ASME
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Summer Heat Transfer Conference

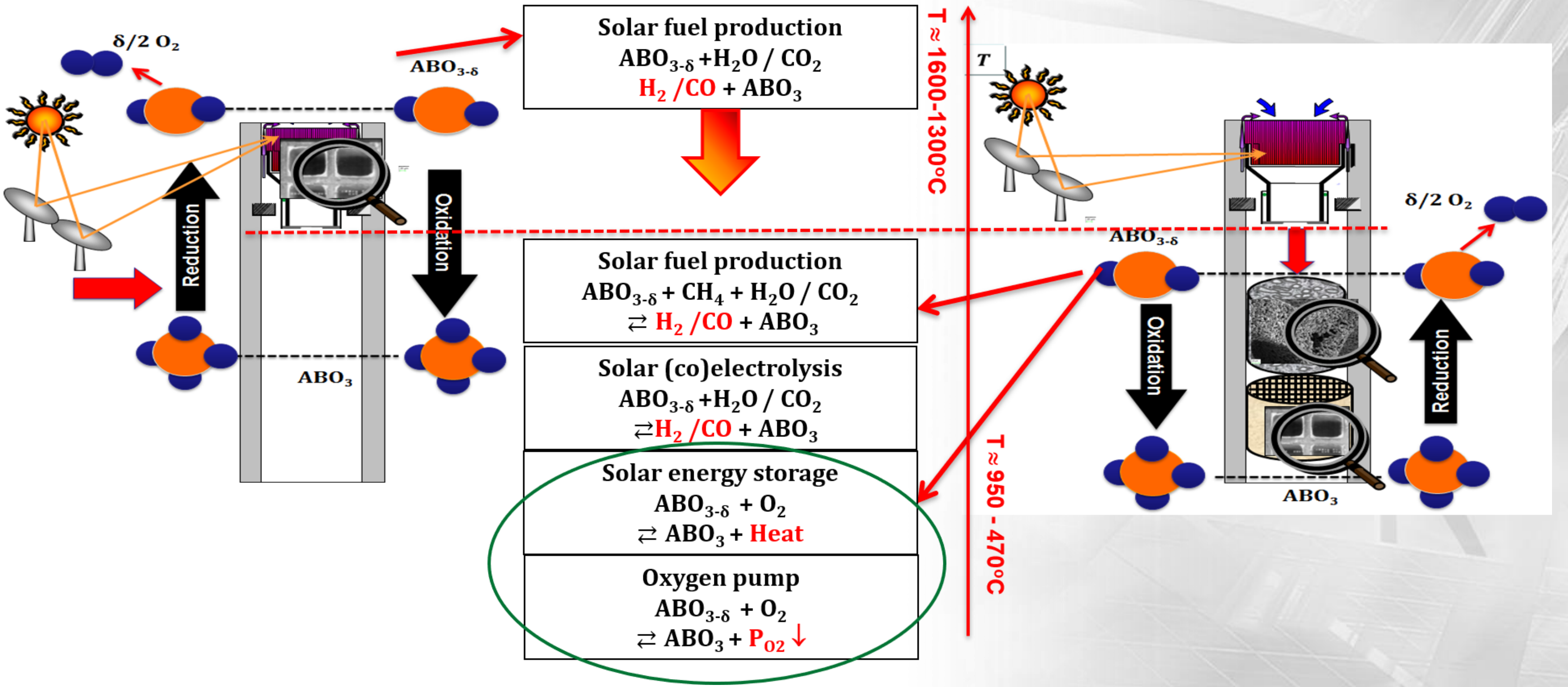
CONFERENCE JULY 11–13

Monolithic Porous Structures of Ca-Mn-Based Perovskites for Thermochemical Energy Conversion

Mathias Pein, Christos Agrafiotis, Martin Roeb, Christian Sattler

DLR – German Aerospace Center, Institute of Future Fuels

Motivation – Perovskites in thermochemical cycles



Motivation - $CaMnO_3$ as storage material

- ΔH = 161 kJ/mol [1]
- Significant reduction in air >760°C
- Cheap, abundant, non-toxic components
- Scalable production (solid state synthesis)
- Is considered as candidate for thermochemical energy storage
  - >0.8 kJ/kg·K of storage capacity for Sr-doped $CaMnO_3$ [2]

[1] *B. Bulfin et al.*, ***J. Mater. Chem. A***, 2017,**5**, 7912-7919
[2] P. Thiel et al., **Journal of Applied Physics**, 2013, 114, 243707

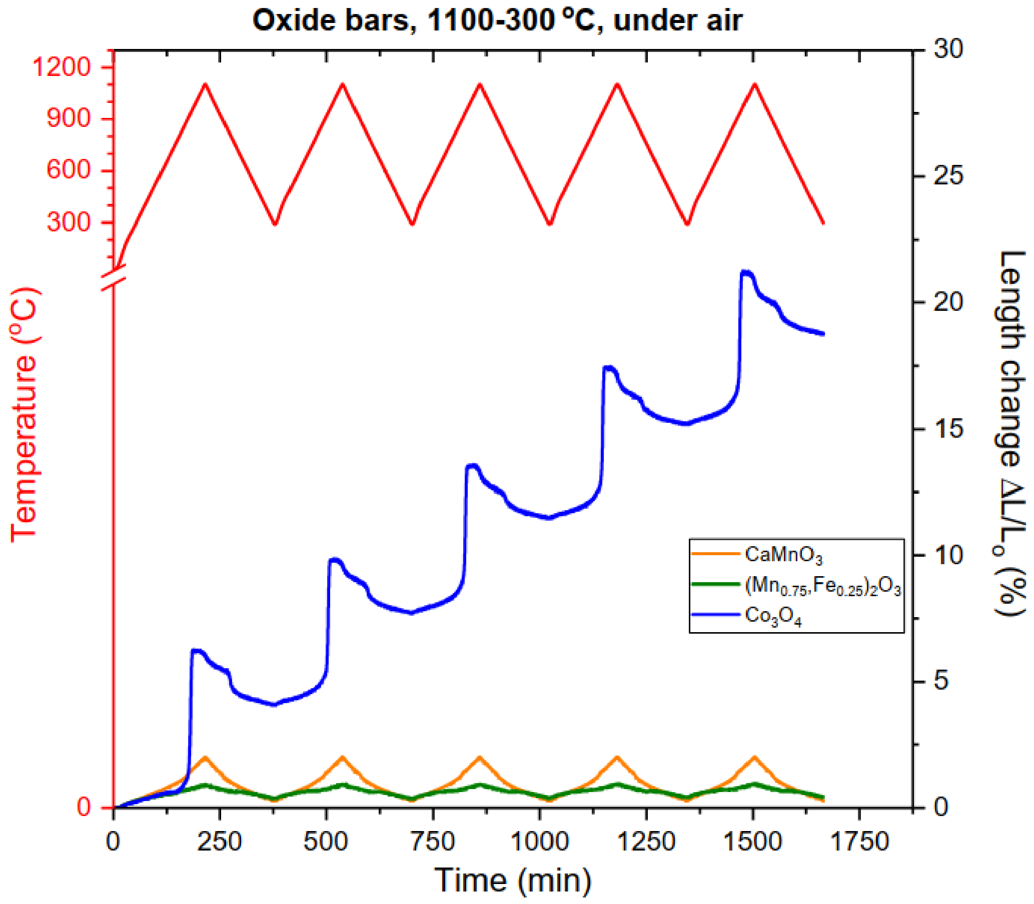
Motivation – Open porous structures in TCES

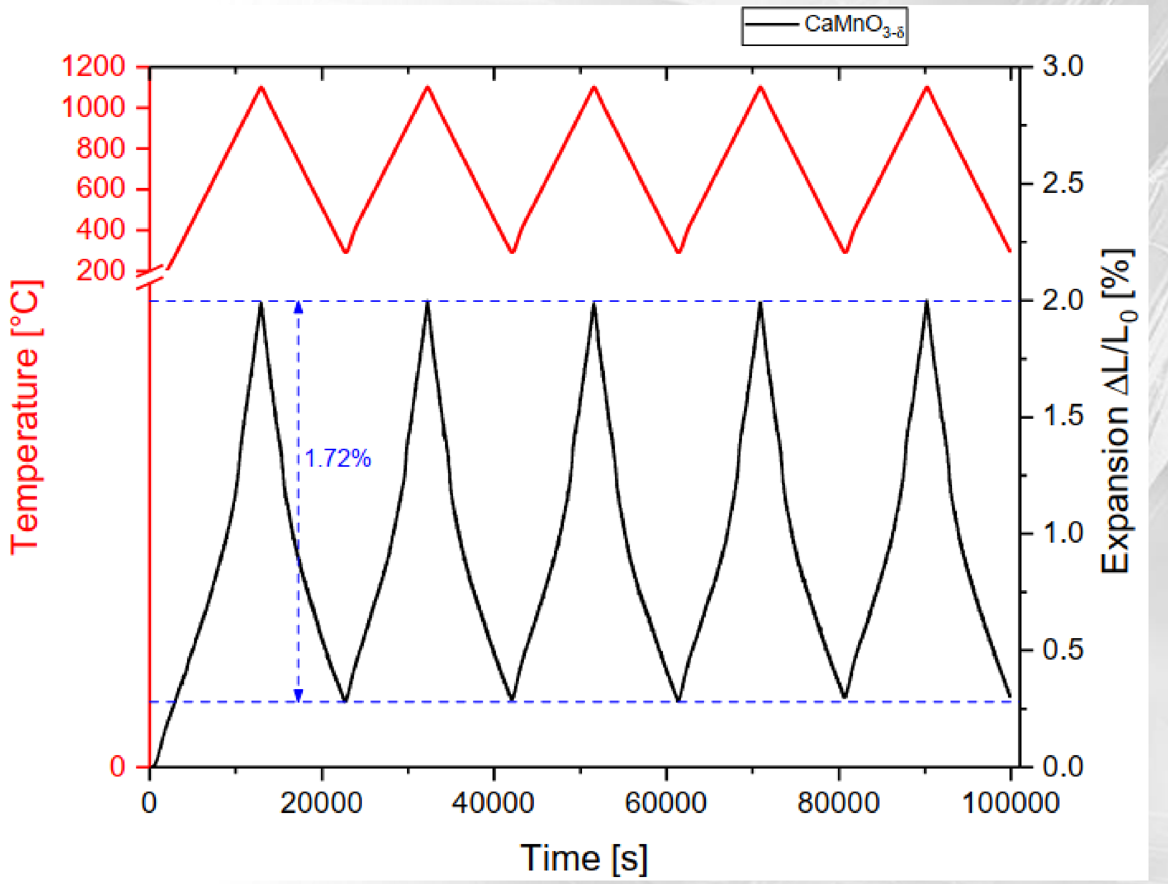
- Allows for higher mass flows of HTF compared to packed bed reactors
- No moving hot solids

- 50 kWh_{th} reactor built in previous project
- Co_3O_4 coated on Cordierite honeycombs
- Monolithic structures from stoichiometric oxides were not stable
- Thermal expansion / contraction causing too much stress

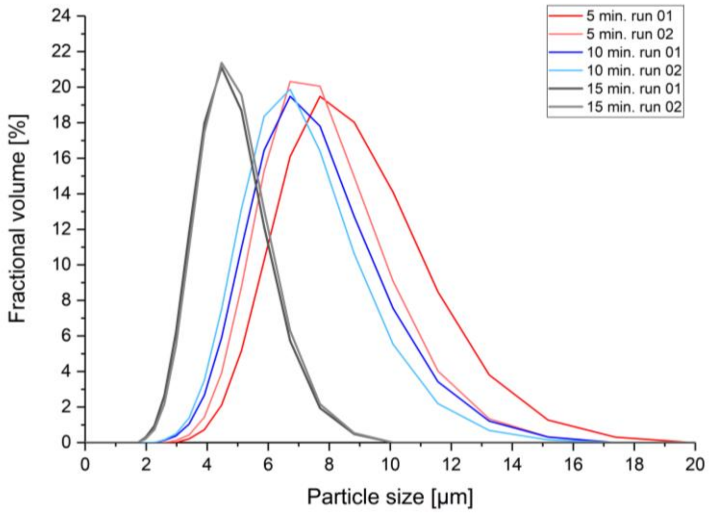
S. Tescari, A. Singh, C. Agrafiotis, L. de Oliveira, S. Breuer, B. Schlögl-Knothe, M. Roeb, C. Sattler, Experimental evaluation of a pilot-scale thermochemical storage system for a concentrated solar power plant, Applied Energy, Volume 189, 2017

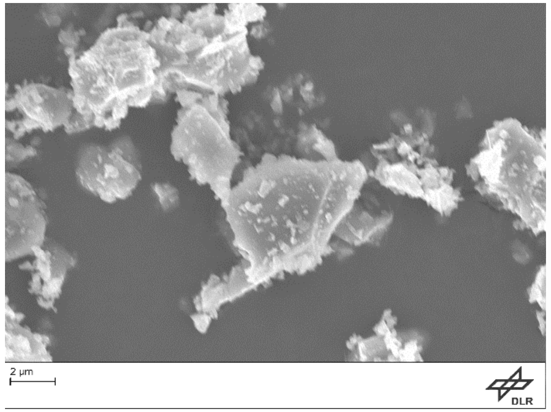
Cyclic thermal expansion





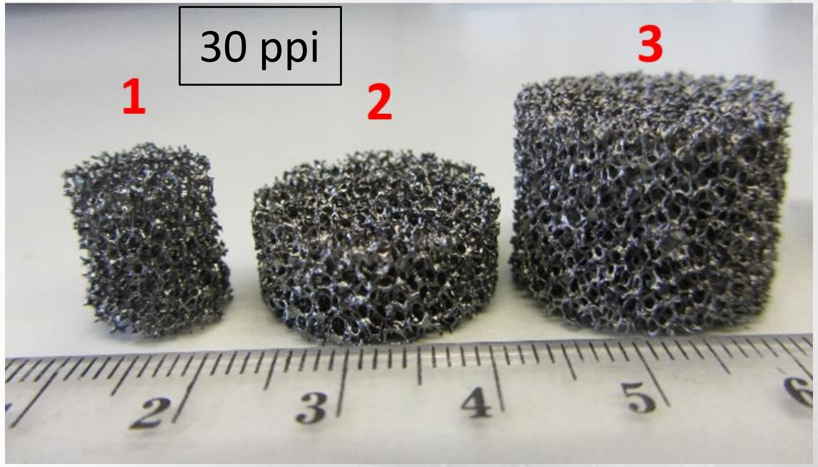
Fabrication of monolithic foams via replica method





Ingredient	wt.-%
Perovskite powder	59
Binder	6
Dispersing Agent	1
H_2O	34

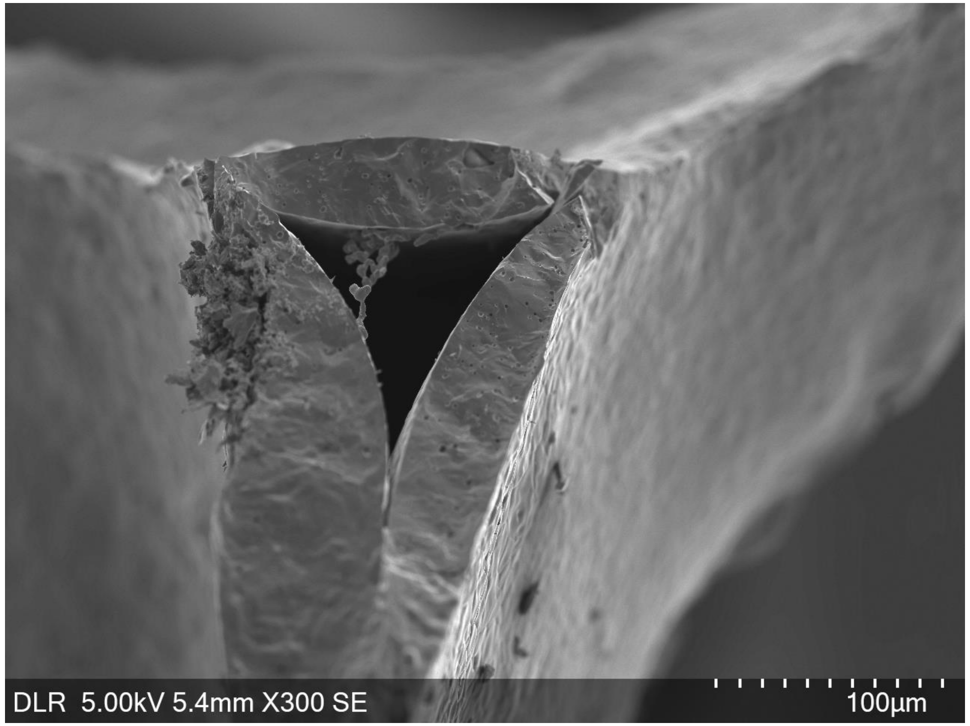
Immerse PU-template in Perovskite slurry → Squeeze out excess slurry → Dry and sinter →

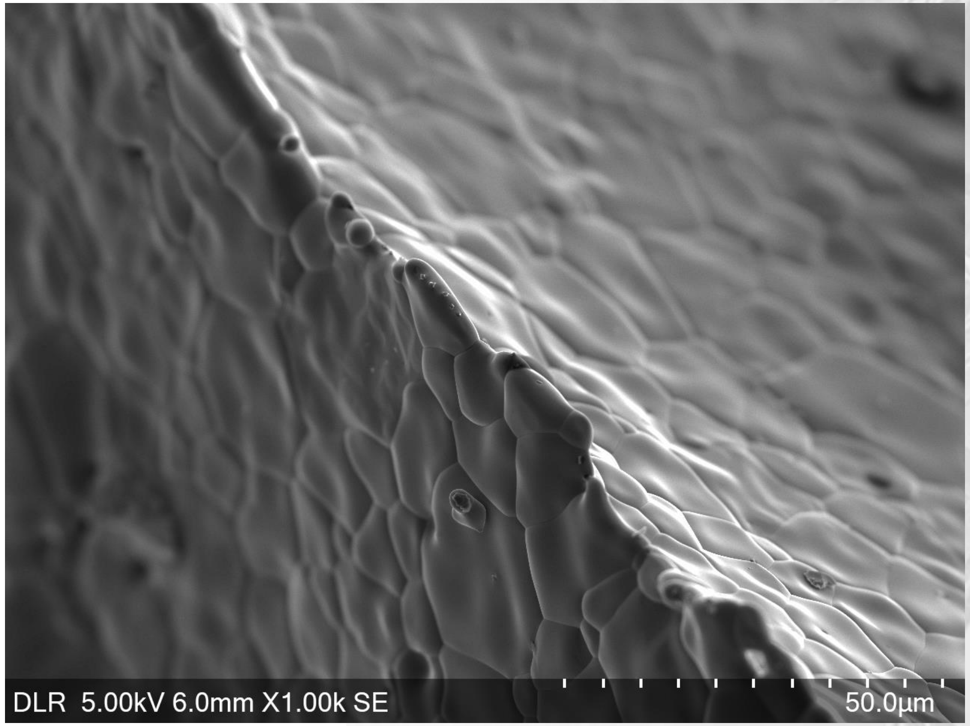


1: Ø1x1.2 cm; 2: Ø2x1 cm; 3: Ø2x2 cm

Pein et al. "Reticulated Porous Perovskite Structures forThermochemical Solar Energy Storage", *Advanced Energy Materials* (2022), p. 2102882. DOI: https://doi.org/10.1002/aenm.202102882.

Microstructure of $CaMnO_3$-specimen

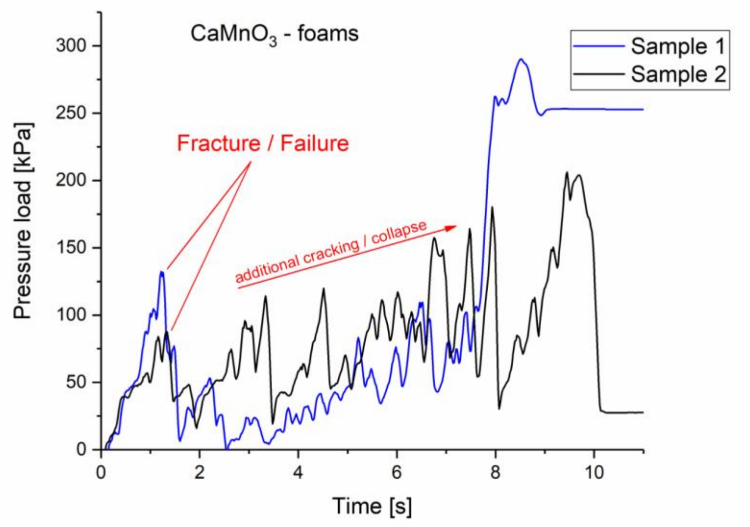


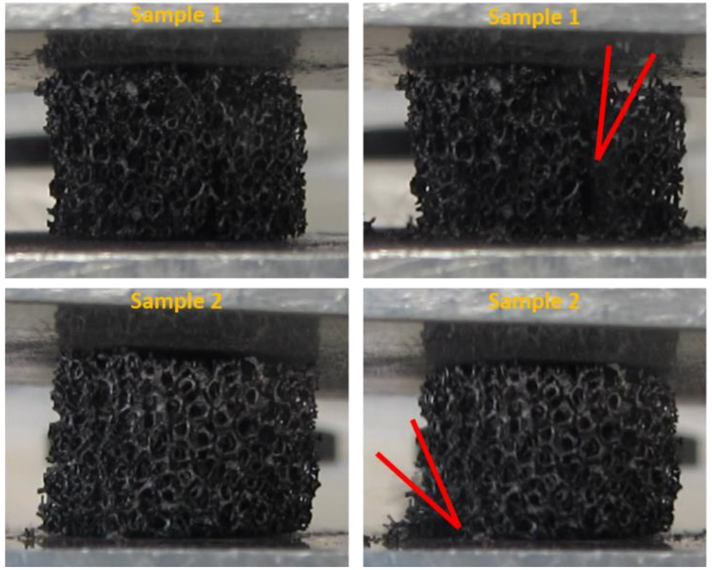


- Struts are ≈ 100µm thick
- Struts appear hollow to some degree
- Smooth surface

- Triangular form of struts
- Sharp edges

Stability of $CaMnO_3$-specimen





- Samples withstand pressure load of approx. 1 bar
- Easy to handle and stackable
- No deformation upon cycling
- Scalability tested up to 10x10x5cm block

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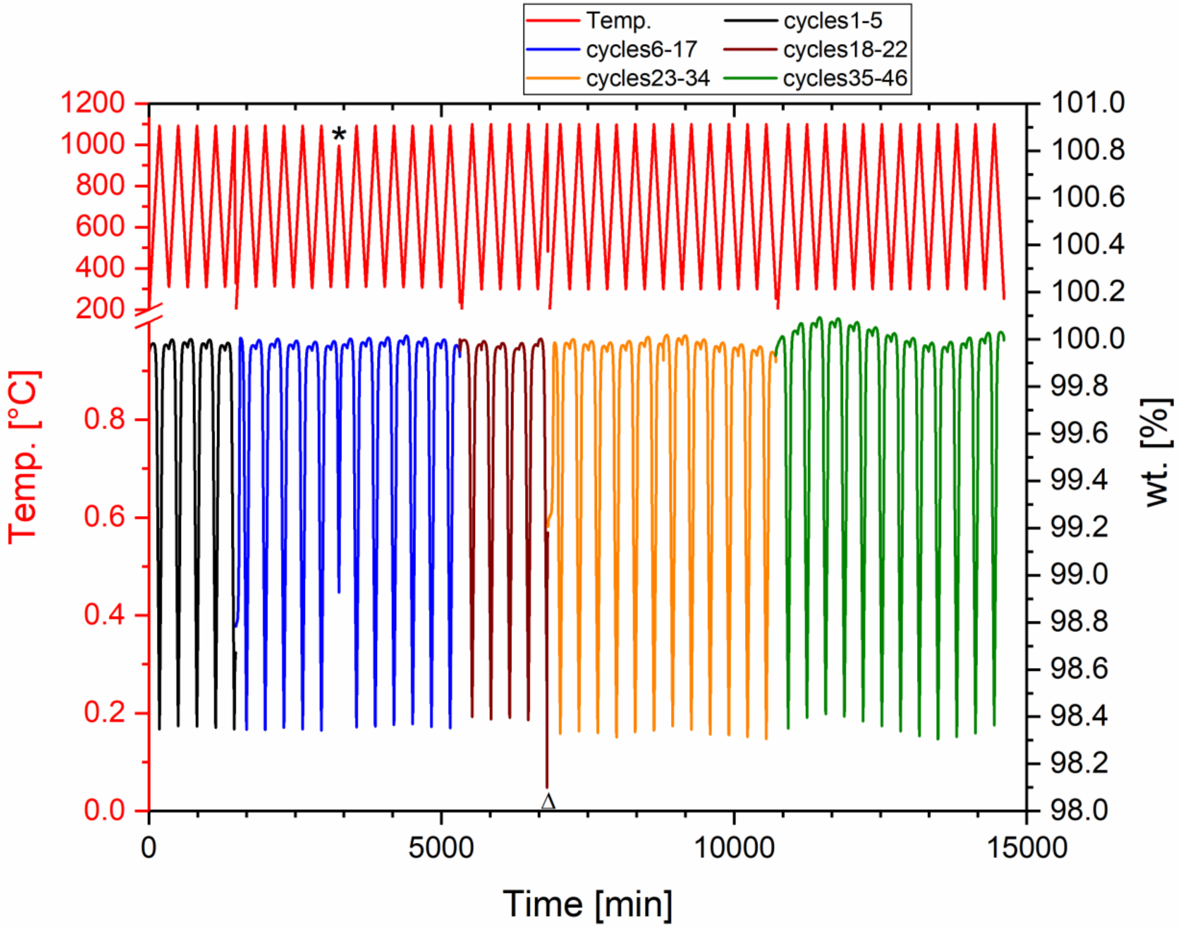
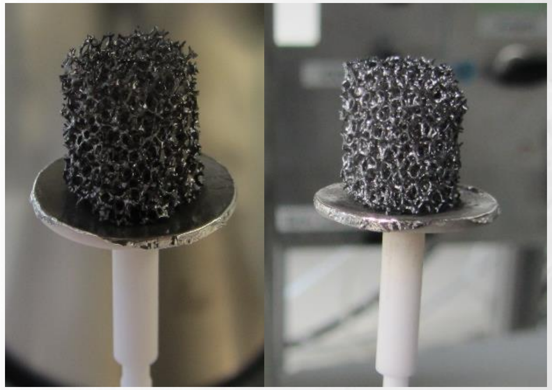
Cyclic stability





- Stable thermodynamics over 46 cycles 300-1100°C
- No deformation of the foam sample

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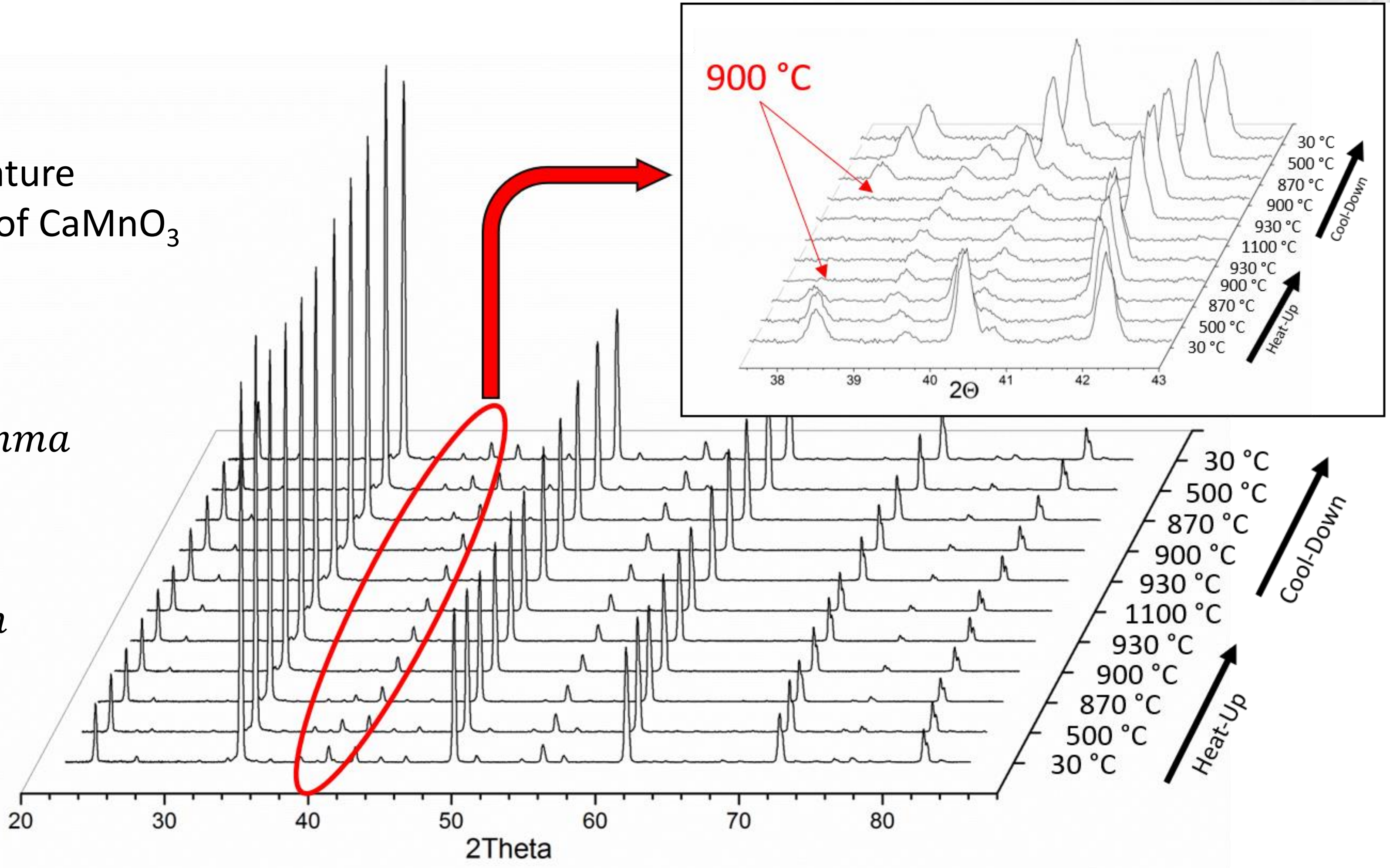
High temperature phase transition

High temperature powder XRD of $CaMnO_3$

Orthorhombic - $Pnma$

Cubic – $Pm\bar{3}m$



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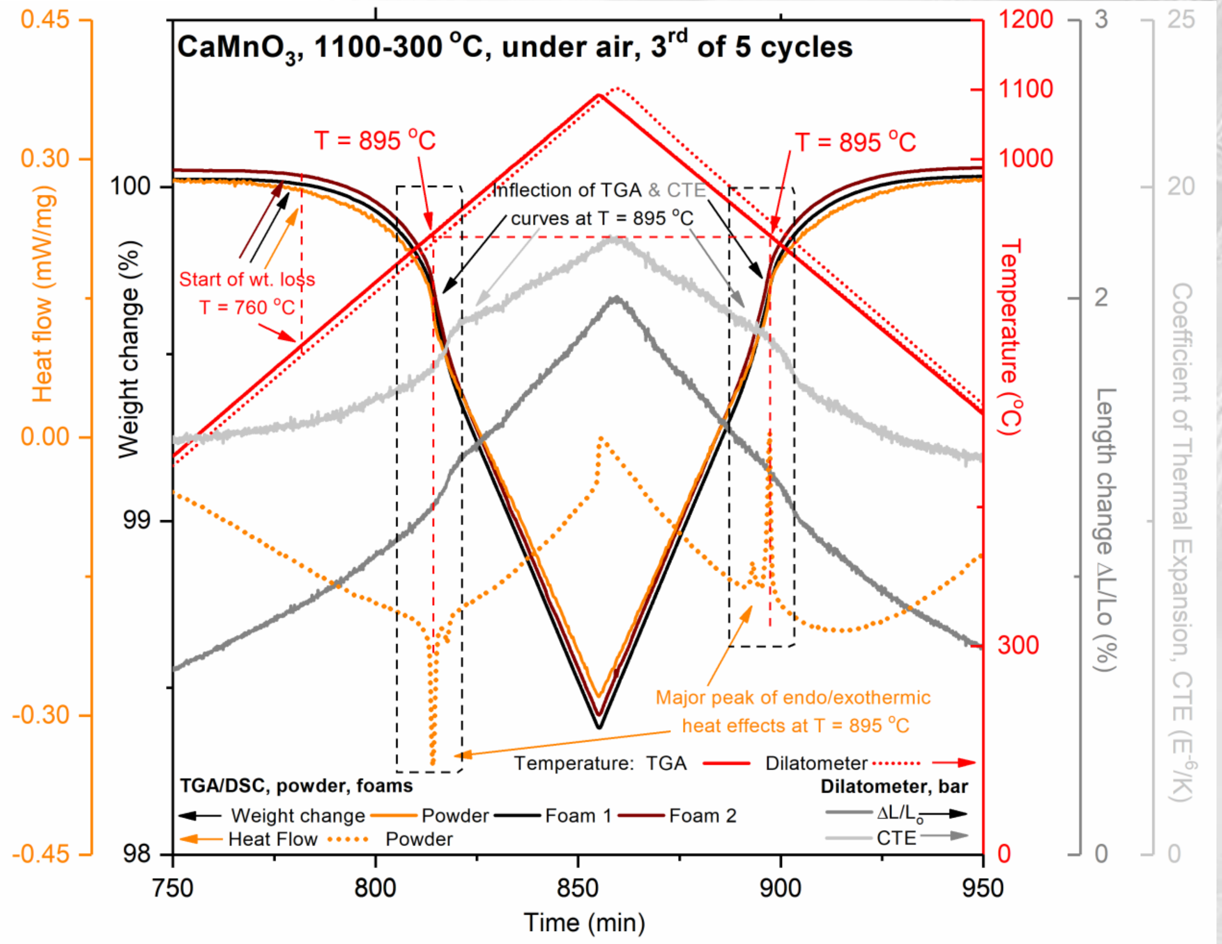
TGA/DSC phase transition

- Phase transition (PT) fully reversible in air
- Heat effects and weight loss/gain at T_{pt}
- PT leads to lattice expansion
- Cubic phase exhibits greater thermal expansion coefficient $\alpha_{cubic} > \alpha_{orthorhombic}$
- Cubic phase has lower formation energy of oxygen vacancies
- Foam and powder exhibit identical thermodynamic behavior



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Outlook: Influence of A-site Sr-substitution in $Ca_{1-x}Sr_xMnO_3$

Increasing Sr-content

- Phase transition *orthorhombic* <-> *cubic* shifts towards lower temperatures
- Heat effects of phase transition get smaller and eventually vanish ($x \geq 0.2$)
- Oxygen vacancy formation energy reduced
- Faster oxidation kinetics
- Small amounts of Sr-content stabilize thermal expansion/contraction at reduced $p(O_2)$

Outlook 2: Oxygen Pumping with foam specimen

- Sr-substituted CaMnO3-Specimen with 0%, 5% and 10% Sr-content tested in lab scale demonstrator
- Oxygen purposefully pumped from reference chamber in Temp.-swing operation
- ≈ 2-fold increase in Δδ of reference material CeO_2
- Experimental campaign ongoing

O_2-pumping reactor:		Reference reactor:	
$T_{Red:}$:	800°C	$T_{Red:}$:	1500°C
T_{ox}:	700°C	T_{ox}:	1000°C

Operating total pressure: 10^{-5} bar

Conclusion

- Mechanically stable open porous monilithic foams from $CaMnO_3$
- Foams exhibit identical thermodynamic behavior as powder
  - No ageing observed over 46 cycles
- Fully reversible thermal expansion and contraction between 300-1100°C under air
- A-site Sr-substitution: production successfully transferred
  - Lowers T_{pt} and reduces heat effects
  - Reduced mechanical stress during thermal cycling around T_{pt}
- Foam specimen proven to work in oxygen pumping demonstrator reactor

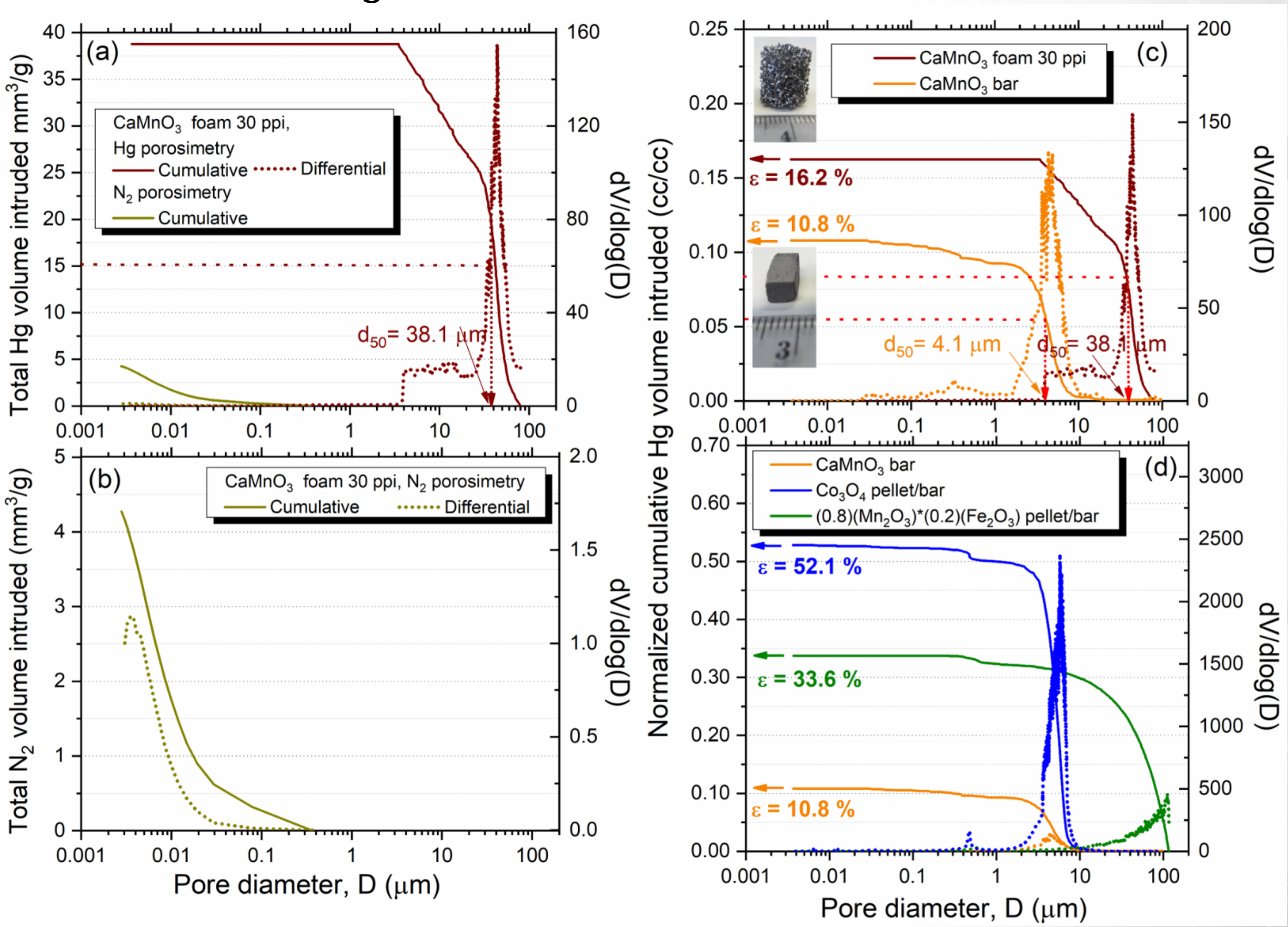
Thank you for your attention

Further information:

- Pein et al. "Reticulated Porous Perovskite Structures forThermochemical Solar Energy Storage", *Advanced Energy Materials* (2022), p. 2102882. DOI: https://doi.org/10.1002/aenm.202102882.

Thanks to all colleagues for contributing to this work

Porosity of $CaMnO_3$-specimen



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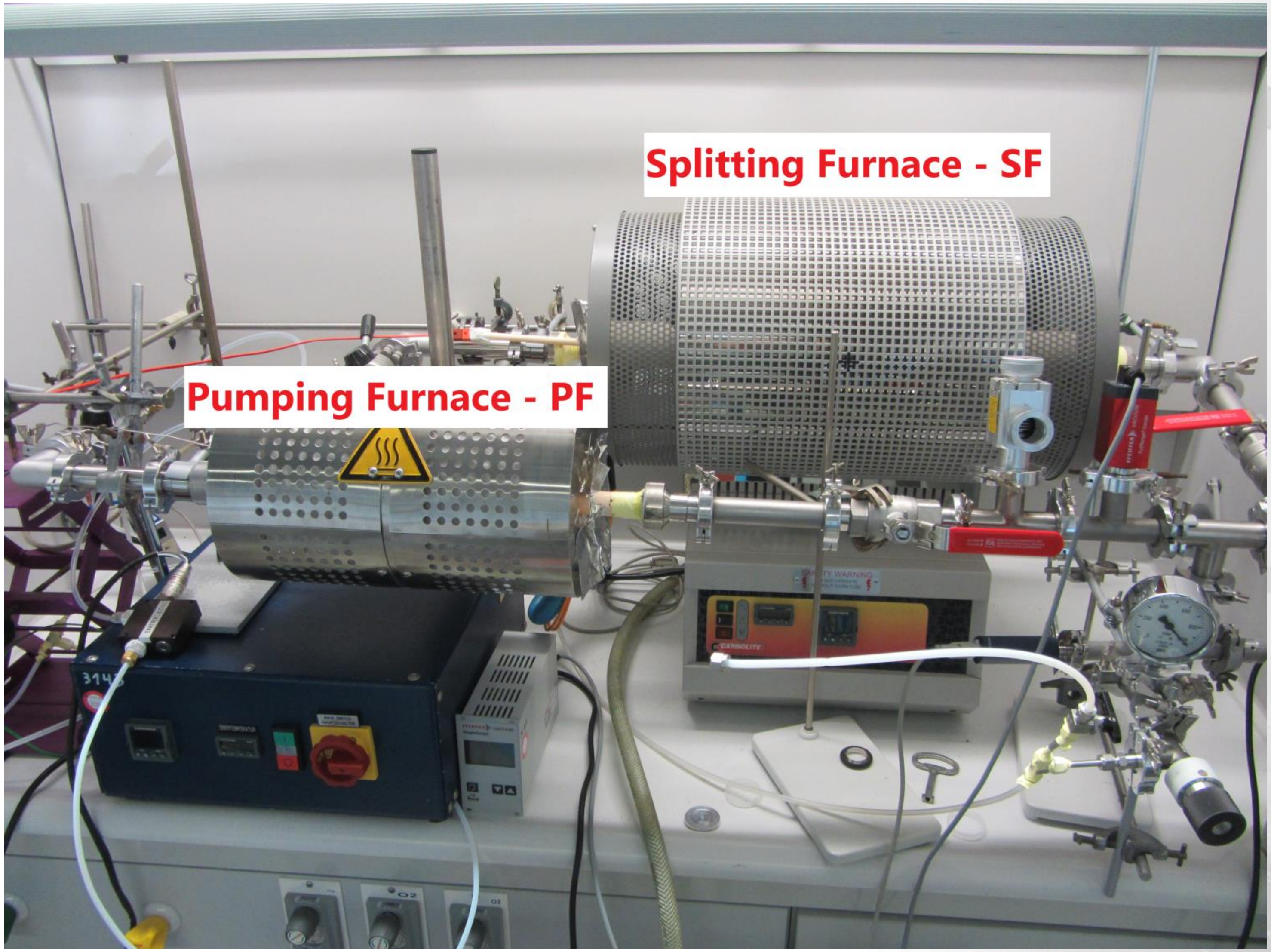
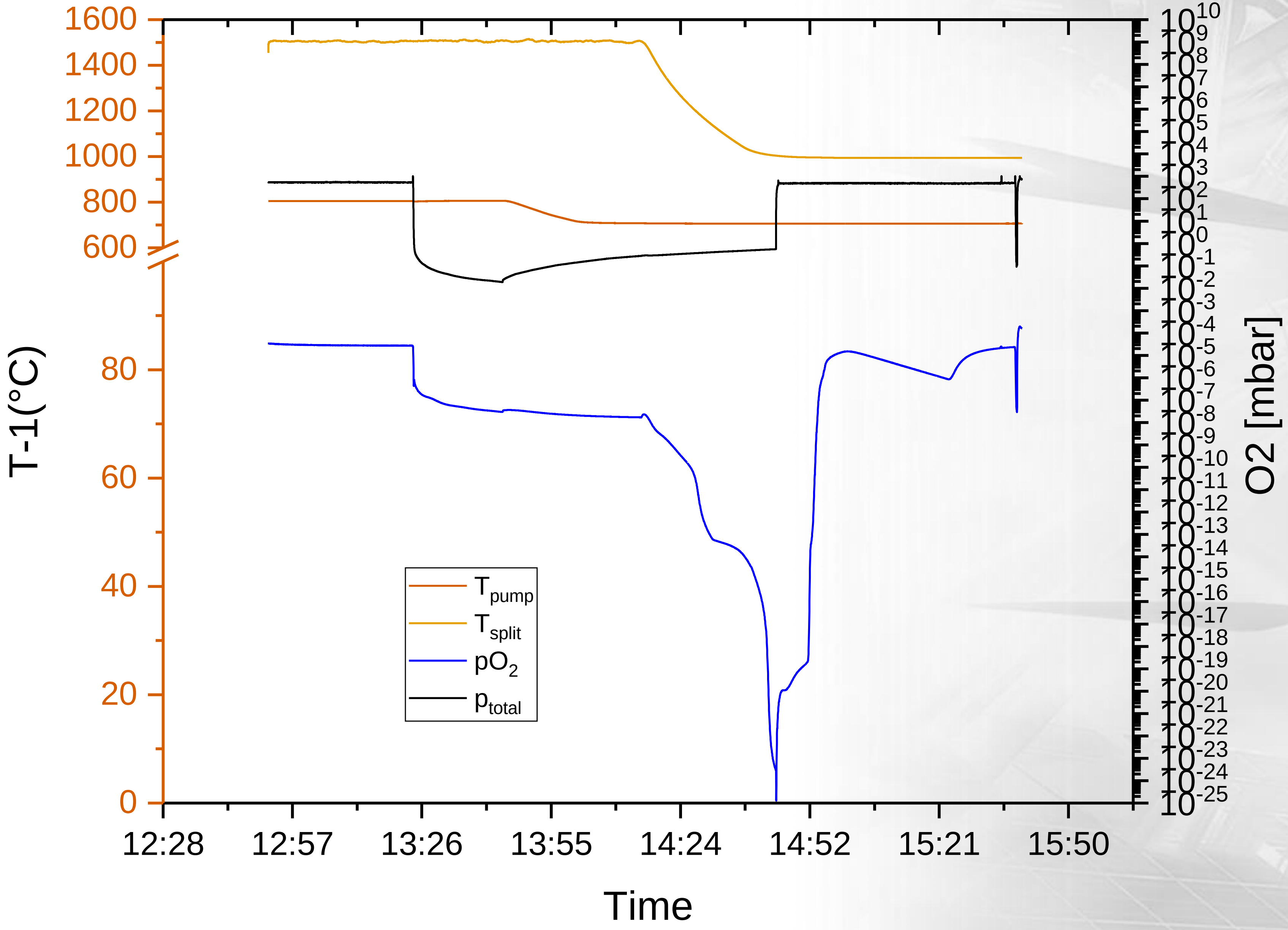
O_2-pumping setup




1600
1400
1200
1000
800
600
80
60
40
20
0
T-1(°C)
12:28
12:57
13:26
13:55
14:24
14:52
15:21
15:50
Time
O2 [mbar]
T pump
T split
pO2
p total