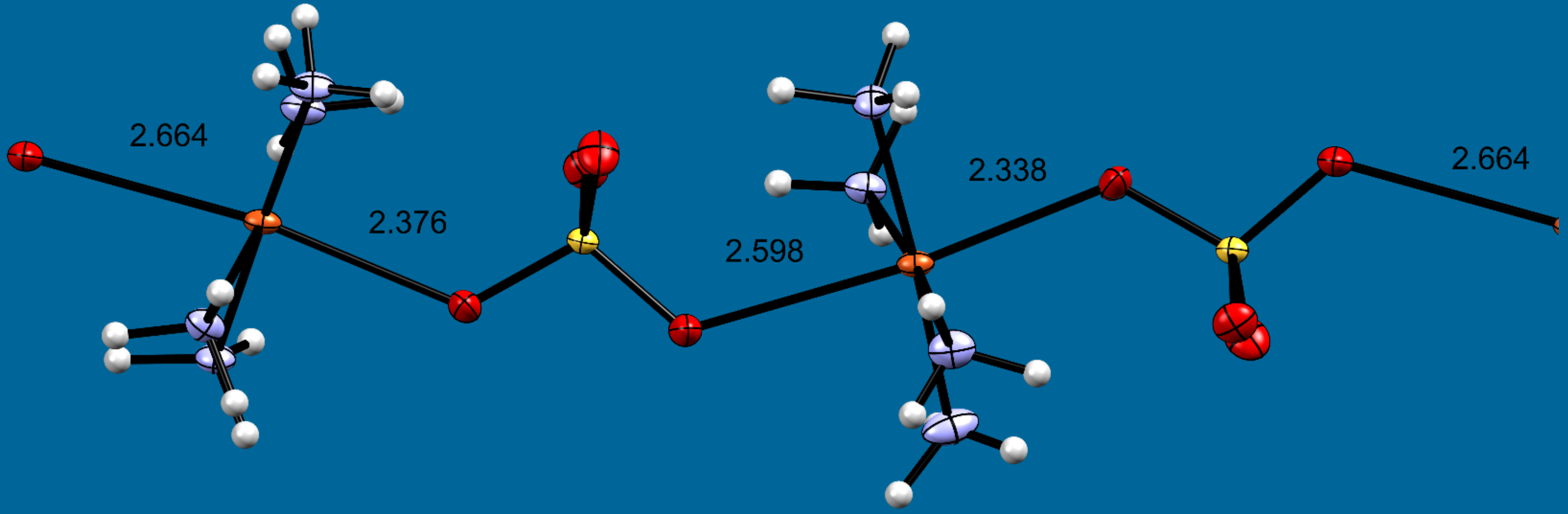
TECHNISCHE UNIVERSITÄT WIEN

Institute of Applied Synthetic Chemistry

Magneto & Thermo Chemistry

Thermochemical Heat Storage by High Performance Salt Ammoniates



Associate Professor
Dr. Peter Weinberger

3rd International Sustainabel Energy Conference 2024, 10.-11.April 2024, Graz, Austria.

Thermochemical Energy Storage

Heat is the most ubiquitously used form of energy

Industrial production

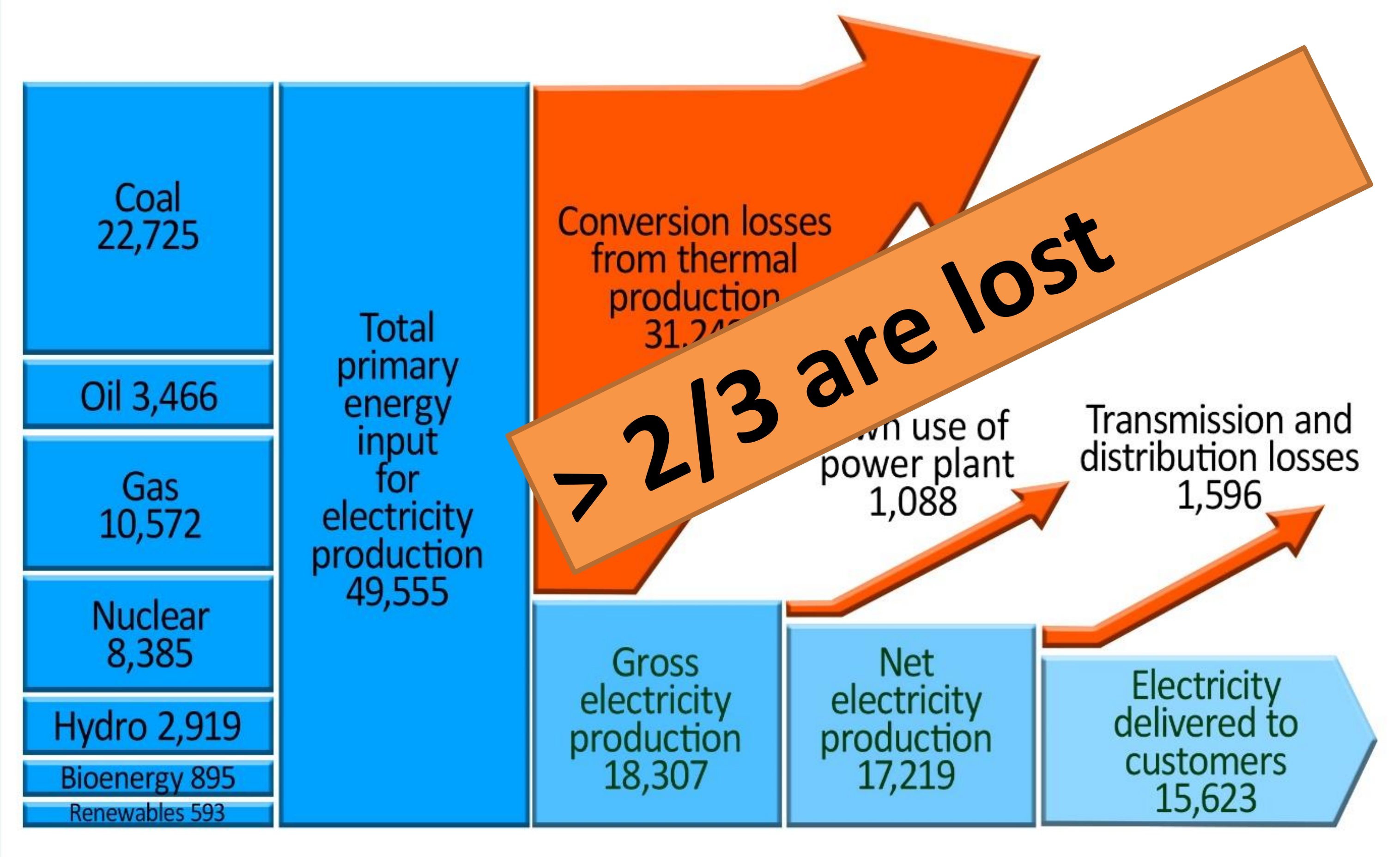
Electricity generation

Cooking

Heating

Thermochemical Energy Storage

Heat is the most abundant energy source for electrical power generation



Annual energy flows in global electricity generation [TWh]

Co-generation and Renewables. Solutions for a low-carbon energy future, IEA, ***2011***

Energy Storage Concepts

Sensible	Latent	Sorption	Reaction

storage capacity, materials costs →

← **TRL, storage volume**

Sensible storage

- Heating / cooling of a liquid / solid material
- H_2O, oil, rock, ...

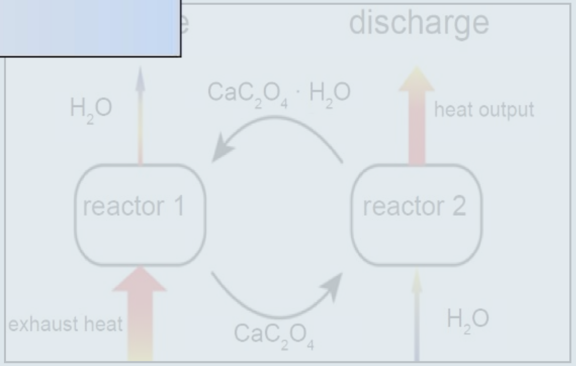
Latent storage

- Phase-change materials
- Paraffin wax ...

Chemical storage

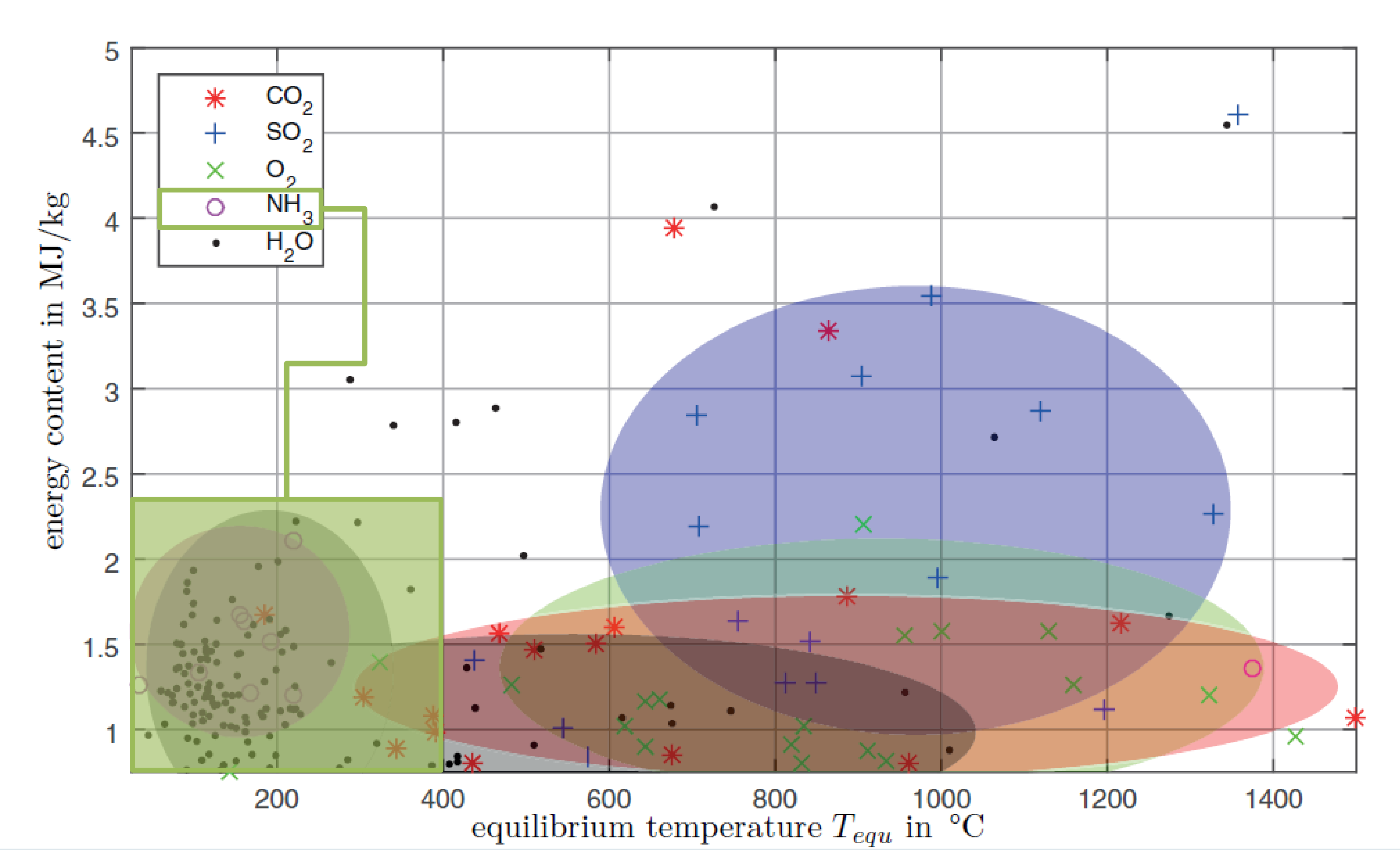
- C + ΔH ↔ A + B
- Hydrates, carbonates, oxides,...

storage capacity



A Systematic Material Investigation

Systematic investigation of potentially suitable materials for thermochemical energy storage with different reactive gasses, based on the HSC-database



Appl. Energy, **2016**, *183*, 113-120.

Thermochemical Energy Storage

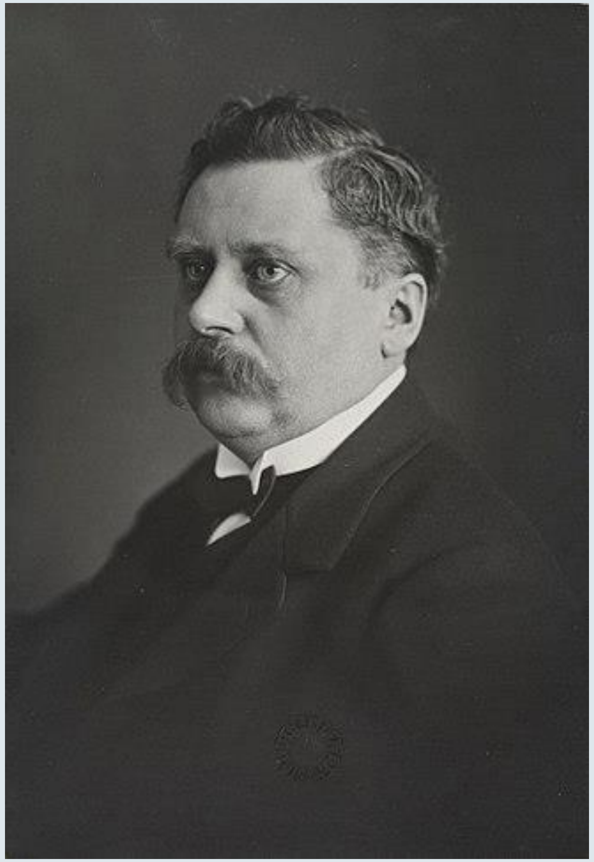
Concept of thermochemical storage

$Mg(OH)_2$

- Higher storage densities
- Broad temperature range
- Lossless (long-term) storage
- Transportation possible

A few reactions intensely investigated in literature

The Beginnings of 3d-NH_3 Complexes



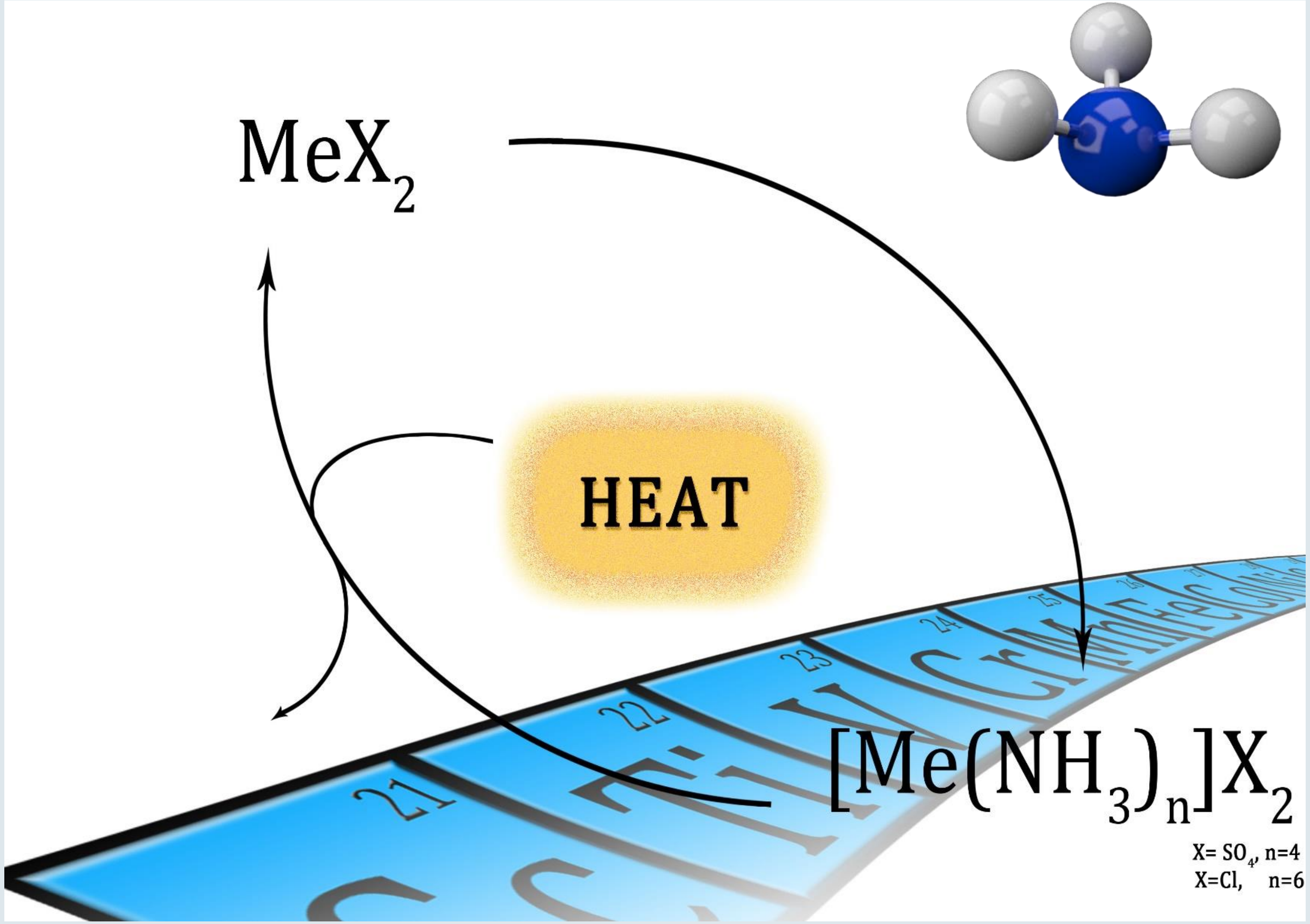
Alfred Werner
1866-1919

$[Cu(NH_3)_4]SO_4 \cdot H_2O$

violeo

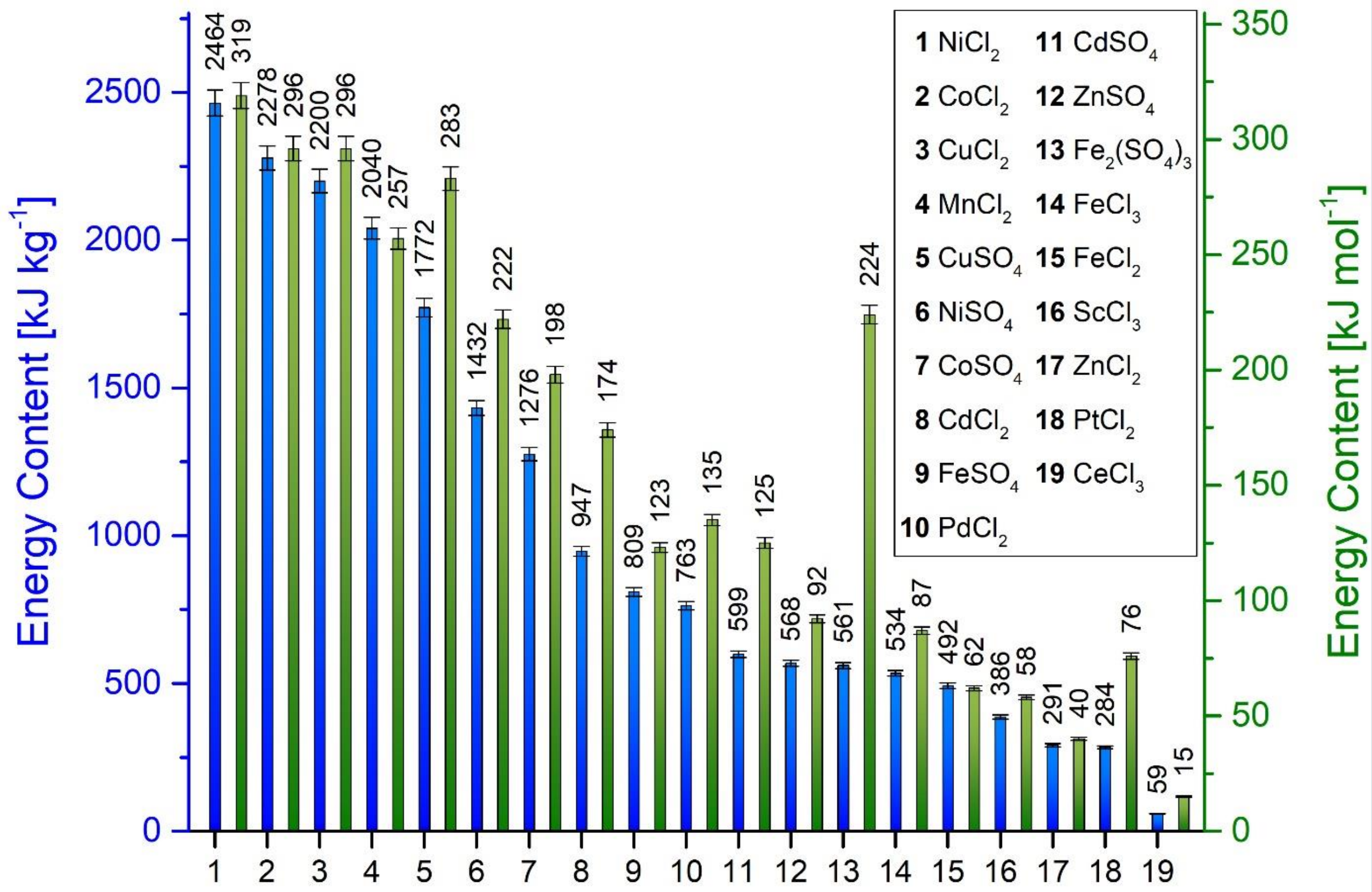
praseo

Transition Metal Ammoniates



Transition Metal Ammoniates

Highest energy content for thermochemical storage materials in this temperature window



For comparison:

CoO / Co_3O_4	844 kJ kg^{-1} [1]
$MgO / Mg(OH)_2$	104 kJ kg^{-1} [2]

[1] 10.1016/j.solmat.2013.12.018
[2] 10.1021/ie404246p

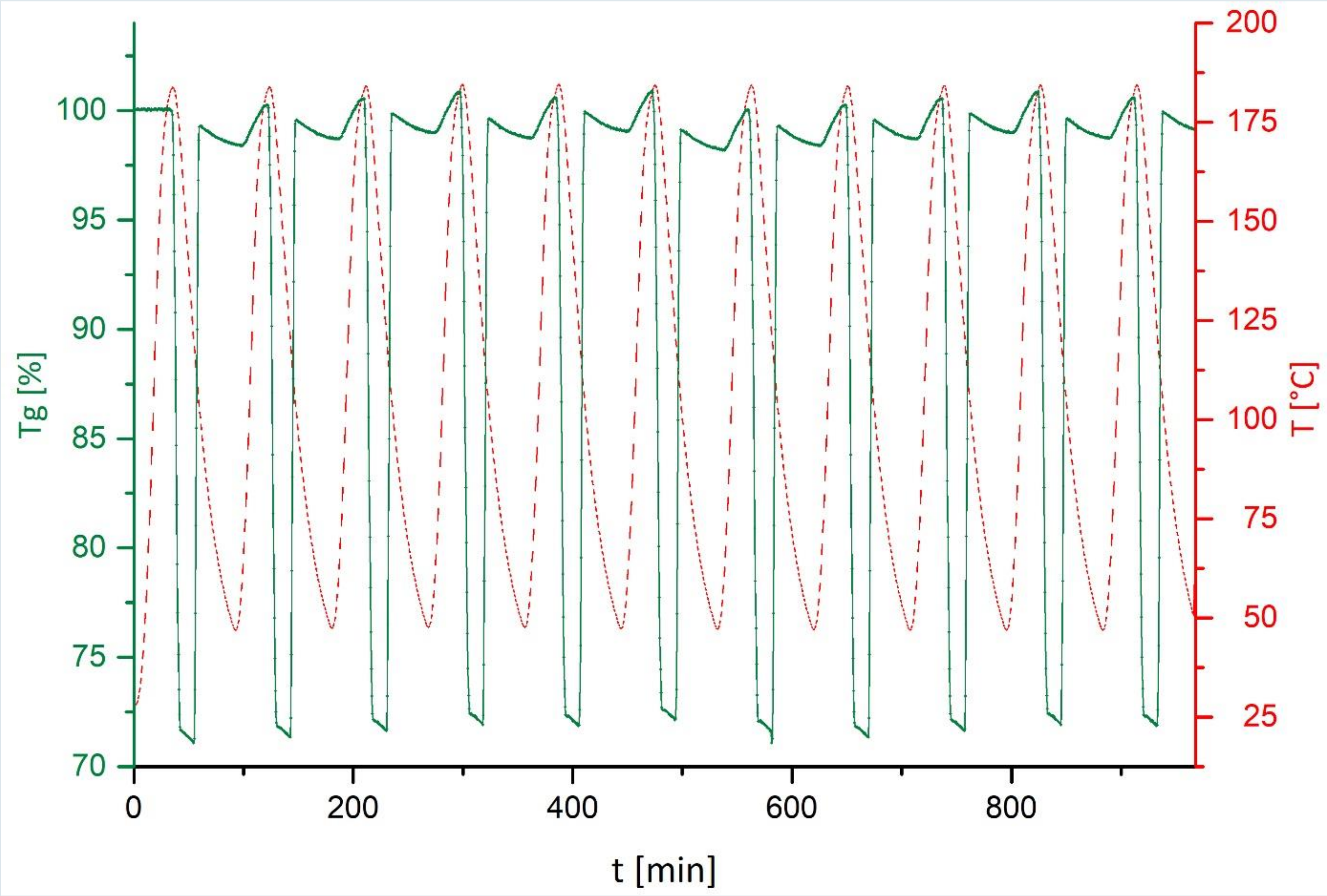
A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$NiCl_2 + 6\ NH_3 \leftrightarrow [Ni(NH_3)_6]Cl_2$

Decreasing maximum temperatures results cycling of

Poor cycle stability due to slow sublimation / decomposition

$[Ni(NH_3)]Cl_2 + 5\ NH_3 \leftrightarrow [Ni(NH_3)_6]Cl_2$

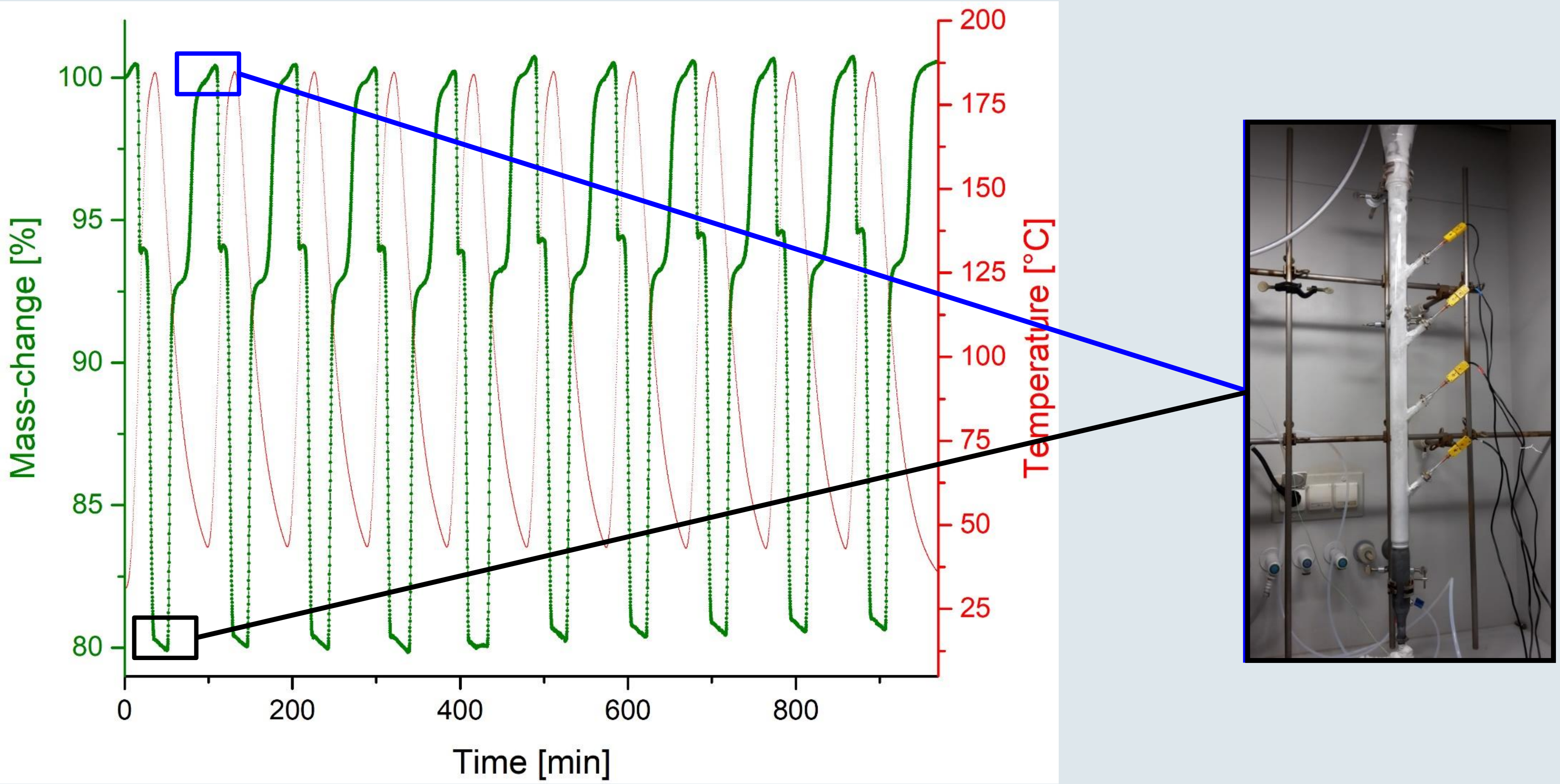


Cycle stability enhanced, energy content decreased

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$CuSO_4 + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]SO_4$

$CuSO_4 + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]SO_4$ perfectly cycle stable

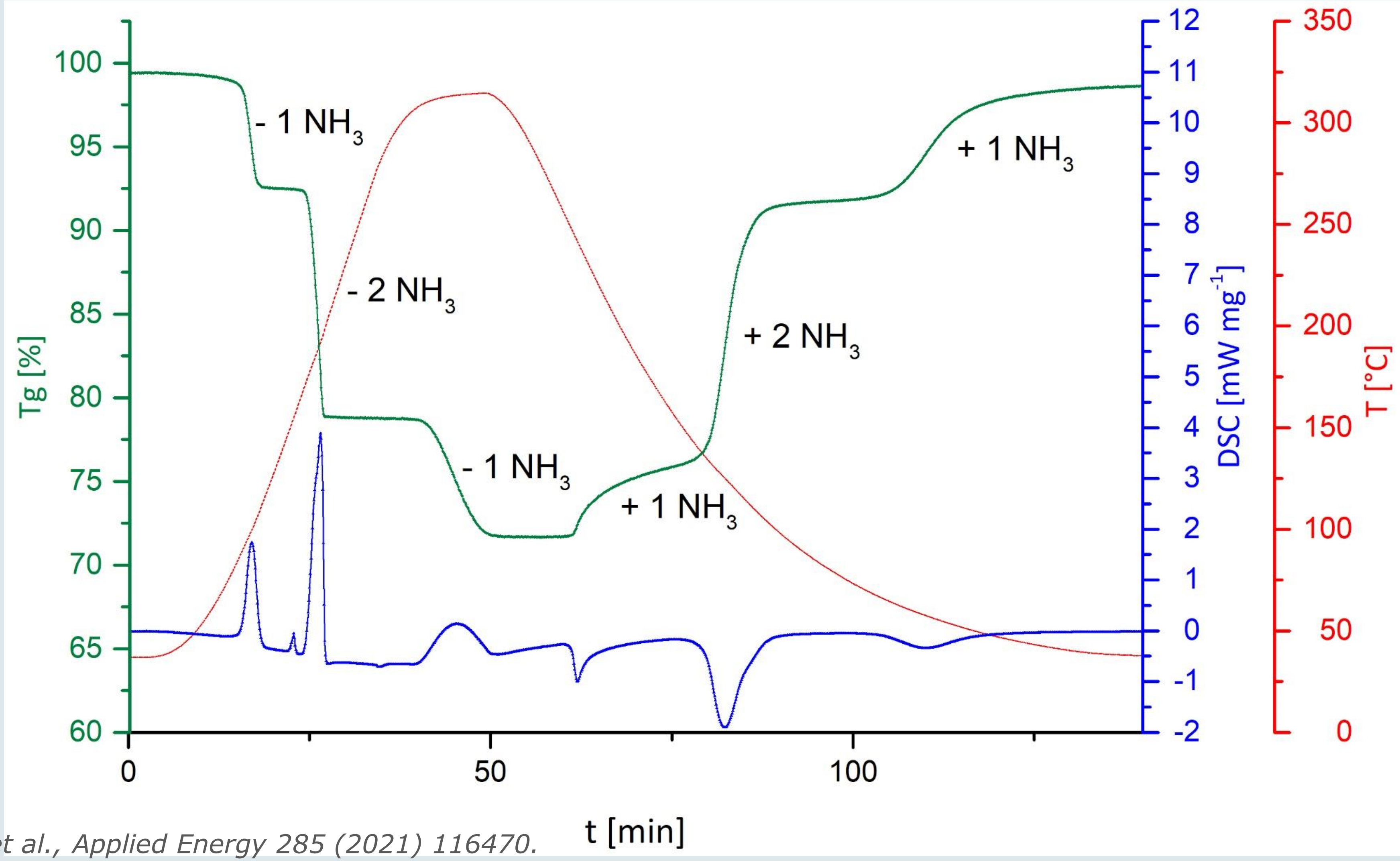


A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$CuSO_4 + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]SO_4$

Decomposition and formation of $[Cu(NH_3)_4]SO_4$ under NH_3-atmosphere

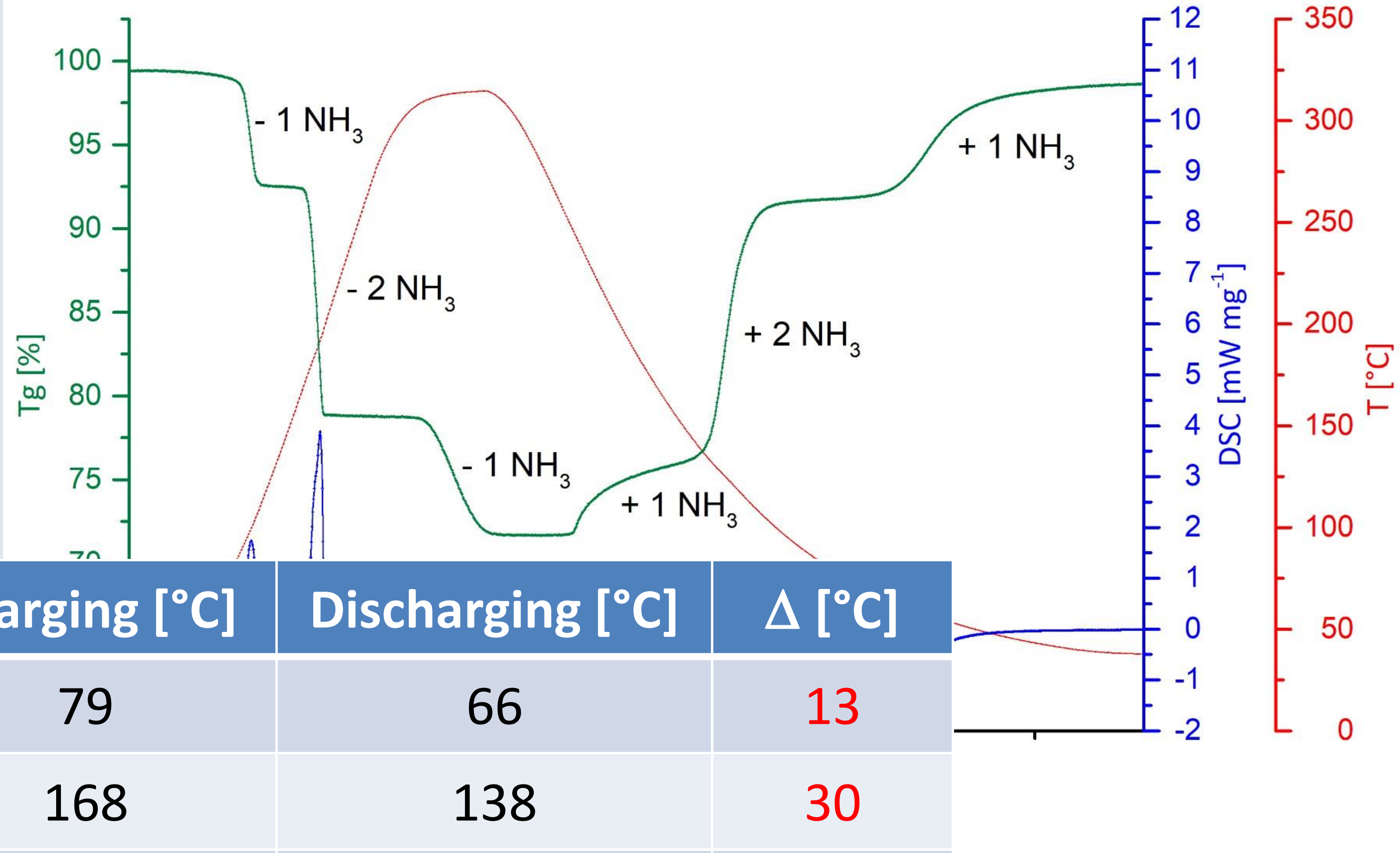
Stepwise removal and uptake of NH_3-ligands



A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$CuSO_4 + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]SO_4$

Application as cascade storage material

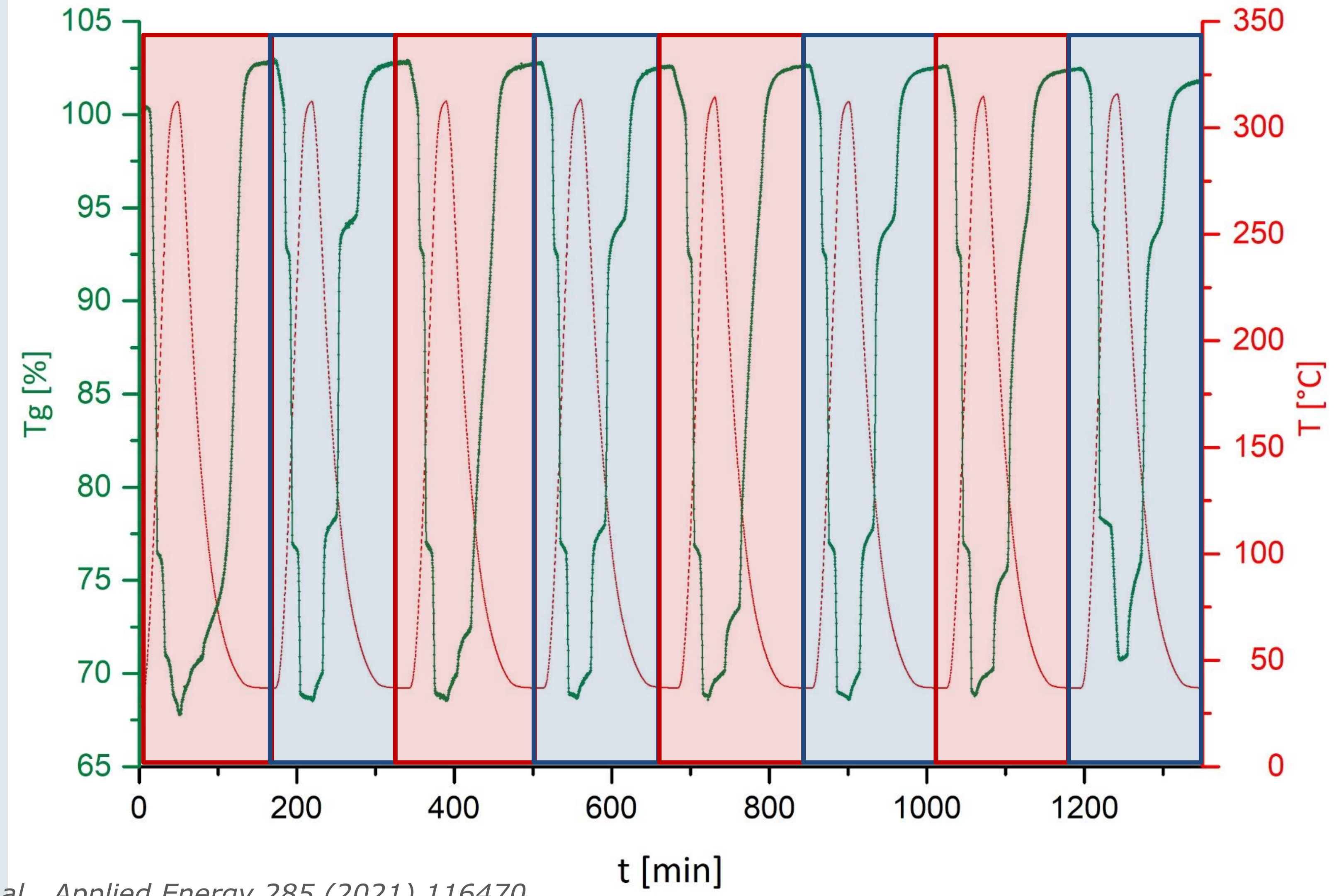


	Charging [°C]	Discharging [°C]	Δ [°C]
1st step (1 NH_3)	79	66	13
2nd step (2 NH_3)	168	138	30
3rd step (1 NH_3)	307	248	59

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$CuSO_4 + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]SO_4$

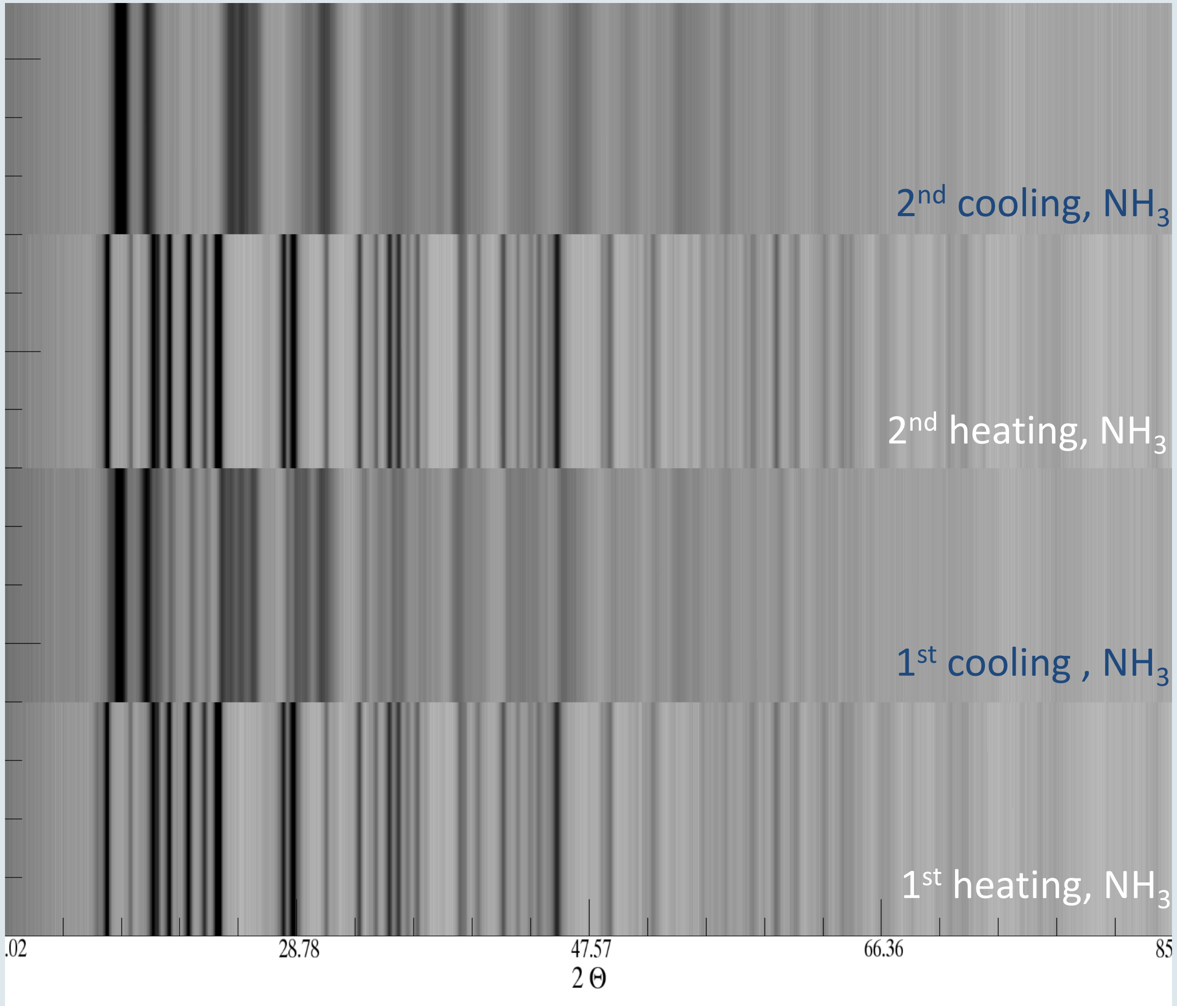
Heating under N_2-atmosphere, cooling under NH_3 atmosphere



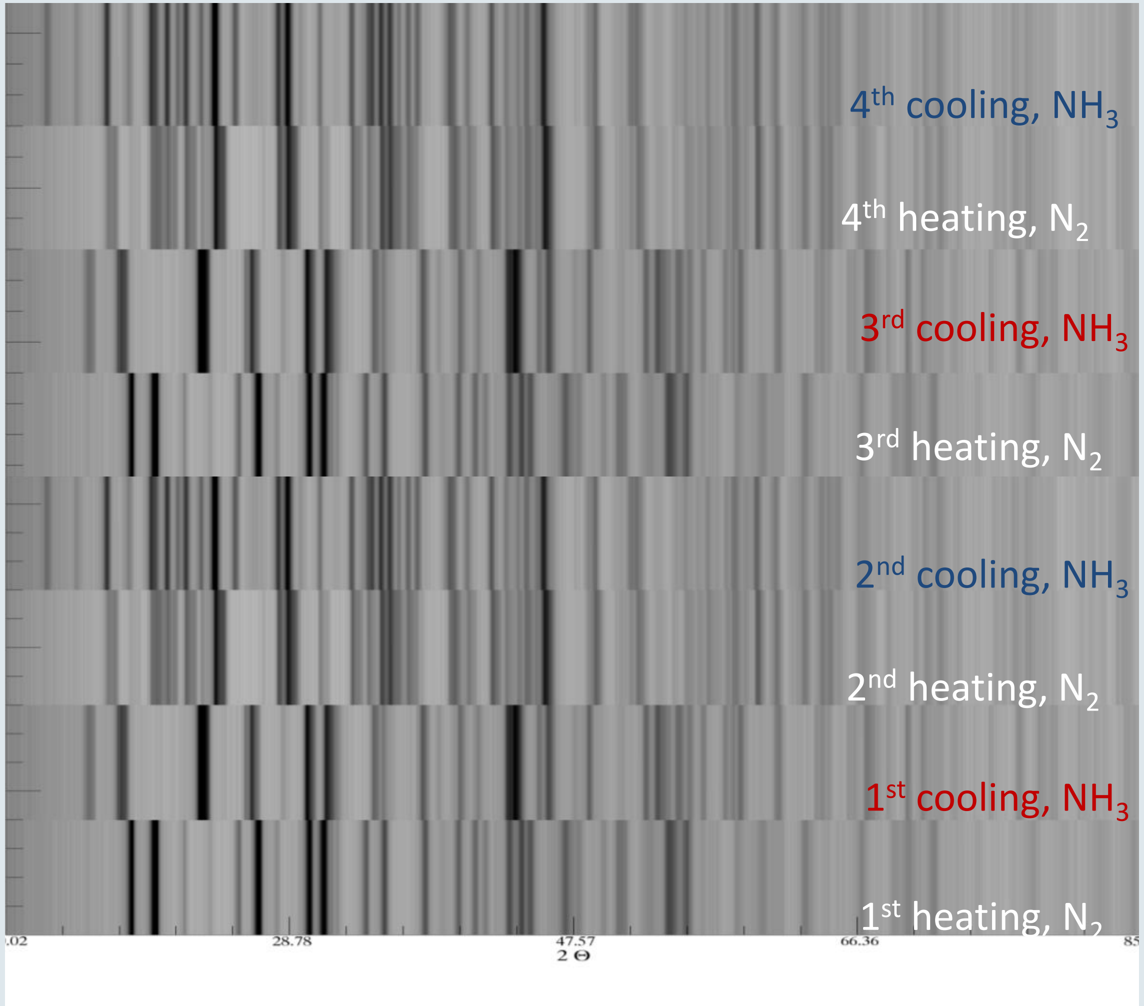
Switching between a 1-step and 3-step process

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

In-Situ P-XRD Study



Cycling under NH_3-atmosphere

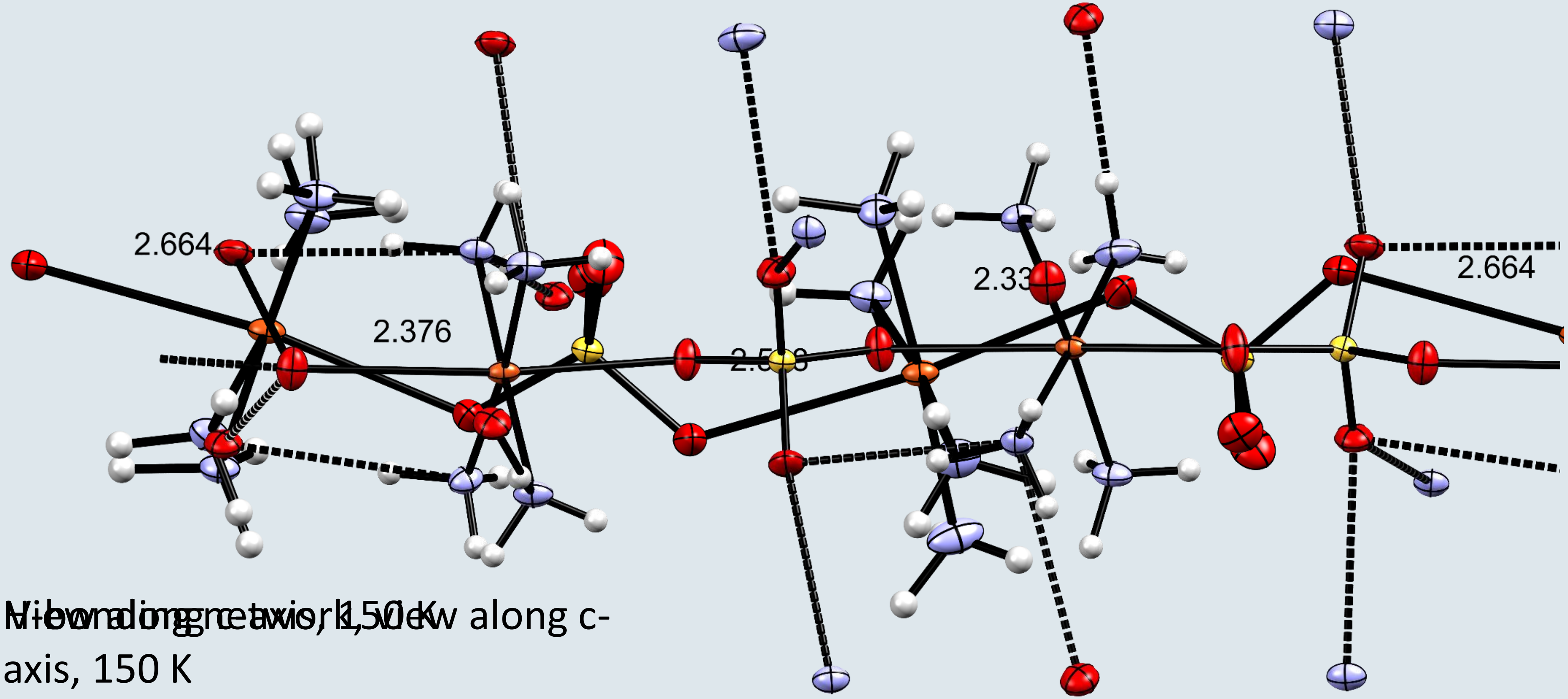


Cycling under N_2 (heating) and NH_3 (cooling)

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

Molecular Structure of $[Cu(NH_3)_4]SO_4$

Single crystals of $[Cu(NH_3)_4]SO_4$ were obtained from MeOH-solution



View along c-axis, 150 K

H-bonding network, 1, view along c-axis, 150 K

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

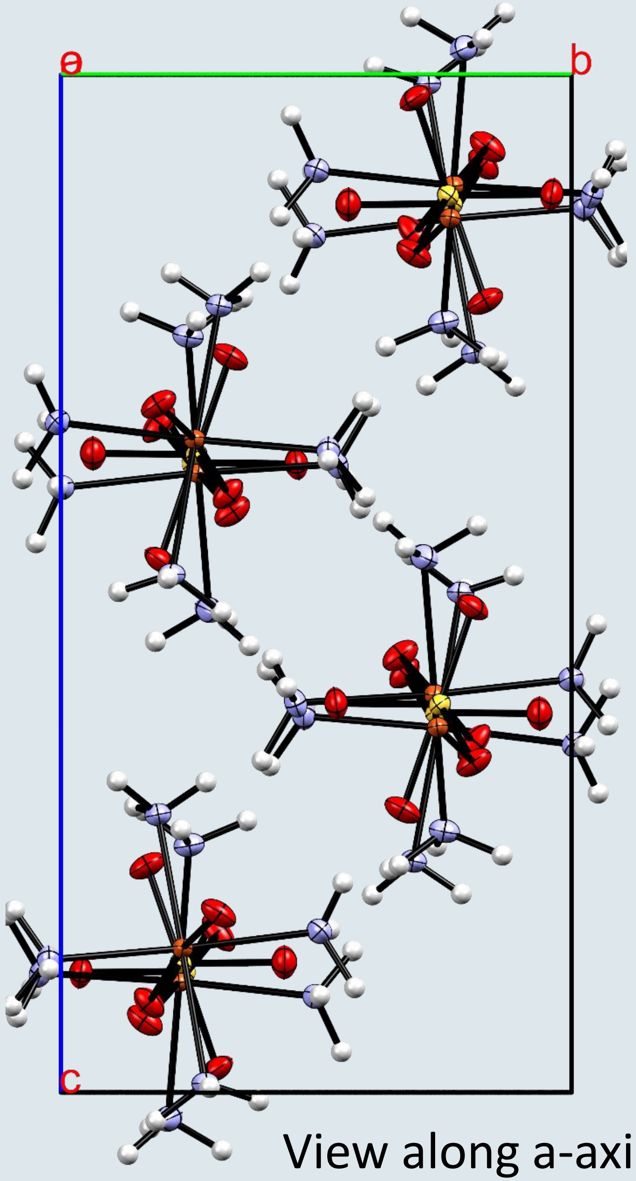
Molecular Structure of $[Cu(NH_3)_4]SO_4$

Single crystals of $[Cu(NH_3)_4]SO_4$ were obtained from MeOH-solution

	P 2_1/c
a [Å]	14.182(3)
b [Å]	7.3078(12)
c [Å]	14.571(3)
β [°]	91.656(4)
V [Å^3]	1509.5
Z	8

Cell-parameters at 150 K

Pseudo mirror- and glidereflection planes in all 3 axes

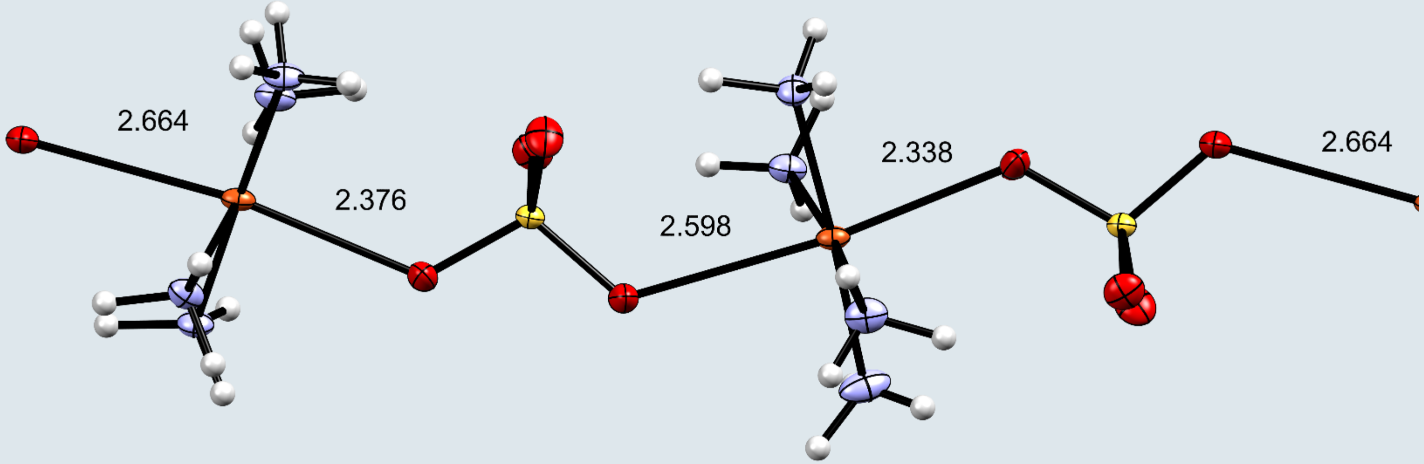


View along a-axis, 150 K

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

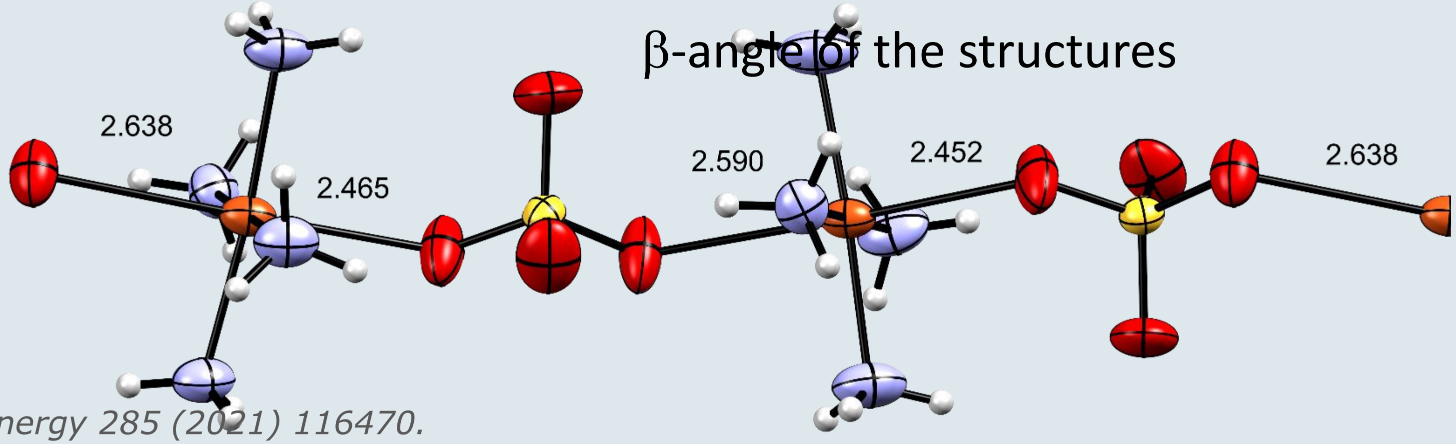
Molecular Structure of $[Cu(NH_3)_4]SO_4$

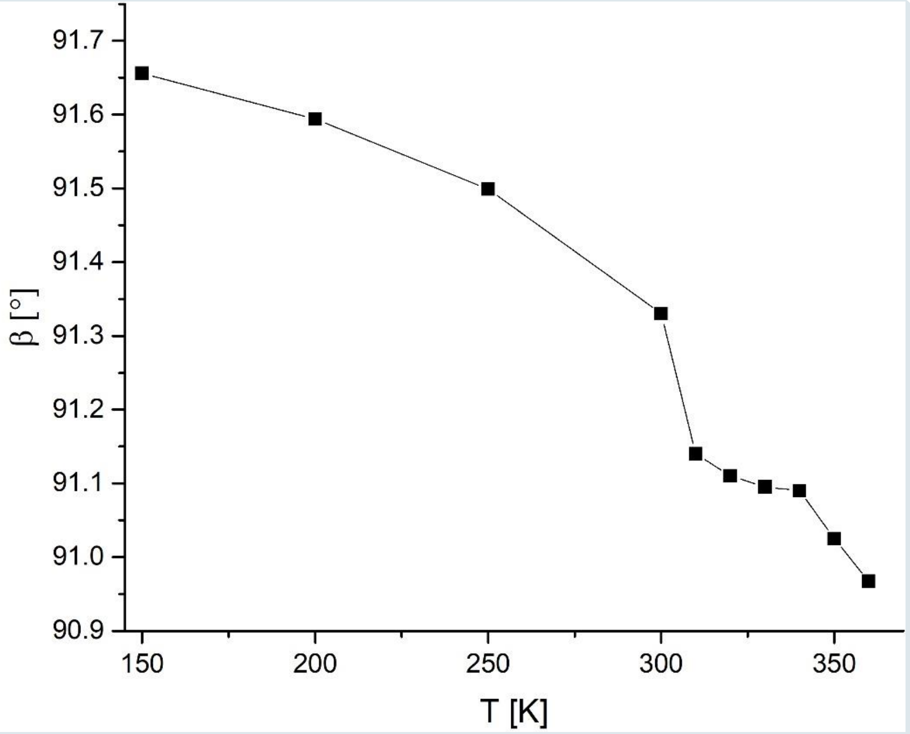
Bond-lengths extend and assimilate on heating



View along c-axis, 150 K

View along c-axis, 360 K



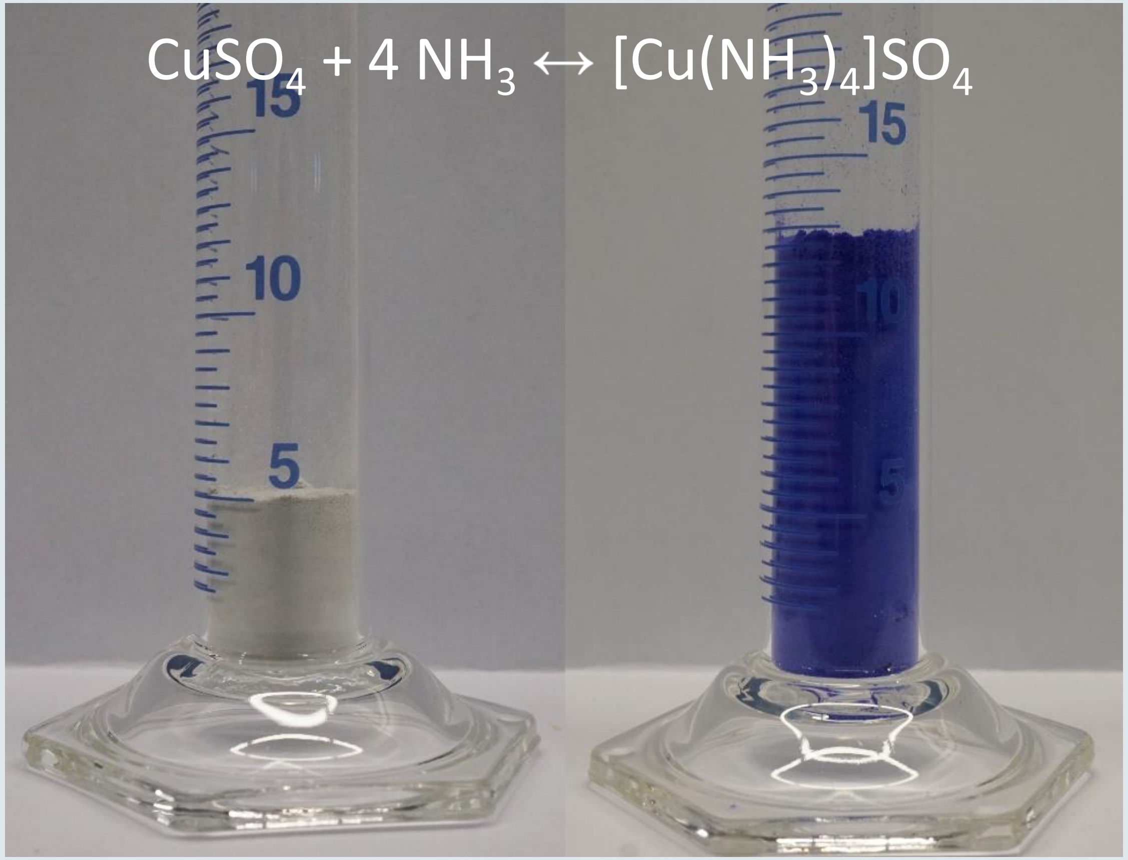


β-angle of the structures

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

Volume Work During Cycling

$CuSO_4$ expands to 2.6-fold volume during reaction with NH_3

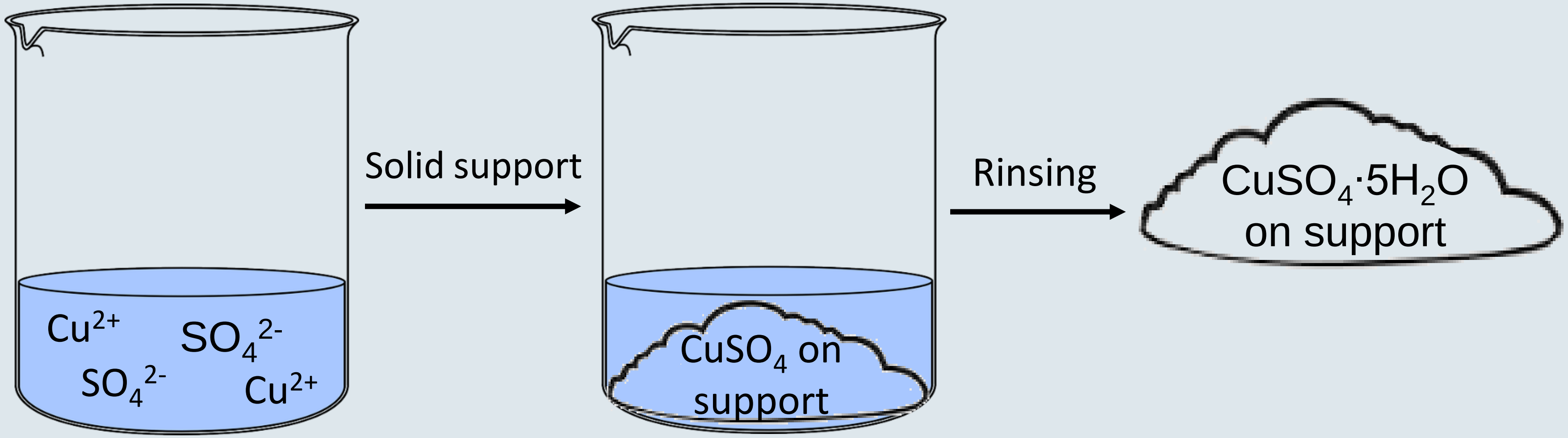


	$CuSO_4$	$[Cu(NH_3)_4]SO_4$
a [Å]	8.3976(1)	14.182(3)
b [Å]	6.70382(9)	7.3078(12)
c [Å]	4.82443(8)	14.571(3)
V [Å^3]	271.6	1509.5

A 327/2016, A345/2017; D. Müller et al., Applied Energy 285 (2021) 116470.

$CuSO_4$ on Solid Support Materials

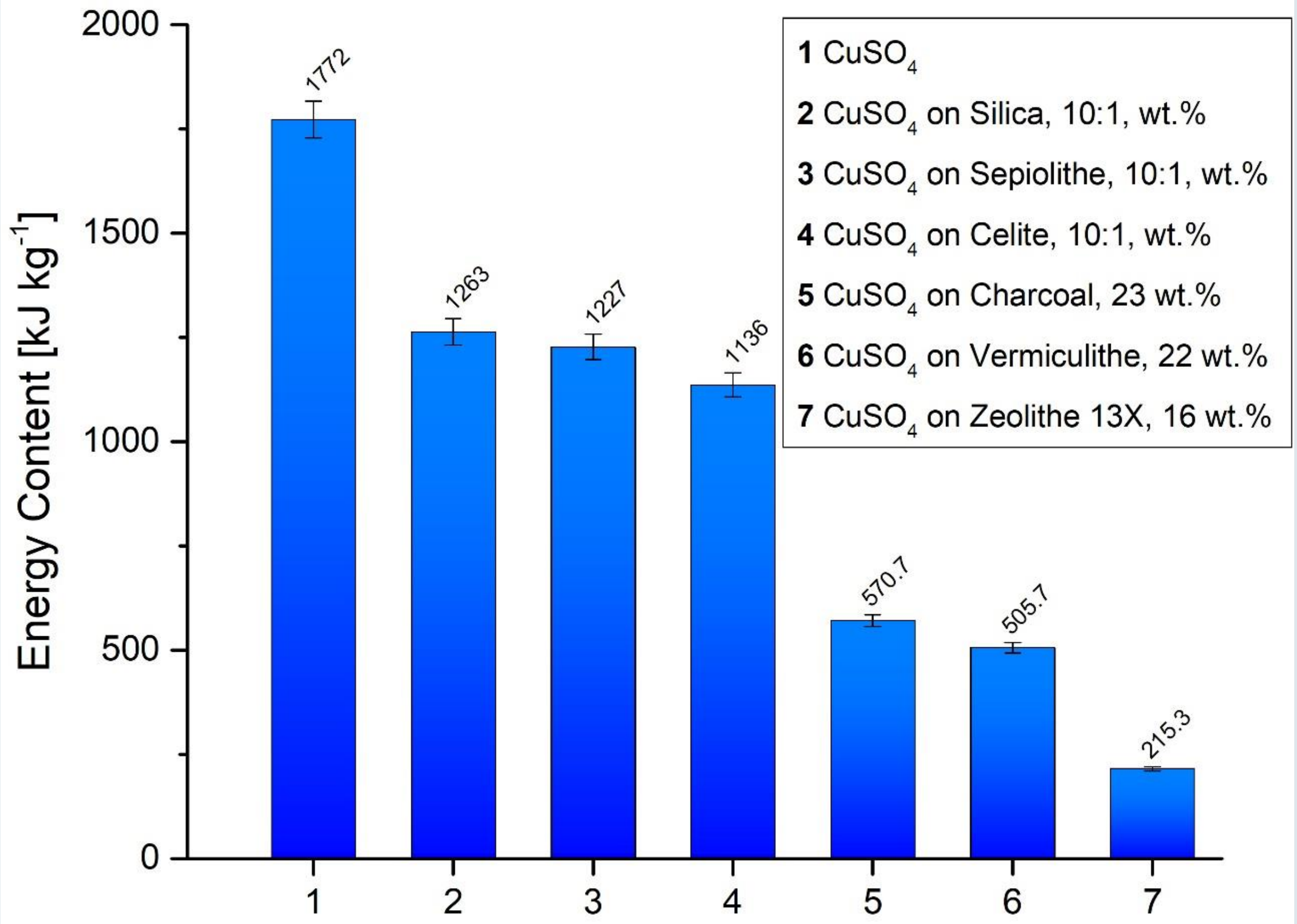
Impregnation / loading of passive, solid support materials with $CuSO_4$

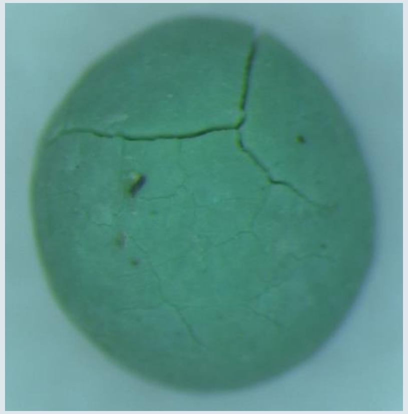


A 327/2016, A345/2017;

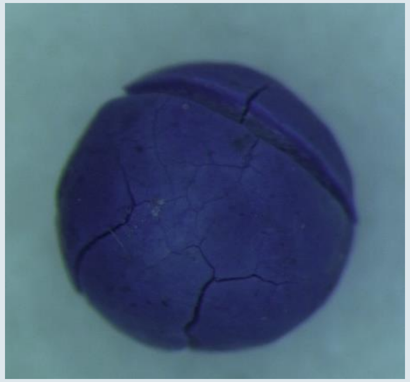
$CuSO_4$ on Solid Support Materials

Various $CuSO_4$ concentrations on the different solids





$CuSO_4$ on zeolithe

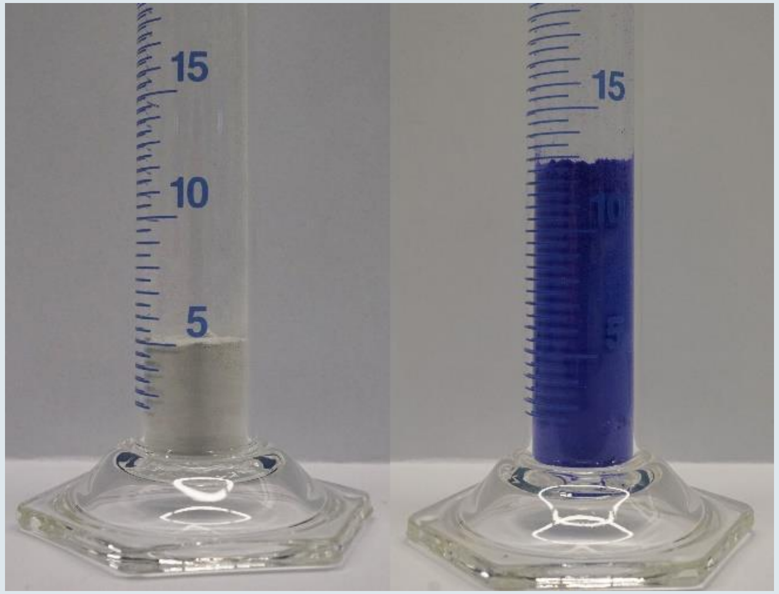


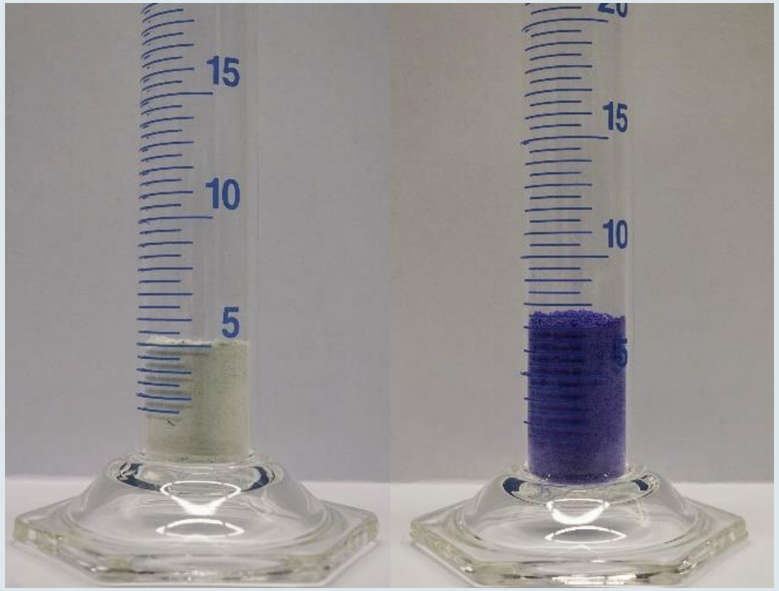
$[Cu(NH_3)_4](SO_4)$ on zeolithe

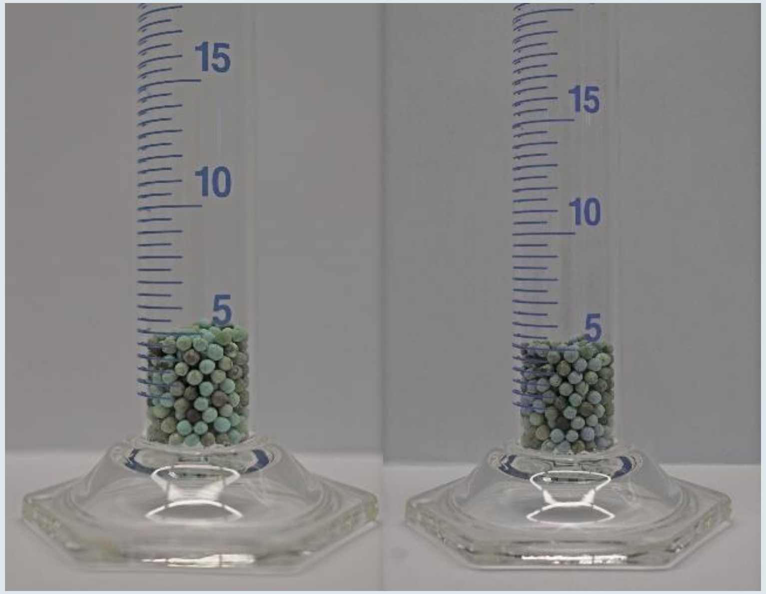
D. Müller et al., Nanomaterials 10 (2020) 2485.

Volume Work During Cycling

Solid support for $CuSO_4$ decreases notably the volume work during cycling







$CuSO_4$	$CuSO_4$ on Sepiolithe	$CuSO_4$ on Zeolithe 13X
	10:1 wt.%	16 wt.%
2.6-fold volume	1.3-fold volume	no expansion
1772 kJ kg^{-1}	1263 kJ kg^{-1}	215.3 kJ kg^{-1}

D. Müller et al., Nanomaterials 10 (2020) 2485.

$CuSO_4$ on Zeolithe 13X

Highly comparable performance between pure $CuSO_4$ and $CuSO_4$ @ 13X

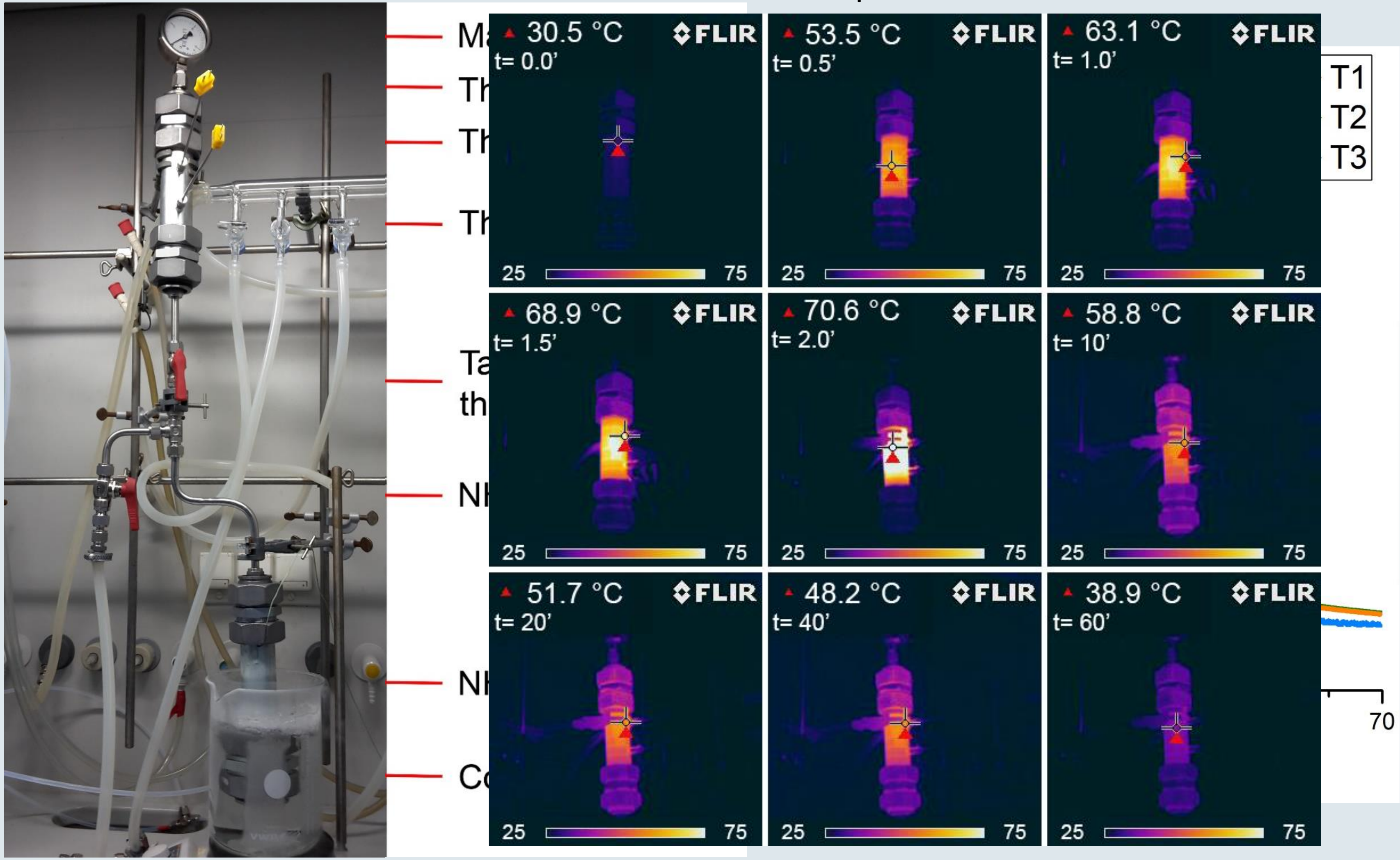
Comparing pure and loaded material

	$CuSO_4$	**$CuSO_4$ @ 13X**
Energy content	1772 kJ kg^{-1}	215.3 kJ kg^{-1}
Storage capacity in 1 m^3	1772 kWh	38.87 kWh
Max. Charging Temperature	380 °C	380 °C
Max. Discharging Temperature	65 °C	65 °C
Max. Peak-Temperature	312 °C	181 °C
Time to Peak-Temperature	93 seconds	90 seconds
Estimated Price per ton	1450 €	1091 €
Bulk density	3.6 t m^{-3}	0.69 t m^{-3}

D. Müller et al., Nanomaterials 10 (2020) 2485.

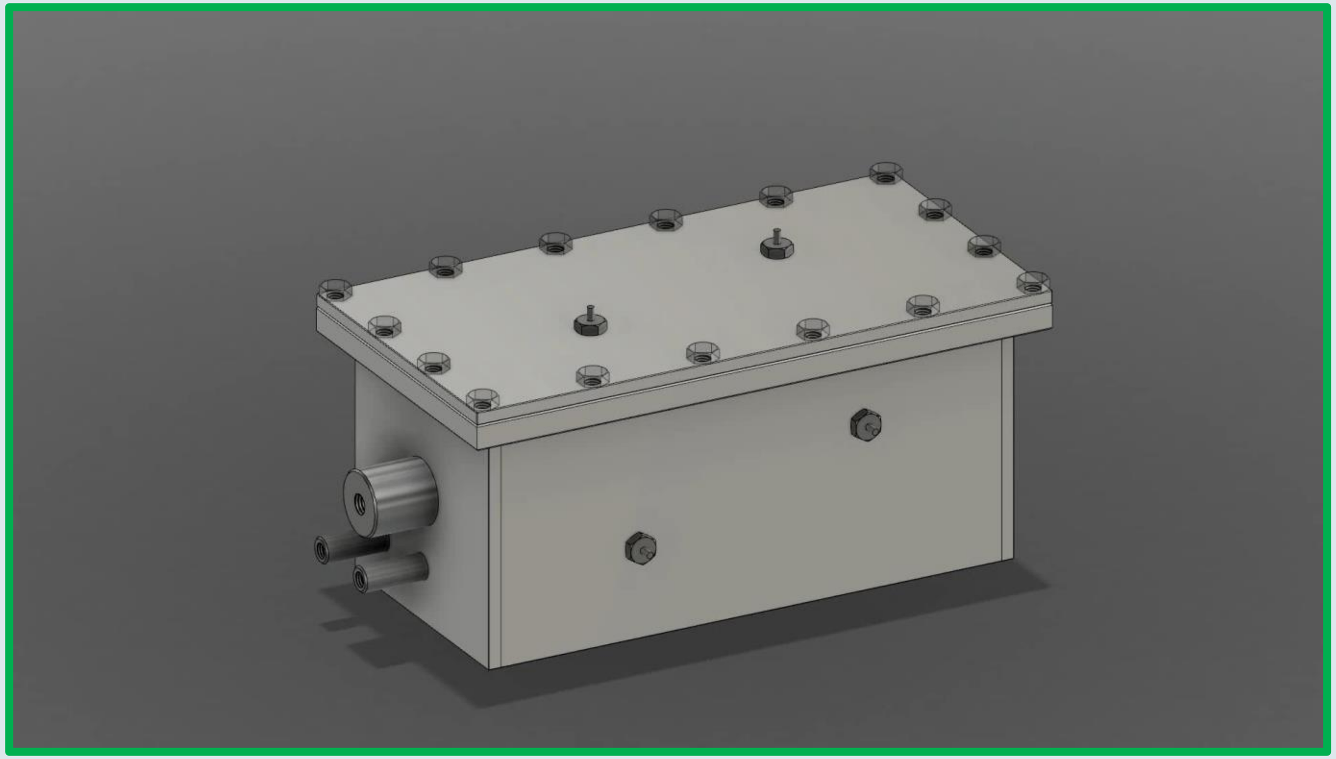
Closed Cycle – A Prototype

Prototype of a closed cycle TCES-process with $CuSO_4$



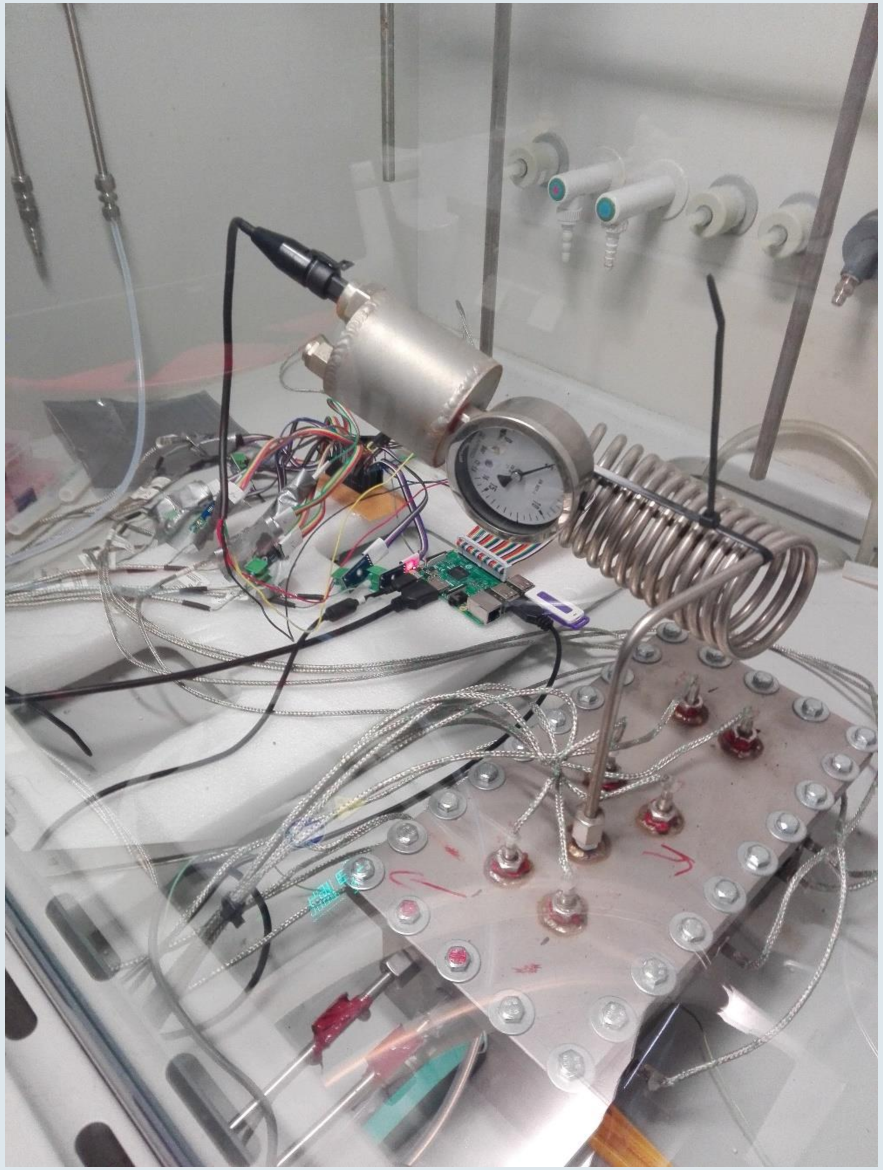
A 327/2016, A345/2017; ISES-Proceedings, ***2018***

A First Prototype in Shoe Box Size

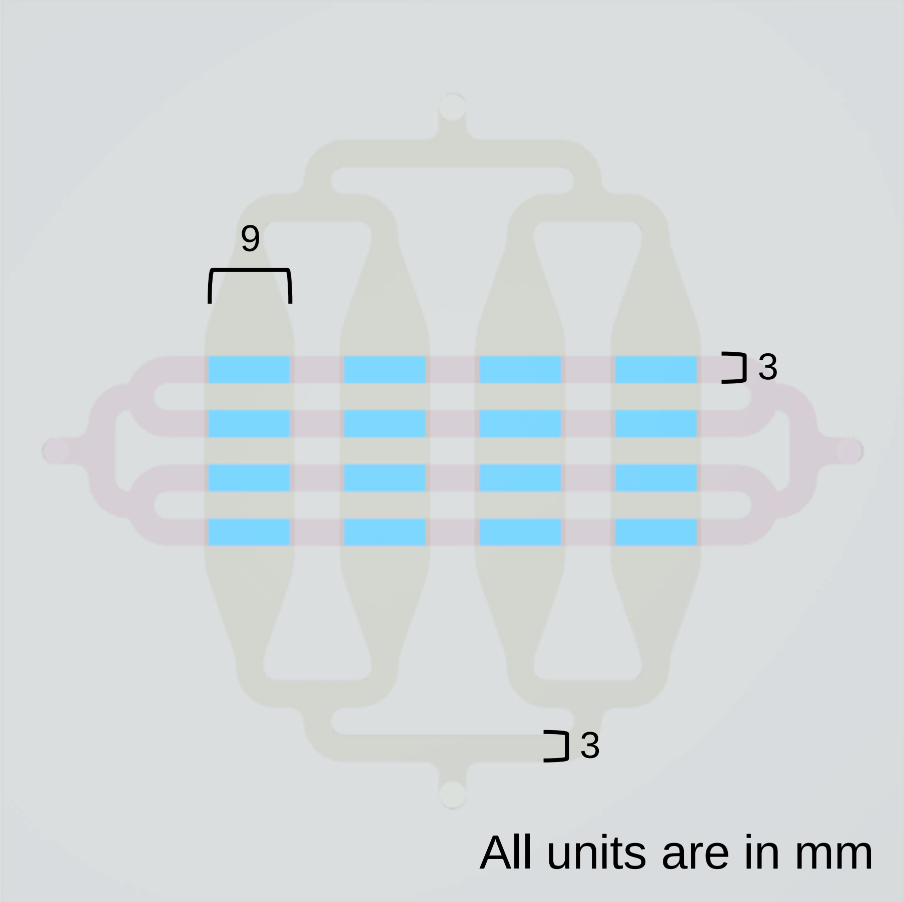


- Thermochemical energy storage using a $CuSO_4$ / $[Cu(NH_3)_4]SO_4$ storage
- 1.77 GJ m^{-3} (0.49 MWh) storage density
- Operates between 25 -350 °C
- Heat release within 20 seconds

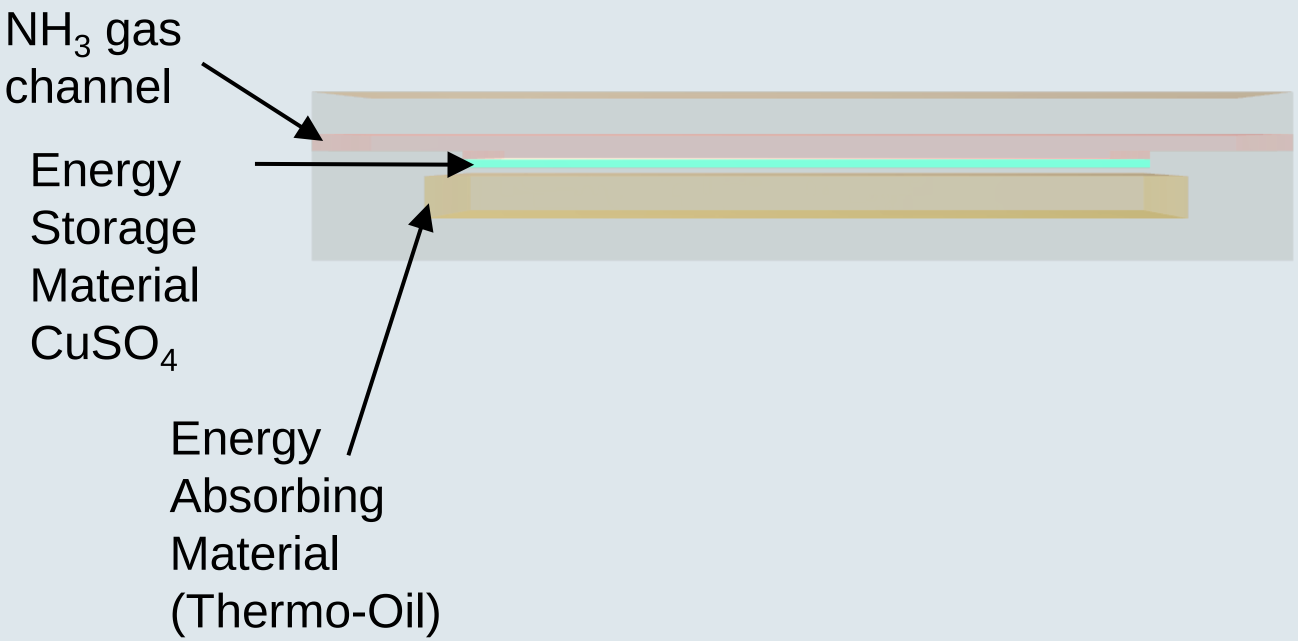
A First Prototype in Shoe Box Size



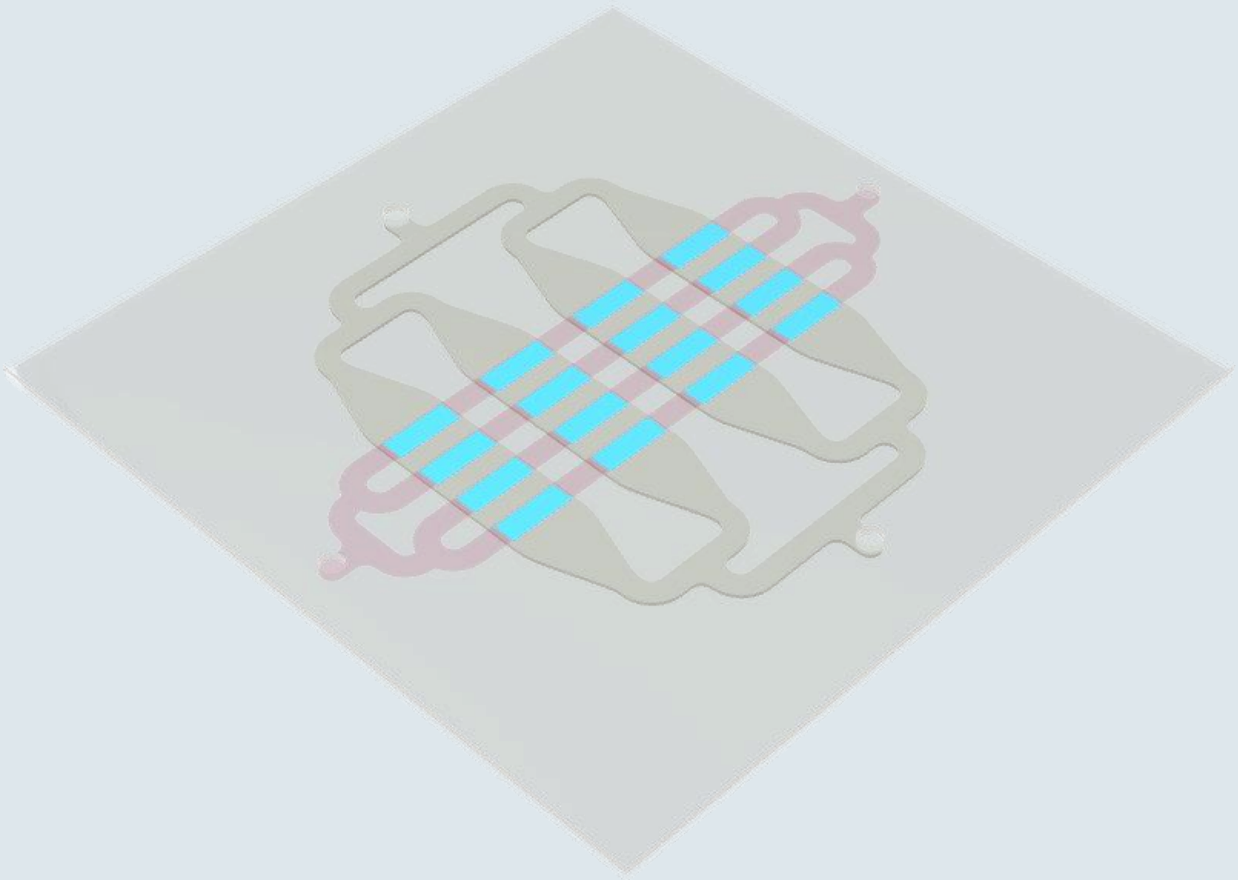
A New Concept using microfluidic Chips



Slice View of the Energy Storage Cell



A New Concept using microfluidic Chips

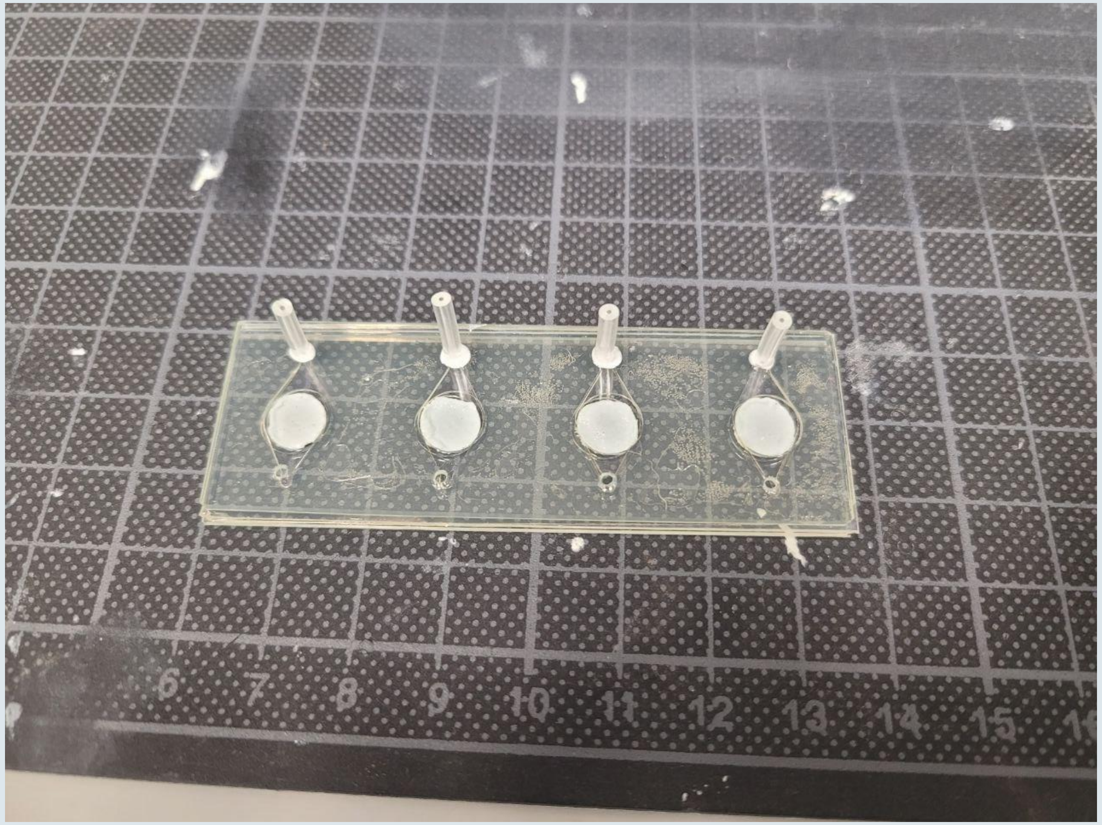


- **Simulation**
- **Single Unit – Proof of Concept**
- **Considerations**
  - Silica Wafer or Ceramics
  - Connector Options
  - Pump Type Evaluation
  - Tubing Material

Patent AT50736/2023 („Vorrichtung zur Speicherung von thermischer Energie “)

A New Concept using microfluidic Chips

Single Unit – Proof of Concept



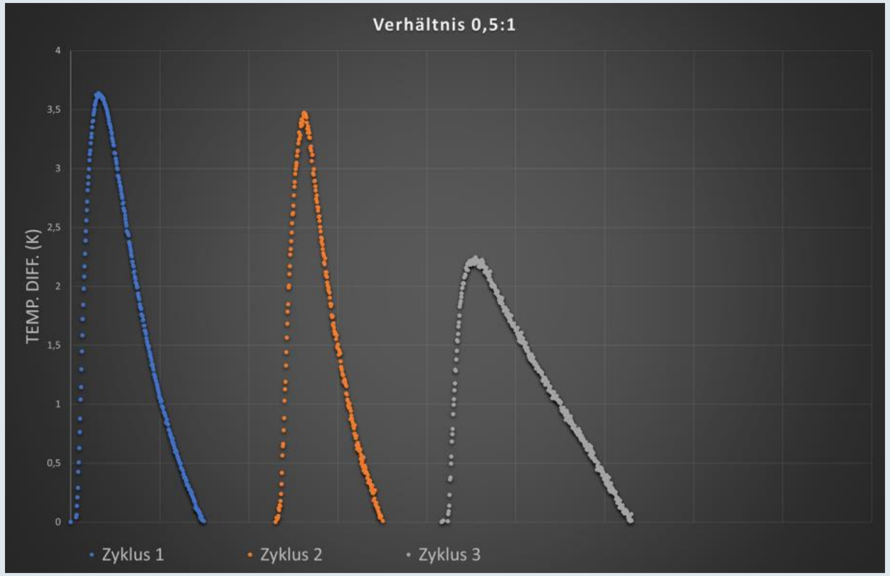
Patent AT50736/2023 („Vorrichtung zur Speicherung von thermischer Energie ")

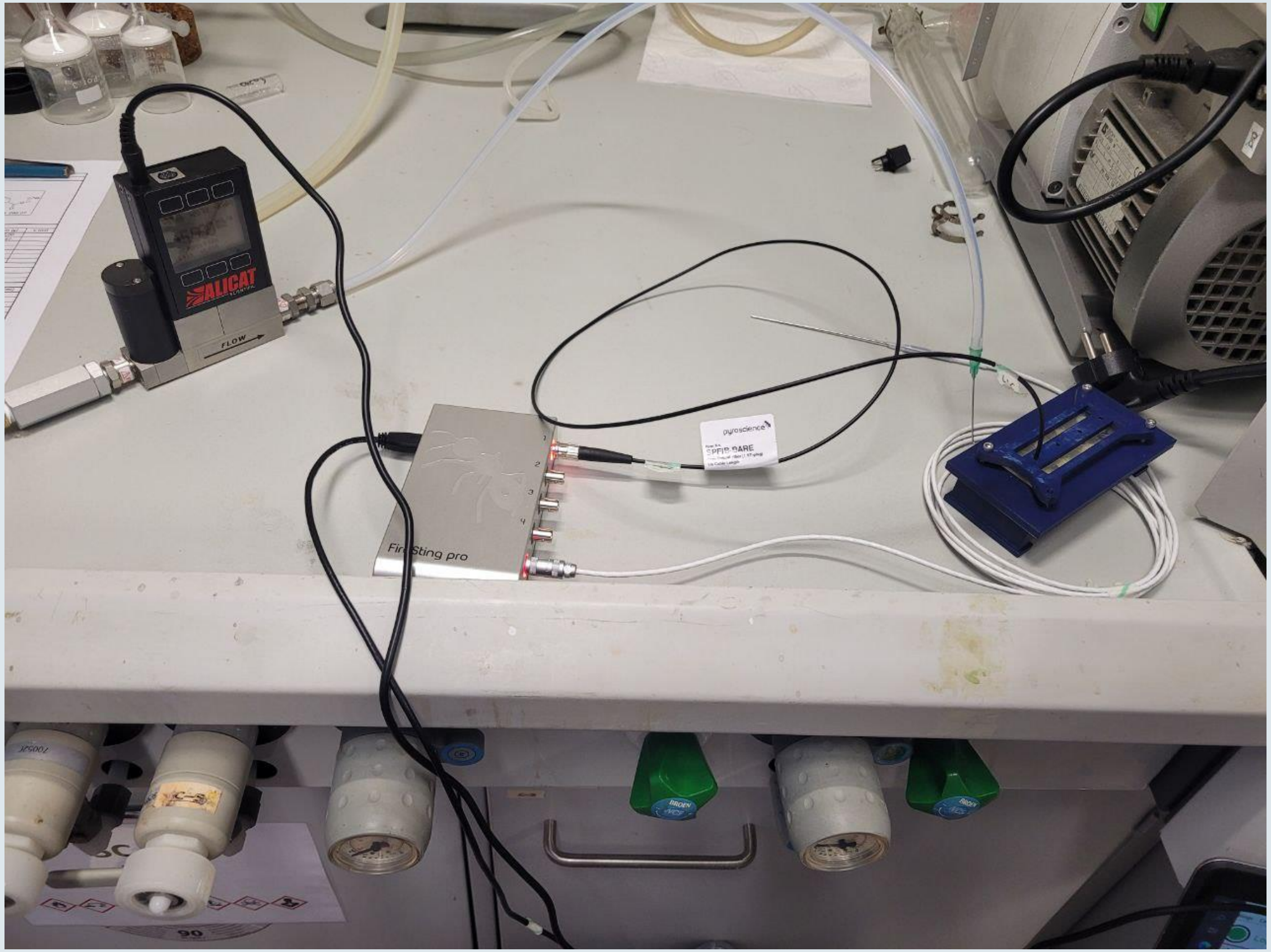
A New Concept using microfluidic Chips

Single Unit – Proof of Concept

Measurement of gas flow and

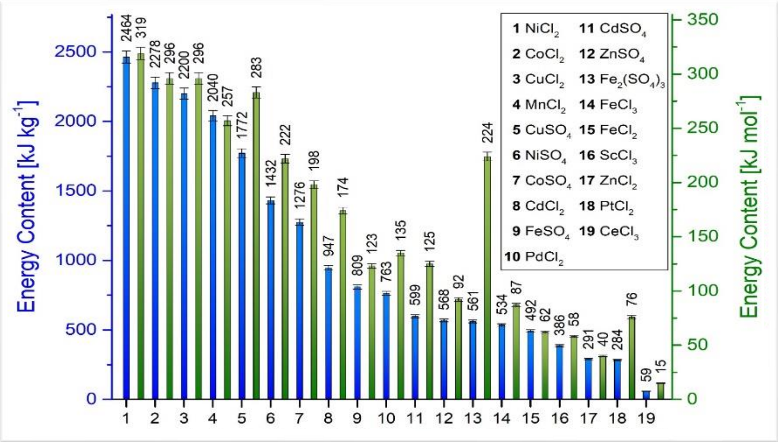
temperature change, cycle stability

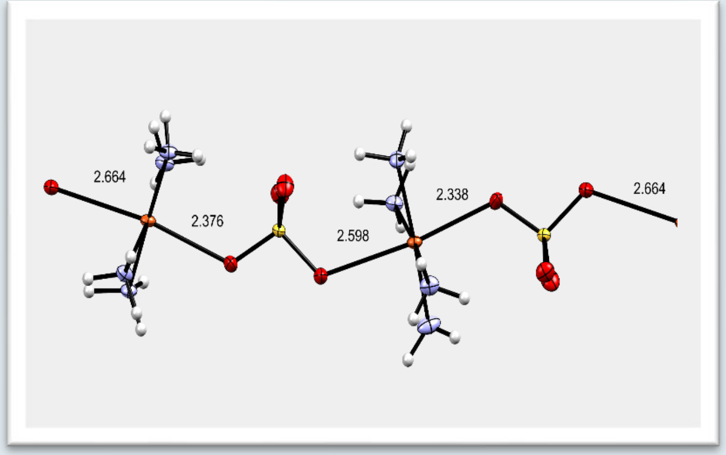




Patent AT50736/2023 („Vorrichtung zur Speicherung von thermischer Energie ")

Conclusion and Outlook





- Ammoniates provide high energy densities
- Cycle stability depends on anion and cycling conditions
- Appealing reaction rates

- $[Cu(NH_3)_4]SO_4$ enables cascade storage
- According to the atmosphere 1-step or 3-step ammoniation

- First prototype demonstrated feasibility, but problem with clogging
- Change of concept to microfluidic devices

Acknowledgement

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Peter Ertl
TU Wien

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FFG Austrian Research Promotion Agency