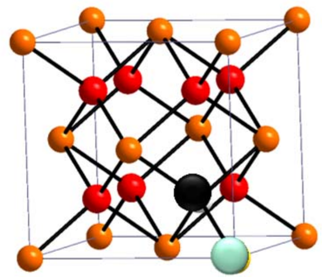
polycrystalline sample rod

oxidized



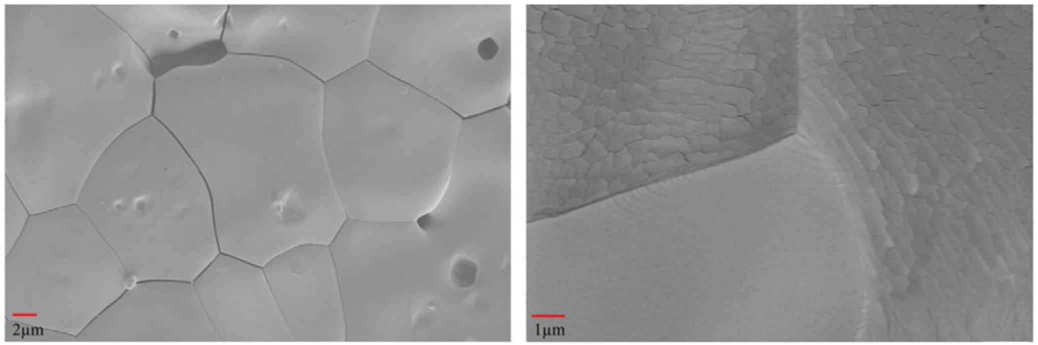
O_O^x M_{Ce}^x

oxygen loss



$V_O^{\cdot\cdot}$ M'_{Ce}

reduced



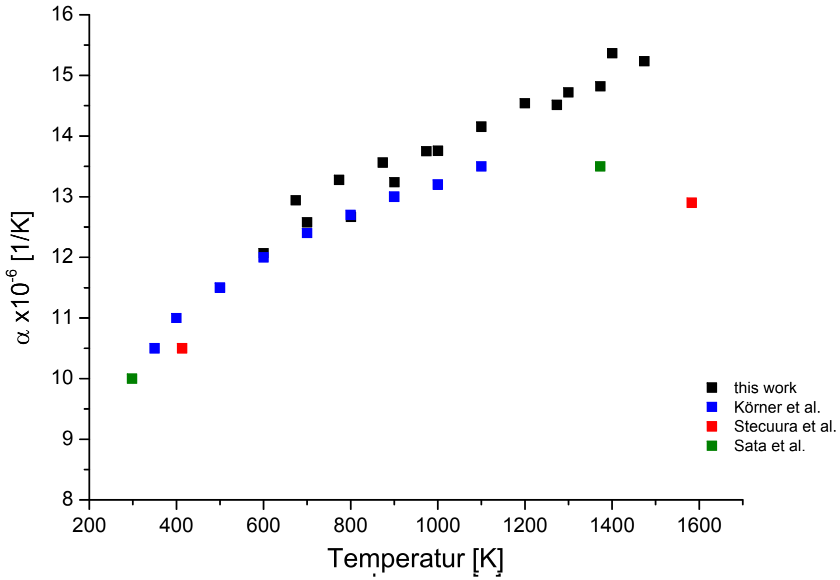
N. Knoblauch et.al., *Solid state ionics*, 2017, 301, 43-52

N. Knoblauch

Thermal and chemical Expansion during reduction

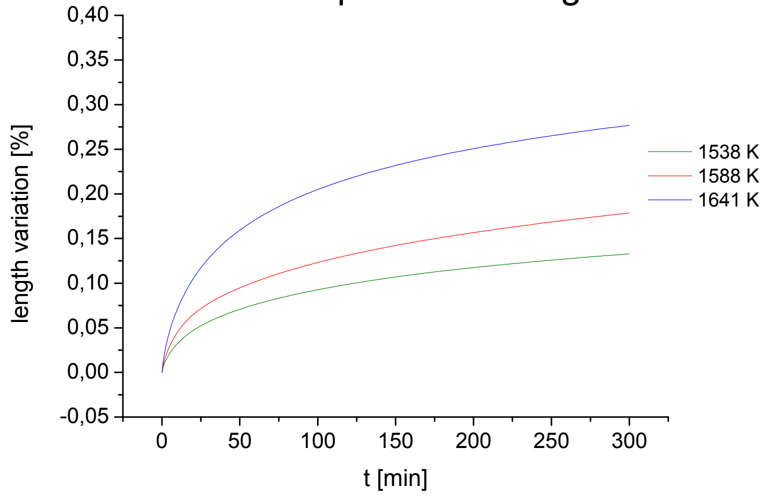
under reduced atmosphere (pO_2 = 2-7x10^{-9} atm)

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$

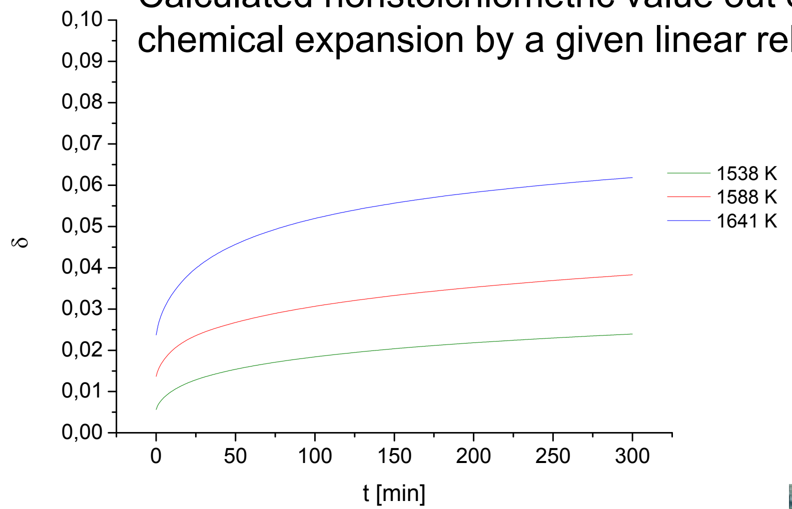


Thermal expansion coefficient

Chemical expansion during isothermal segment



Calculated nonstoichiometric value out of the chemical expansion by a given linear relationship

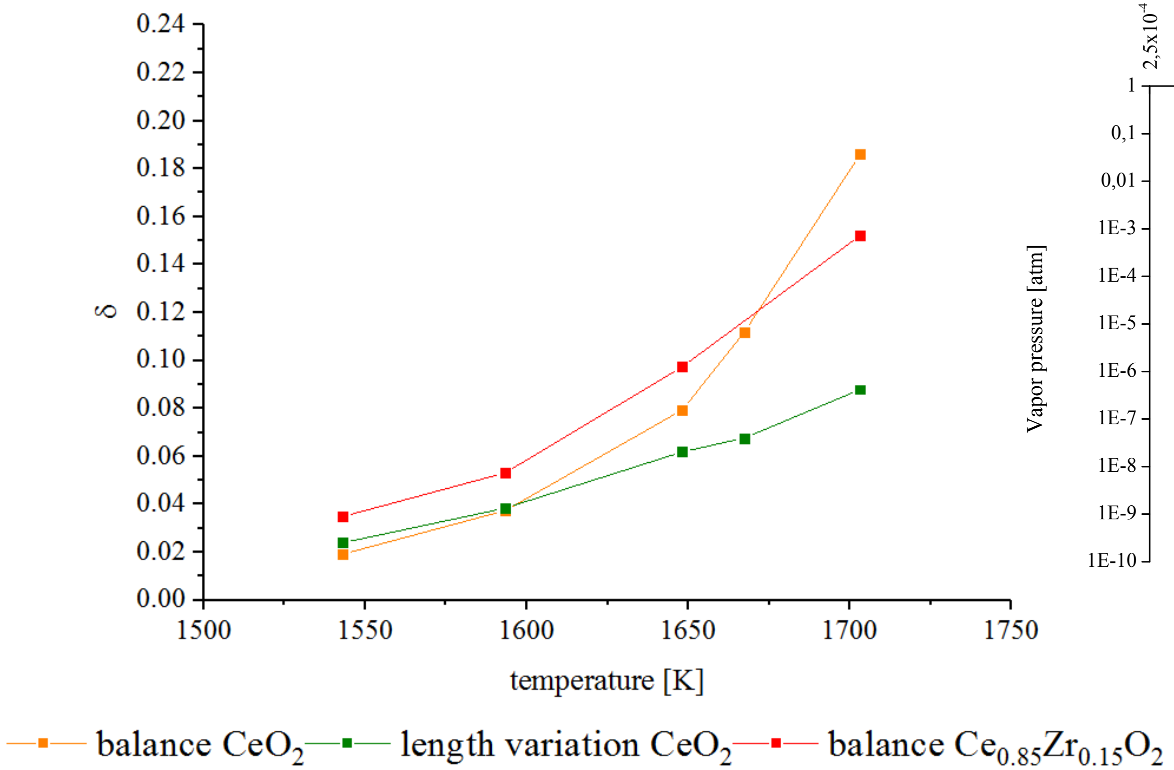


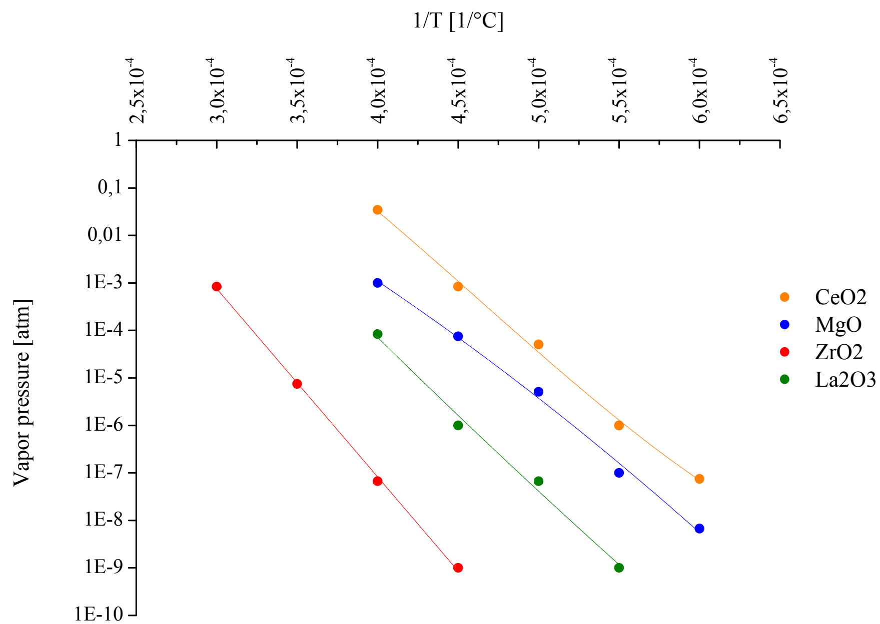
N. Knoblauch et.al., *Solid state ionics*, 2017, 301, 43-52

N. Knoblauch

Degradation of (Ce,Zr)O2 Redox Ceramics by selective sublimation

In a previous study on redox characteristics of ceria data suggest sublimation of ceria at high temperature above 1660K and low pO_2 (2–7 × 10−9 atm) [Knoblauch, N.; Simon, H.; Schmücker, M., Solid State Ionics 2017,301, 43–52, DOI10.1016/j.ssi.2017.01.003].





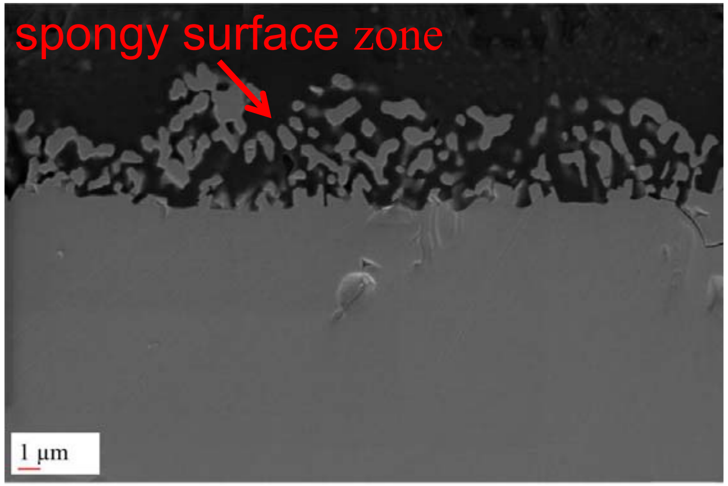
N. Knoblauch et.al., Inorganics, Special Issue "Cerium-based Materials for Energy Conversion“ coming soon

N. Knoblauch

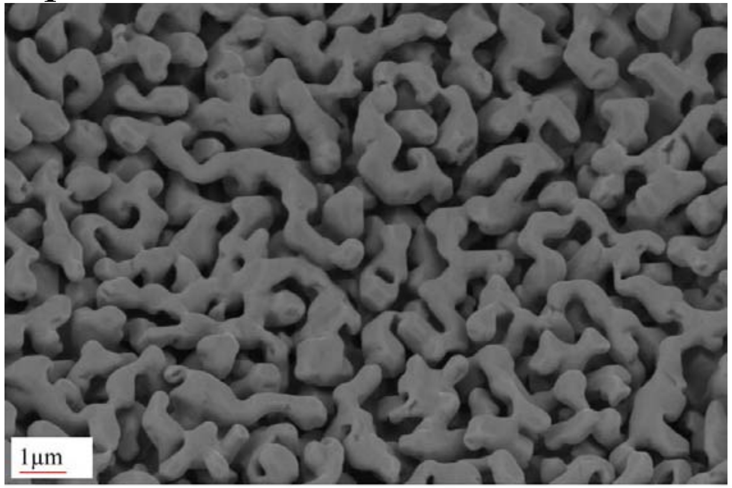
Characterisation by SEM

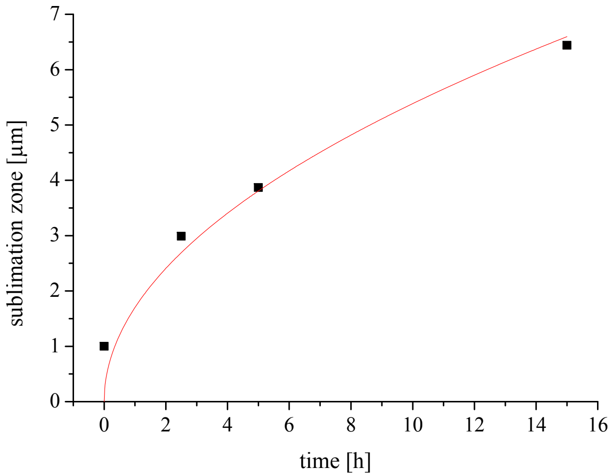
e.g. reduced $Ce_{0.85}Zr_{0.15}O_2$ (1683K (pO2=2,96E-9 atm)

cross section



top view





Measured length of spongy surface zone after reduction at 1683K for various length of time

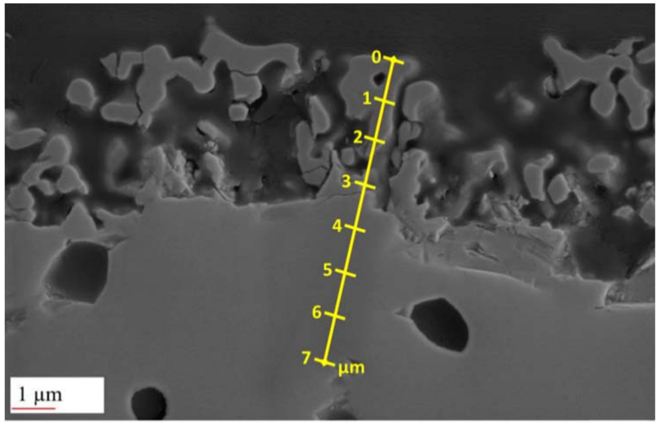
	time [h]	length [µm]
1	2,5	2,99
2	5	3,87
3	15	6,44

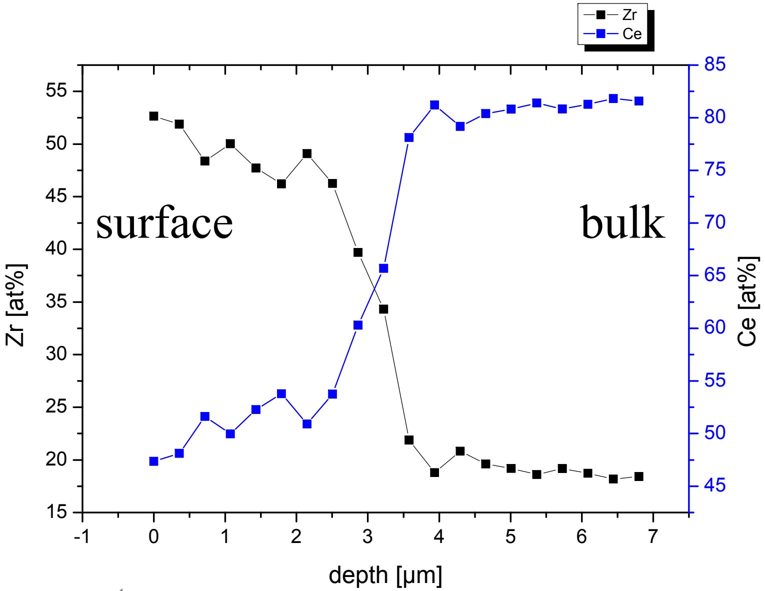
N. Knoblauch et.al., Inorganics, Special Issue "Cerium-based Materials for Energy Conversion" coming soon

N. Knoblauch

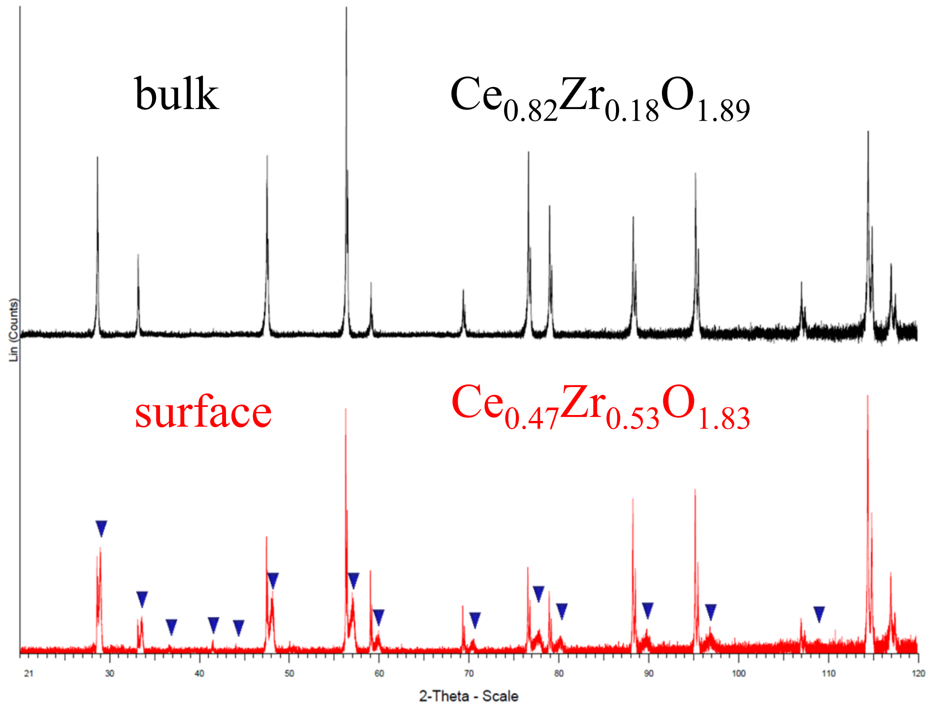
Characterisation by EDX and x-ray diffraction

e.g. reduced $Ce_{0.85}Zr_{0.15}O_2$ (1683K (pO2=2,96E-9 atm)





! $Ce_2Zr_2O_7$ Pyrochlore formation at the surface



N. Knoblauch et.al., Inorganics, Special Issue "Cerium-based Materials for Energy Conversion“ coming soon

J. Vieten

Development of new materials
Perovskites for redox cycles

$A^{2+}M^{3+/4+}O_{3-\delta}$

Reduction from perovskite to brownmillerite:

$$4\ AMO_3 \overset{\Delta H}{\leftrightarrow} 4\ AMO_{2.5} + O_2$$

gradual reduction possible -> non-stoichiometry δ

Cu Co Fe Mn Ti ΔH

Air separation | **Water splitting**

Oxygen pumps | **CO_2 splitting**

0 100 200 500 kJ/mol O

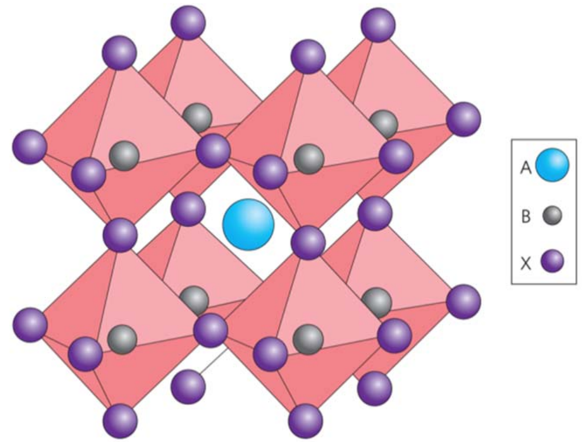


Image: Eames et al.

➢ $A^{2+}M^{3+/4+}O_3$: **Reaction enthalpy** mainly governed by choice of **transition metal** $M^{3+/4+}$

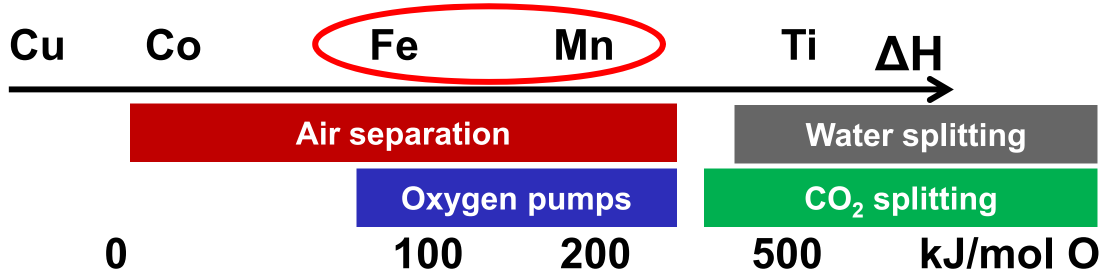
Bulfin, B. et al. (**2017**). "Applications and Limitations of Two Step Metal Oxide Thermochemical Redox Cycles; A Review." Journal of Materials Chemistry A

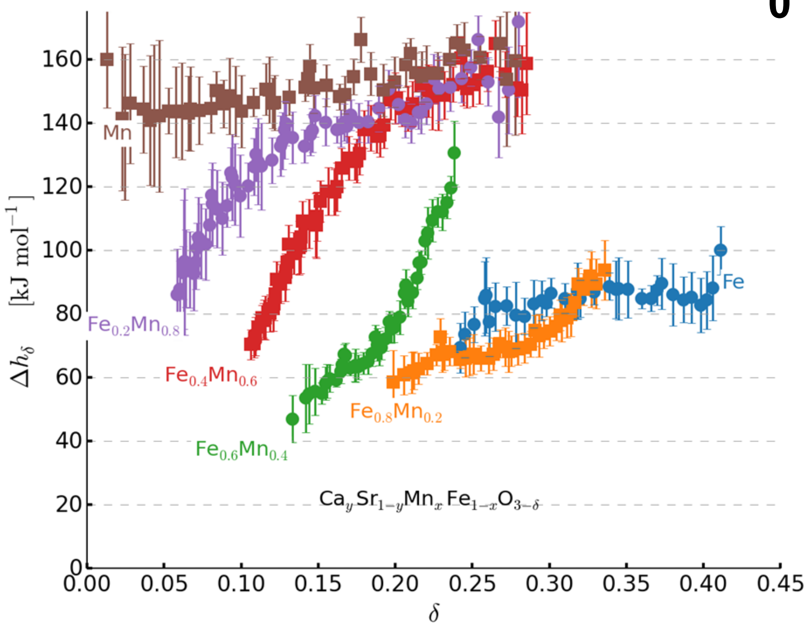
J. Vieten

Tailored thermodynamic properties
Mn-Fe solid solutions

*in the fully oxidized state

$Sr_yCa_{(1-y)}Mn_xFe_{(1-x)}O_{3-\delta}$





ΔH per mol O

same crystal structure in oxidized state

Materials suitable for oxygen pumping, selection according to operation parameters

Vieten, J. et al. (**2016**). "Perovskite oxides for application in thermochemical air separation and oxygen storage." Journal of Materials Chemistry A 4(35): 13652-13659.
Vieten et al. (**2017**), Redox thermodynamics and phase composition in the system SrFeO3 − δ — SrMnO3 − δ. Solid State Ionics, 308, 149-155

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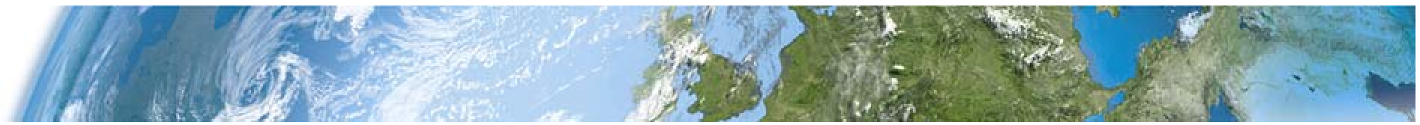
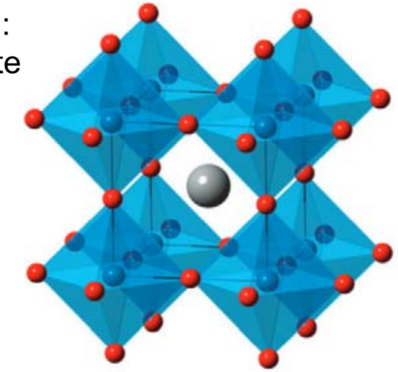


S. Richter

Tassel, Kageyama 2011:
Square planar coordinate iron oxides



Selection of redox material

- Low reduction temperatures[1]
- Non-stoichiometric redox characteristics
- Scalable synthesis

Strontium Iron Oxide
$SrFeO_{3-\delta}$

[1]Vieten et al. 2016, J. Mater. Chem. A

S. Richter

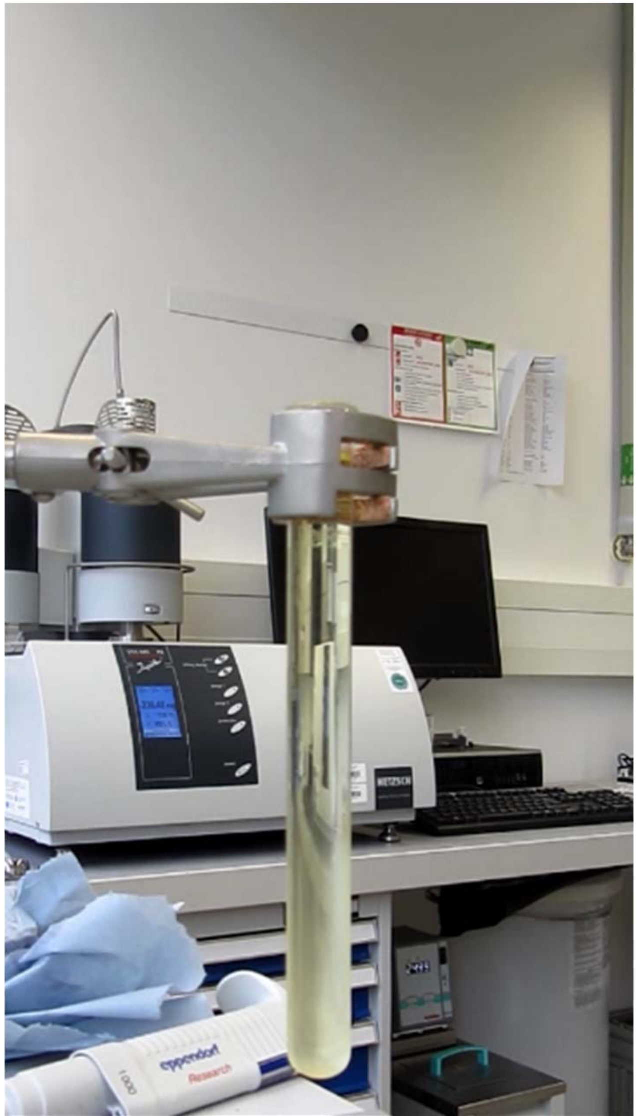
$SrFeO_{3-\delta}$ synthesis

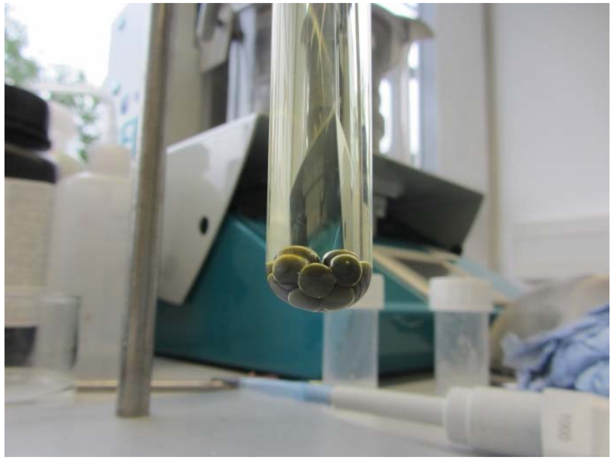
- High temperature solid state reaction
- Precursors: $SrCO_3$ & Fe_3O_4
- Mesoscale synthesis
- Manual pestling of annealed material
- Ball milling

S. Richter

Granulation

- Drip casting
- Slurry dripped into cooled oil bath
- Separation from oil





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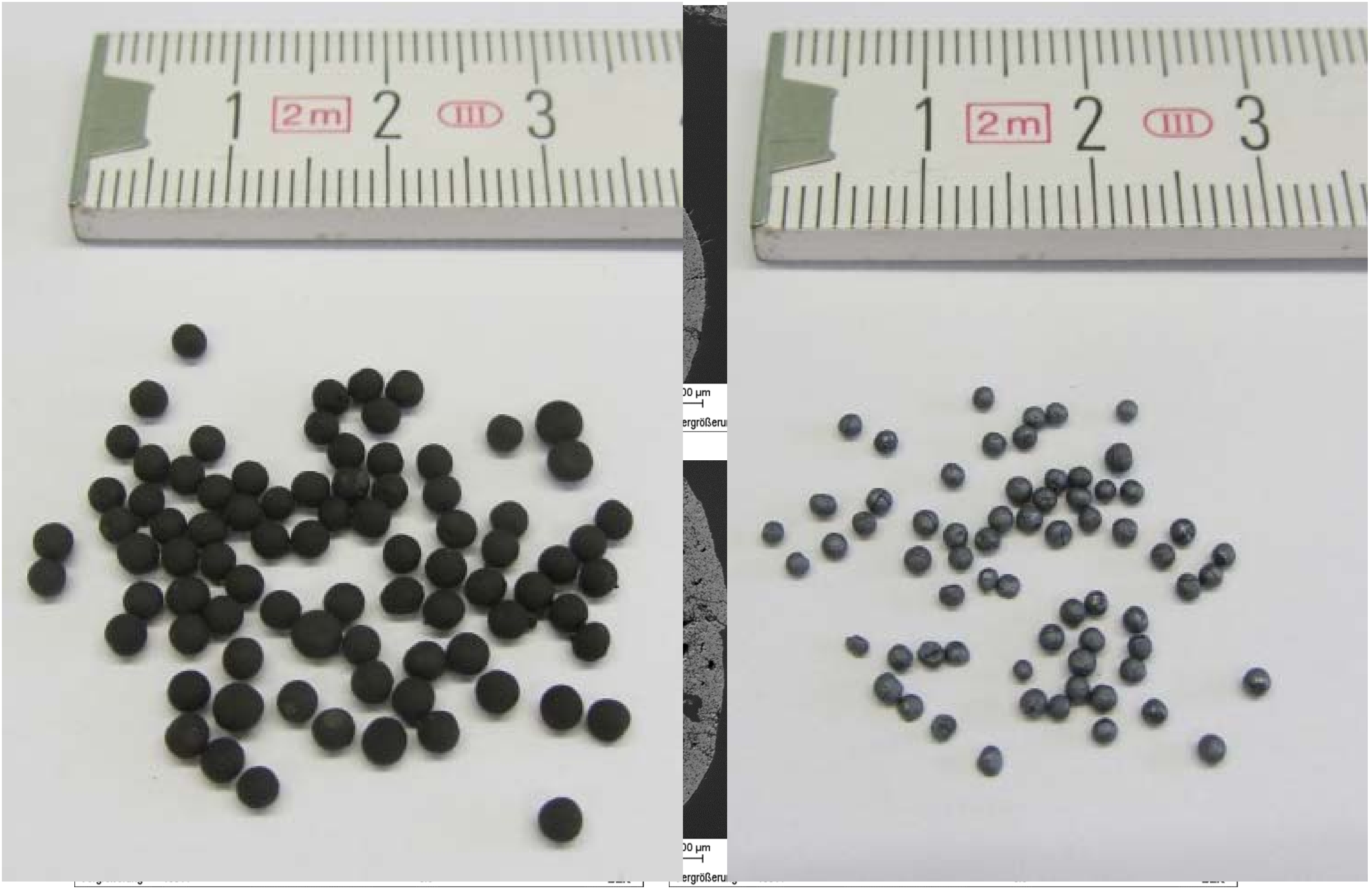
Granulation – post treatment

- Washing
- Drying
- Sintering

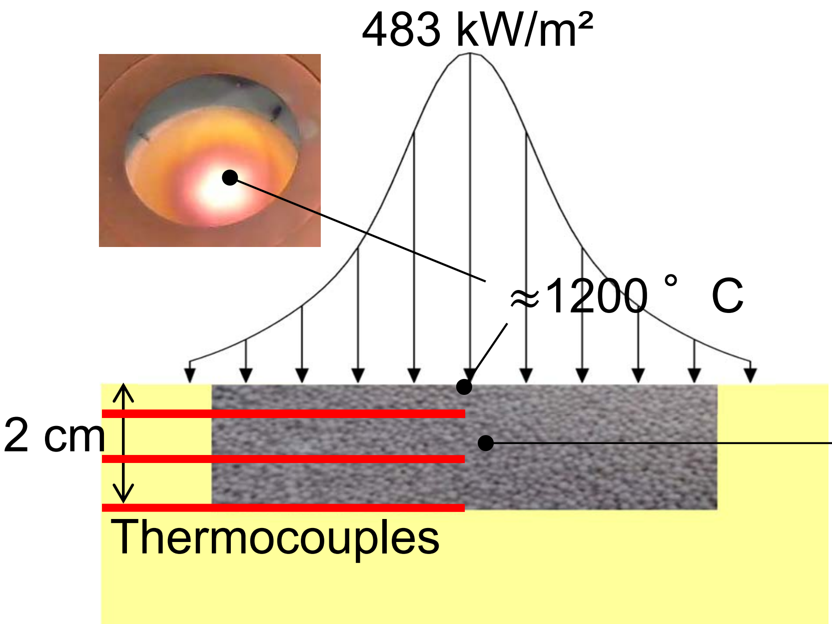


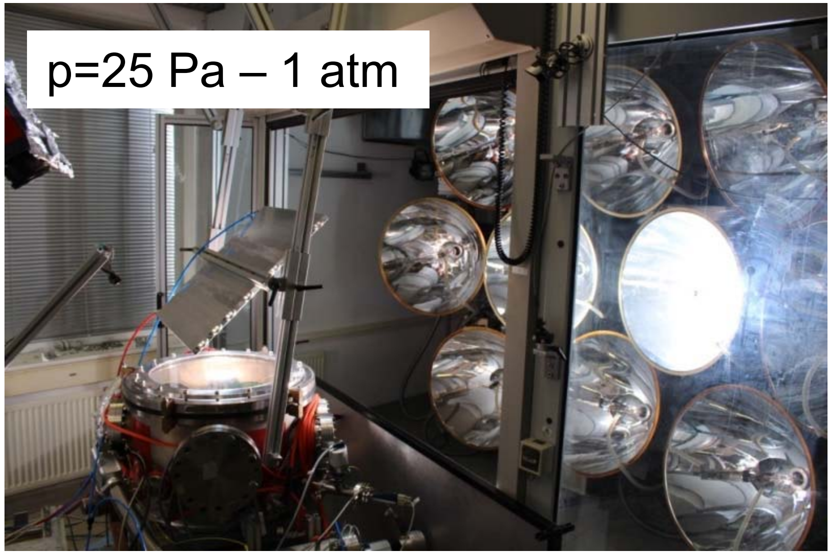
J. Grobbel

Heat transfer properties of Ceria particles at low pressures

Fixed Bed Experiment with Ceria

Investigate effective conductivity as function of temperature and pressure
$k_{bed}\,(p,T)$





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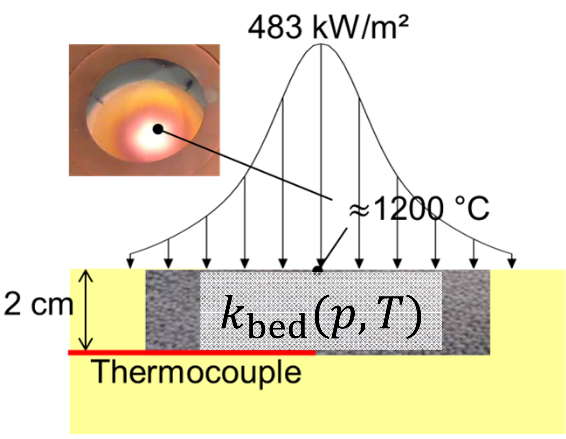
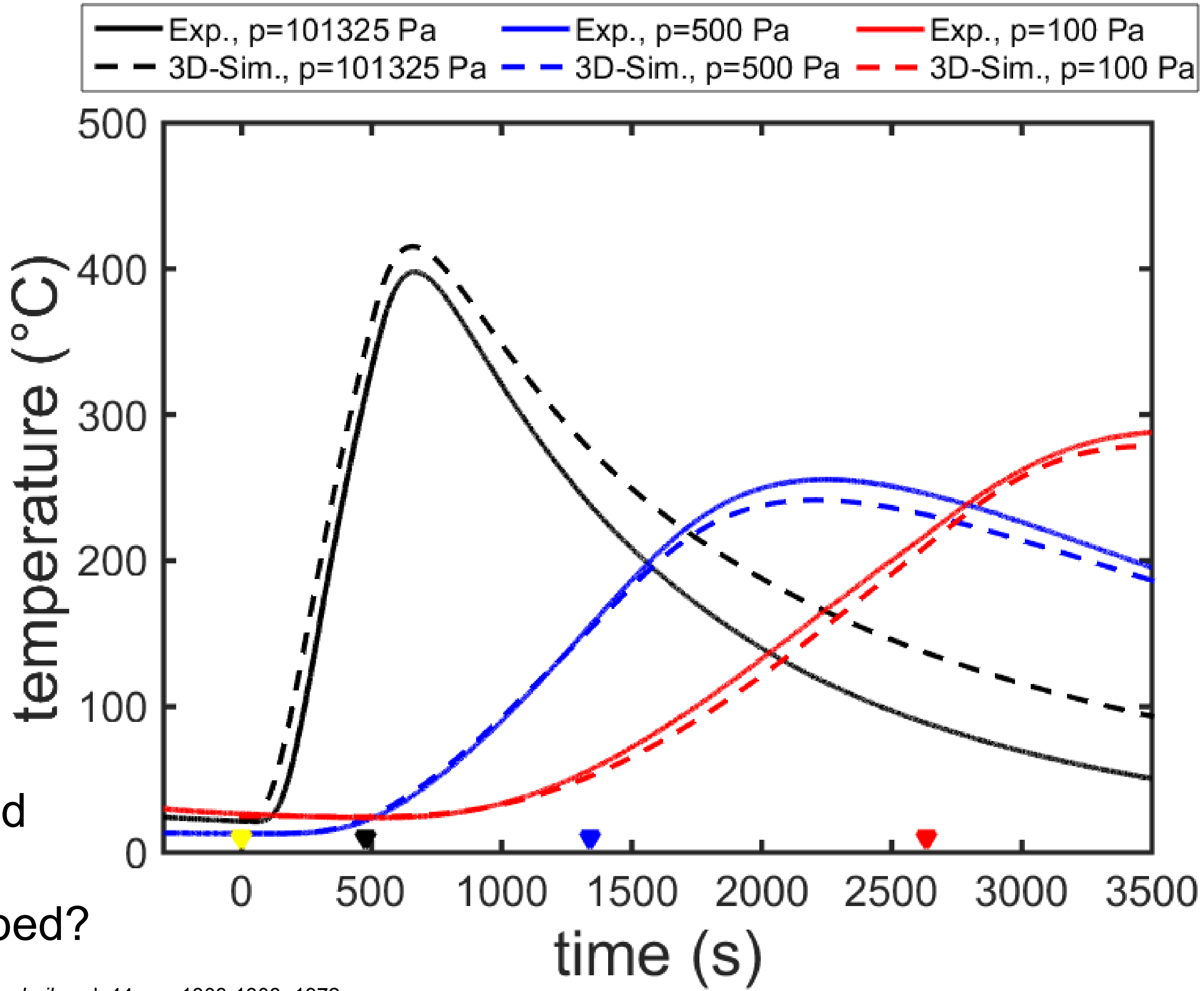
Comparison with Simulation





- Simulation with continuum model [1,2]
- Very low heat transfer → particle mixing required
- How to model a moving bed?

[1] P. Zehner and E. U. Schlünder, *Chemie Ingenieur Technik,* vol. 44, pp. 1303-1308, 1972.
[2] R. Bauer, Düsseldorf: VDI-Verl., 1977.

Grobbel et al., Solar Energy, coming soon

Summary

- Thermodynamic data from TGA measurements
- Reduction extent from dilatometry experiments
- Degradation by selective sublimation
- Tailored perovskites for oxygen pumping
- Production of spherical Strontium Iron Oxide particles
- Pressure dependence of effective thermal conductivity in particle bed

- Other topics of DLR within SolarSynGas
    - Indirect particle based concept
    - Particle-particle heat exchanger
    - Indirect particle reactor
    - Sweep gas demand
    - Vacuum pumping requirements
    - Thermo-chemical pumping
    - Air separation
    - …

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Thank you very much for your attention!