Stability mapping with examples of PCMs and TCMs

IEA SHC Webinar 21+23 November 2023

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PCM/TCM Stability: definition and relevance in TES systems

TES Expected Lifetime (2030)

	Cycles 2018	Cycles 2030	Cycles 2018	Cycles 2030	Years 2018	Years 2030
Sensible	10 000	>10 000	1000-3000	3000-5000	10-30	20-30
Latent	3000-5000	4000-5000	1000-3000	3000-5000	10-20	>25
Thermochemical	<100	500-1000	<100	500-1000	15-25	20-25

Source: SoA & international roadmap (IRENA 2020)

IRENA, Innovation Outlook. Thermal energy storage. *International Renewable Energy Agency, Abu Dhabi*, 2020.

TES system durability *(application)*

- ❑ **Time to maintain its performance** according to design standards
- ❑ Within established **operational conditions**

Material (PCM/TCM) Stability

- ❑ Ensures **consistent properties**, avoiding any impact on TES system performance or changes beyond expected limits.
- ❑ Considering **operational conditions**

Long-term stability is key for both PCMs and TCMs to penetrate the energy market

PCM/TCM Stability Evaluation: SoA

- **Few works have already made an initial effort to compile methodologies and present interesting approaches to address stability. (Focused on PCMs)**

https://doi.org/10.1016/j.rser.2015.04.187

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

ELSEVIER

Review on the methodology used in thermal stability characterization of phase change materials

Gerard Ferrer [a,1], Aran Solé [a,1], Camila Barreneche [a,b,2], Ingrid Martorell [a,1,3], Luisa F. Cabeza [a,*,1]

2014

Summary of contents in Annex

https://doi.org/10.1002/er.4589

SPECIAL ISSUE RESEARCH ARTICLE

WILEY ENERGY RESEARCH

Development of a new methodology for validating thermal storage media: Application to phase change materials

Rocío Bayón | Esther Rojas

2019

https://doi.org/10.3390/app13158682

applied sciences

MDPI

Article

Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach

Harald Mehling

2023

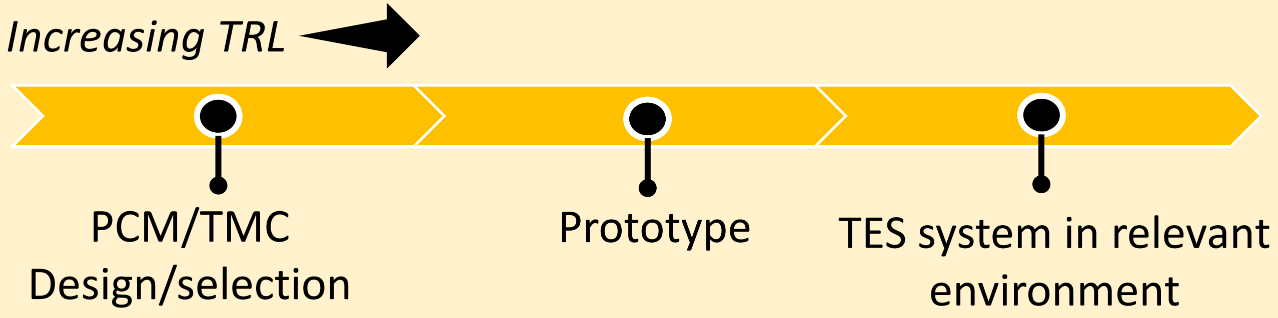
To date, there is no common standard or guideline for evaluating the stability of PCMs/TCMs

PCM/TCM Stability Evaluation

Application approach:

- **Properties affecting TES performance**
- **Testing within defined operational conditions**

Early stages of PCM/TCM development hinders the use of the application approach



phenomena inherent to the material → Environment/Op. conditions → External elements for integration

Degradation/vaporization/sublimation temperature; aging; thermal cycling stability; compatibility with HTFs/HX/other elements…

Application focus brings into play both operational conditions and external agents affecting PCM/TCM

Extended info in Annex

Representative Cases

PCMs — TCMs

Fraunhofer ISE; CIC energiGUNE (Member of Basque Research & Technology Alliance); Ciemat (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas); National Institute of Chemistry; Curtin University

Sugar Alcohols	Org. Plastic Crystal	Fatty Acids	Zeolite NaY	Metal Carbonates
Aging evaluation and mechanism understanding	Dealing with potential stability issues	Lifetime models to predict PCM long-term behavior	Adsorption/desorption cycling with water vapor	Decomposition/carbonation reaction
S. Gamisch, M. Kick, F. Klünder, J. Weiss, E. Laurenz, T. Haussmann: Thermal Storage: From Low-to-High-Temperature Systems; Energy Technol. 2023 https://doi.org/10.1002/ente.202300544	Serrano. A, Montero. G, Santos. S, Dauvergne. JL, Palomo del Barrio. E. Assessment of Plastic Crystal System for Medium-Temperature Thermal Energy Storage (80ºC-190ºC). Eurosun 2022. Kassel. Serrano, A., Duran, M., Dauvergne, J. L., Doppiu, S., & Del Barrio, E. P. (2021). Tailored transition temperature plastic crystals with enhanced thermal energy storage capacity. Solar Energy Materials and Solar Cells, 220, 110848. https://doi.org/10.1016/j.solmat.2020.110848	Bayón R, Bonanos A, Rojas E. Assessing the Long-Term Stability of Fatty Acids for Latent Heat Storage by Studying their Thermal Degradation Kinetics. Proceedings Eurosun 2020 Quant, L. Bayón, R., García R. J., Rojas, E. 2022. Kinetic analysis of TGA measurements when evaporation is a degradation process in PCM. Eurosun 2022. Kassel. **Annex**	Ristić, A., Fischer, F., Hauer, A., & Logar, N. Z. (2018). Improved performance of binder-free zeolite Y for low-temperature sorption heat storage. Journal of Materials Chemistry A, 6(24), 11521-11530. https://doi.org/10.1039/C8TA00827B	Williamson, K., Møller, K. T., D'Angelo, A. M., Humphries, T. D., Paskevicius, M., & Buckley, C. E. (2023). Thermochemical energy storage in barium carbonate enhanced by iron (iii) oxide. Physical Chemistry Chemical Physics, 25(10), 7268-7277. https://doi.org/10.1039/D2CP05745J K. Williamson, et al., Energy Storage Rocks: Metal Carbonates as Thermochemical Energy Storage, European Materials Research Society Fall Meeting (September 2022). Warsaw - Poland **Annex**

Representative Cases

Aging experiments: Erythritol

https://doi.org/10.1002/ente.202300544

Fraunhofer ISE

Testing conditions	Aging at elevated temperatures 10, 20 and 30 ºC above melting temperature (120 °C)
Properties to follow stability	Latent heat + transition temperature
Testing device	Oven + post-analysis (DSC: differential scanning calorimetry)
Techniques to understand mechanism	DSC, TGA (thermogravimetric analysis), ATR (Attenuated total reflection) and Raman-spectroscopy

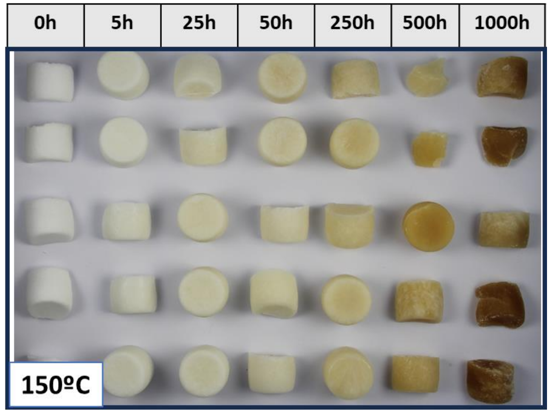
Sugar Alcohols

Plastic Crystals (solid-solid)

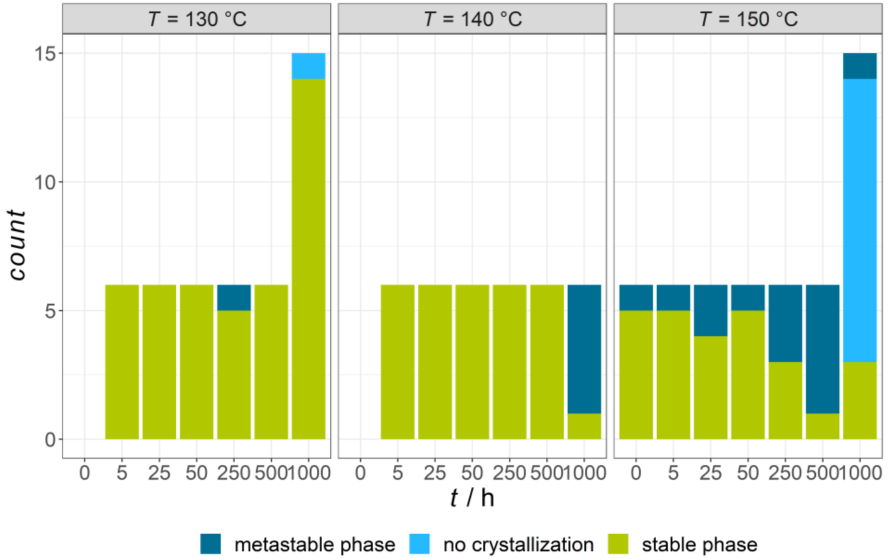
Fatty Acids

Zeolite NaY

Metal Carbonates



- Stable phase at 120ºC
- Metastable phase at 106ºC



S. Gamisch, M. Kick, F. Klünder, J. Weiss, E. Laurenz, T. Haussmann: Thermal Storage: From Low-to-High-Temperature Systems; Energy Technol. 2023

Increasing aging temperature and time increases the probability of metastable phase

↓

Reduced melting point

+

Decrease in the enthalpy of fusion

Aging evaluation and mechanism understanding

SOLAR HEATING & COOLING PROGRAMME INTERNATIONAL ENERGY AGENCY

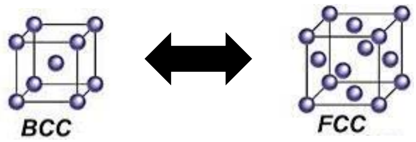
energy storage IEA Technology Collaboration Programme

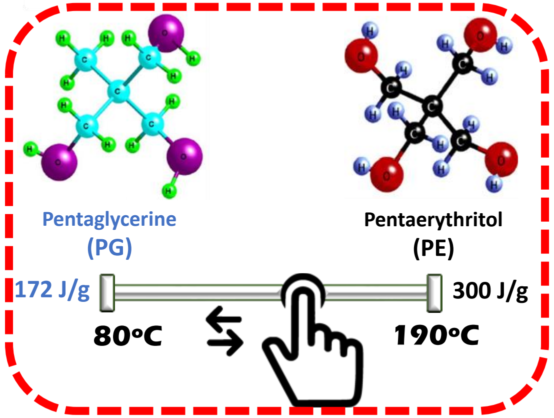
Representative Cases

https://doi.org/10.1016/j.est.2022.105677

Approach in solid-solid PCMs

"Crystal Phase" *"Plastic Phase"*





Sugar Alcohols

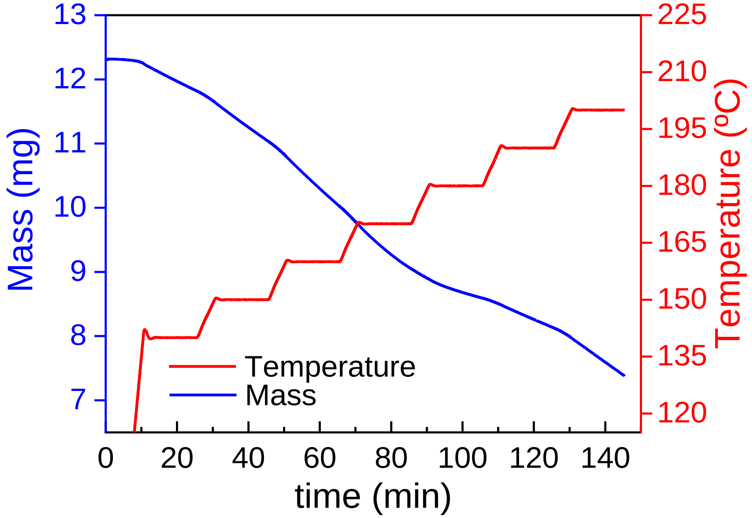
Plastic Crystals (solid-solid)

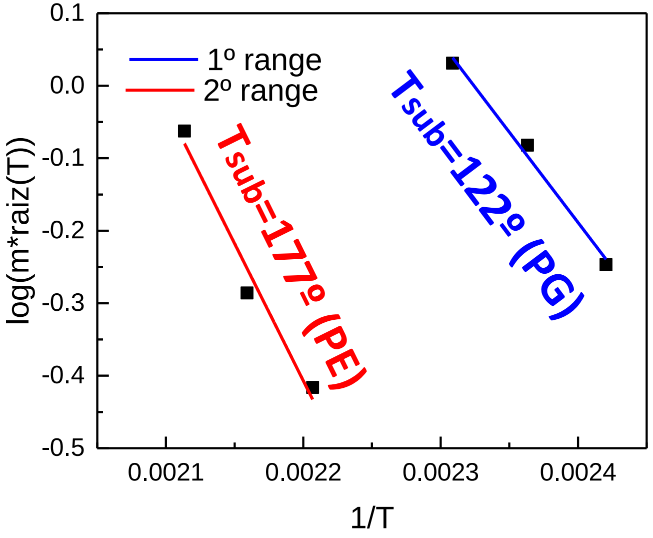
Fatty Acids

Zeolite NaY

Metal Carbonates

TGA by isothermal steps (open system)





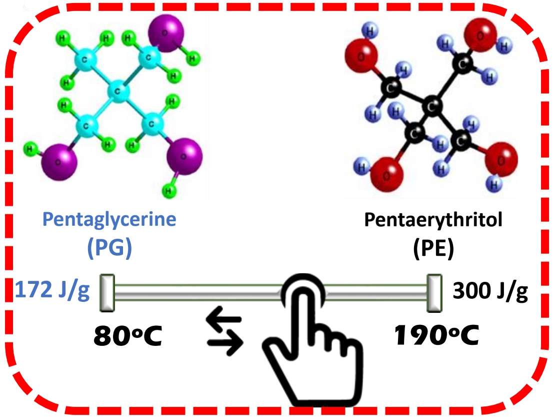
Sublimation

✓ Sublimation temperature

External elements (coatings) are required to mitigate sublimation

Representative Cases

Approach in solid-solid PCMs

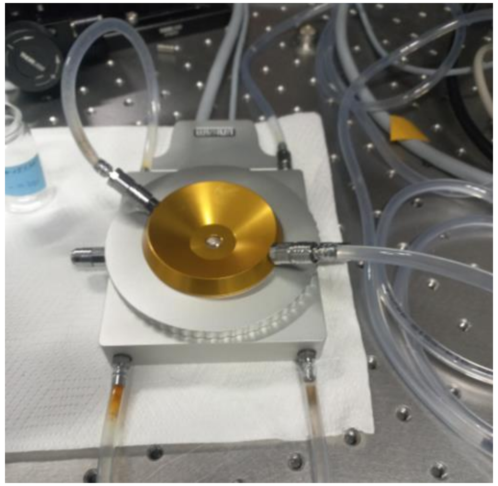


CIC energiGUNE
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

- Sugar Alcohols
- **Plastic Crystals (solid-solid)**
- Fatty Acids
- Zeolite NaY
- Metal Carbonates

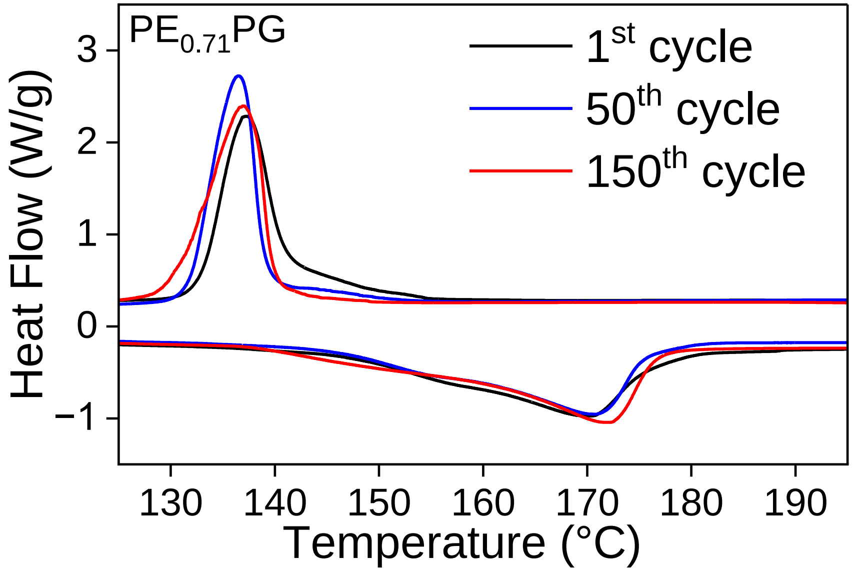
Coatings with low vapor permeability prevent sublimation

Linkam oven (closed system)



x150 thermal cycles
120ºC-200ºC at 10ºC/min

DSC analysis



Accelerated test: Good stability in closed systems

Representative Cases

Prediction of mass loss: Fatty Acids

Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Annex

Sugar Alcohols

Plastic Crystals (solid-solid)

Fatty Acids

Zeolite NaY

Metal Carbonates

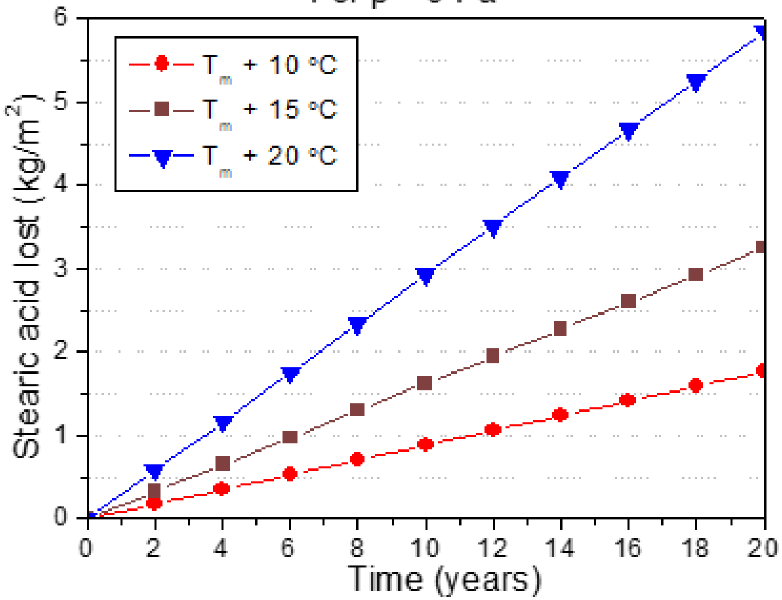
Aging evaluation and mechanism understanding

Degradation observed

1. **Evaporation (physical)**
2. Colour change (chemical)

Evaporation kinetics by using collision theory approach

Lifetime model to predict long-term behaviour



Lifetime models required to predict PCM long-term behavior

Representative Cases

Water vapour adsorption/desorption

NATIONAL INSTITUTE OF CHEMISTRY

https://doi.org/10.1039/C8TA00827B

Sugar Alcohols

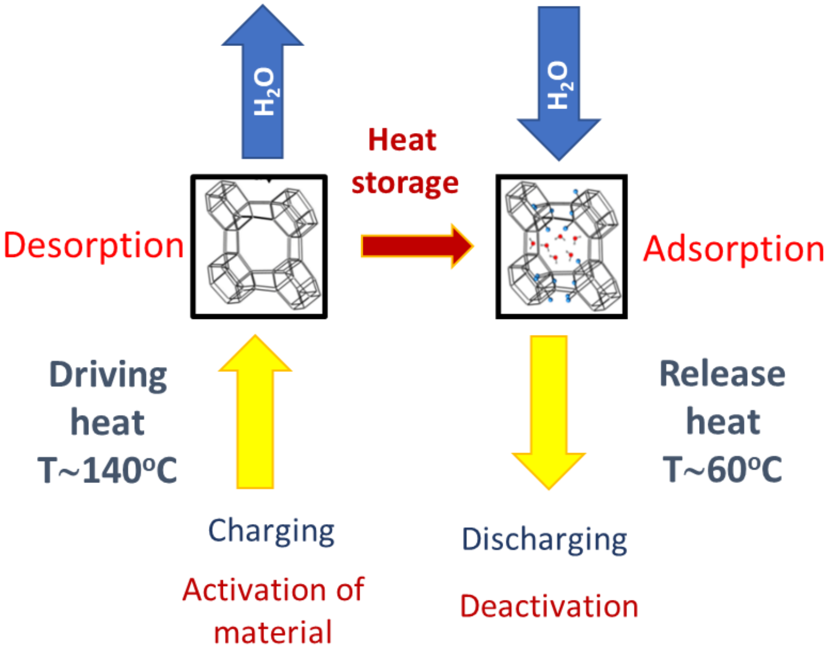
Plastic Crystals (solid-solid)

Fatty Acids

Zeolite NaY

Metal Carbonates

Granulated binder-free Zeolite NaY



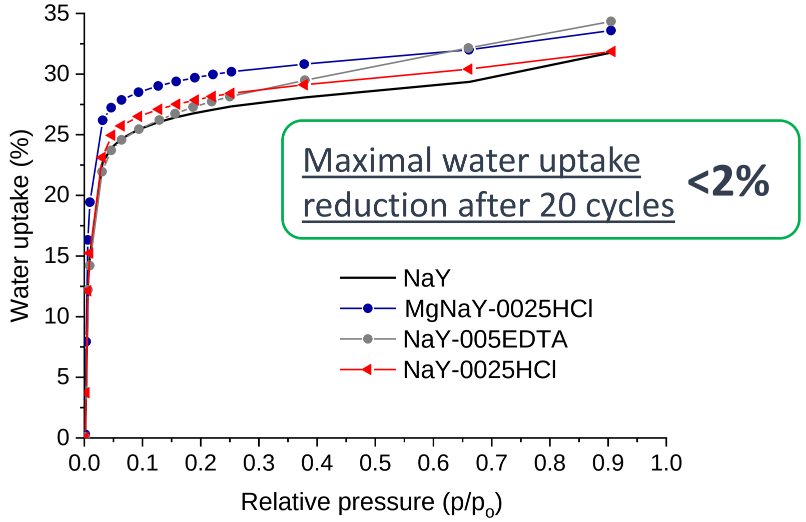
Zeolite modifications

(to decrease desorption temperature)

- Mild acid treatment (HCl)
- Chemical treatment with chelating agent (H_4EDTA)

Cyclic hydrothermal stability

- 20 adsorption/ desorption cycles
  - Thermal cycles: 40ºC-140ºC
  - P_{H2O} = 1.23 kPa (cte)
- Comparing the water uptakes of the samples before and after cycling



Water isotherms of samples after 20 cycles gravimetrically measured at 25ºC.

Good hydrothermal stability after 20 cycles under selected conditions

Representative Cases

$BaCO_3$ & $BaCO_3 \cdot M_xO_y$

Decomposition/Carbonation reaction

$$MCO_{3(s)} + \Delta H_r \leftrightarrow MO_{(s)} + CO_{2(g)}$$

Curtin University

Annex

Sugar Alcohols

Plastic Crystals (solid-solid)

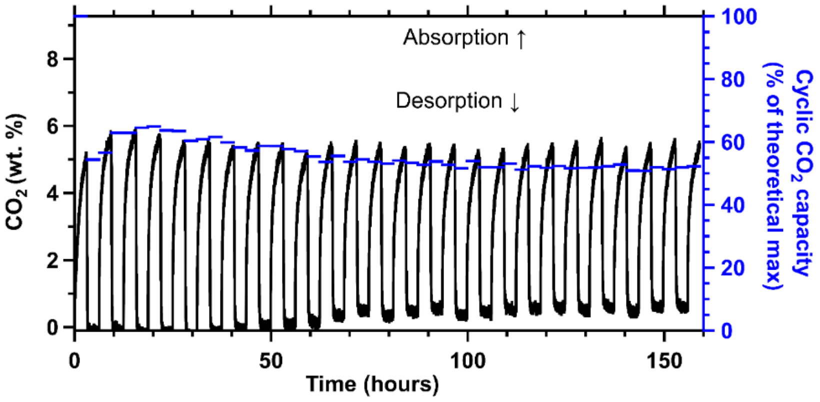
Fatty Acids

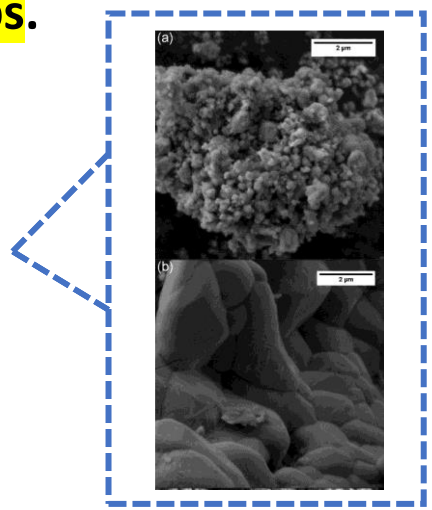
Zeolite NaY

Metal Carbonates

TGA: Limitation of pressure (1 bar)

CO_2 Cycling 1085 °C, **0.4 bar des., 2.2 bar abs.**

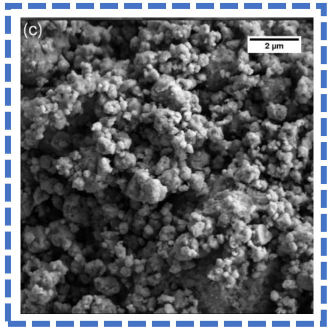




$BaTiO_3$+$BaCO_3$ (1 cycle)

$BaTiO_3$+$BaCO_3$ (50 cycles)

$BaTiO_3$+$BaCO_3$ **+0.02 Ni** **(75 cycles)**



Variable operating conditions in ad hoc device. 75 cycles without sintering when adding Ni.

Conclusions

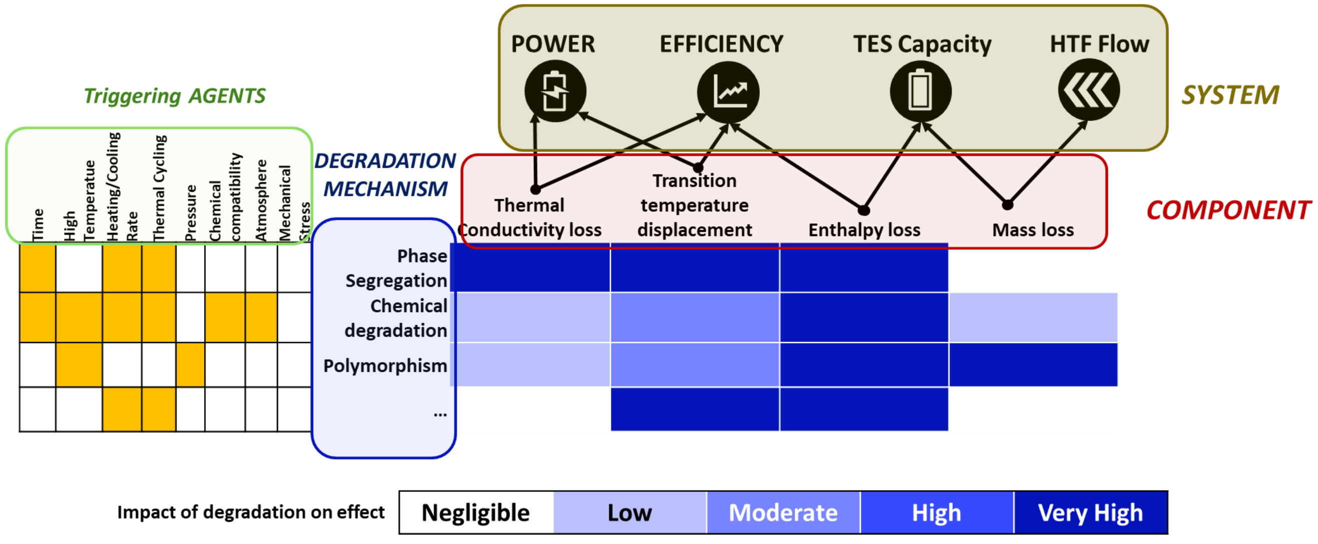
- ❑ **Recommendations for stability testing are required**

Ongoing Work

Exploring potential degradation mechanisms for each PCM/TCM type. Including degradation factors and effects on the material.

Identifying triggering agents and understanding their effects allows for more efficient stability testing, longer-term predictions, and streamlined problem-solving.

Task 67/40 Subtask D
Lead by Dr. Christoph Rathgeber
(christoph.rathgeber@zae-bayern.de)



How degradation can be accelerated?
Testing protocols recommendations

Annex

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PCM/TCM Stability Evaluation: SoA

https://doi.org/10.1016/j.rser.2015.04.187

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Review on the methodology used in thermal stability characterization of phase change materials

Gerard Ferrer [a,1], Aran Solé [a,1], Camila Barreneche [a,b,2], Ingrid Martorell [a,1,3], Luisa F. Cabeza [a,*,1]

2014

- ❑ Focus on PCM **thermal cycling stability**
- ❑ **Review** of test results and procedures containing:
  - Testing Equipment
  - Techniques to characterize PCM and to follow PCM degradation
  - Testing conditions

https://doi.org/10.1002/er.4589

SPECIAL ISSUE RESEARCH ARTICLE

WILEY ENERGY RESEARCH

Development of a new methodology for validating thermal storage media: Application to phase change materials

Rocío Bayón | Esther Rojas

2019

- ❑ Proposing new **methodology for validating thermal storage media** (focus on PCM), consisting of:
  - PCM characterization
  - Preliminary assessment test
  - Accelerated life testing (lifetime models required to predict PCM long-term behavior).
- ❑ Applicable to sensible and TCMs

https://doi.org/10.3390/app13158682

applied sciences

MDPI

Article

Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach

Harald Mehling

2023

- ❑ Reflections on:
  - **Stability/aging/degradation**
  - What is tested, why is it tested, and what is the focus?
- ❑ Proposing a new systematic approach based on:
  - Functions and properties to be tested.
  - Finding degradation effects and underlying mechanisms.

Representative Cases

Aging experiments: Erythritol

Source: S. Gamisch, M. Kick, F. Klünder, J. Weiss, E. Laurenz, T. Haussmann: Thermal Storage: From Low-to-High-Temperature Systems; Energy Technol. 2023; DOI: 10.1002/ente.202300544

Fraunhofer ISE

Sugar Alcohols

Fatty Acids

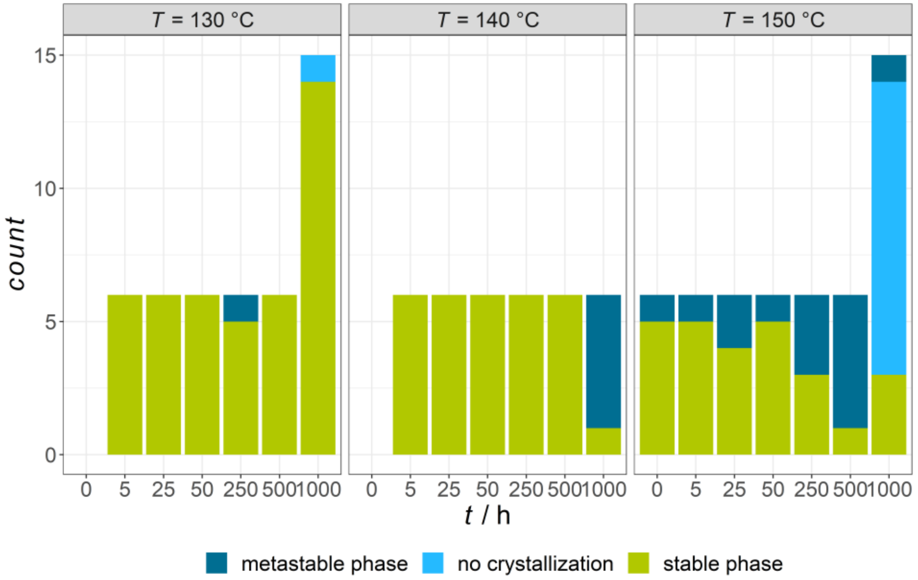
Plastic Crystals (solid-solid)

Zeolite NaY

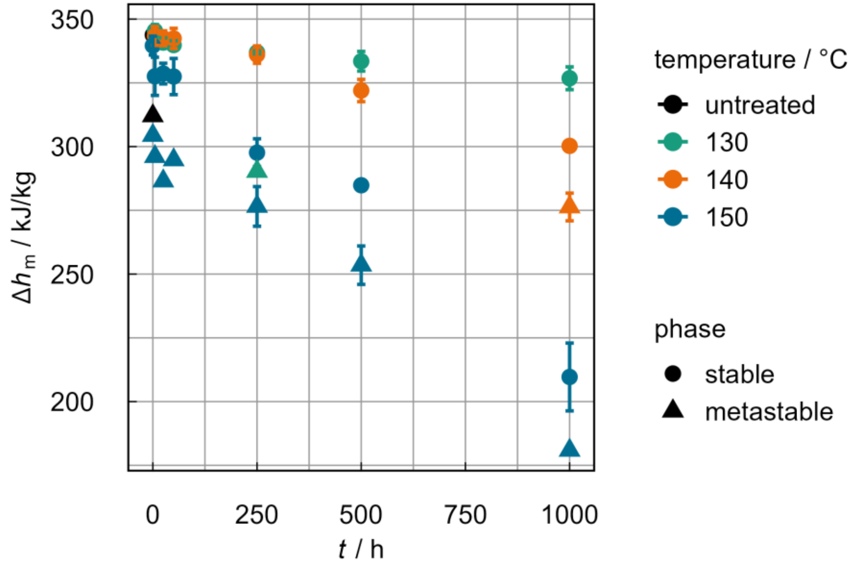
Metal Carbonates

Polymorphic phases in Erythritol:

- Stable phase at 120ºC
- Metastable phase at 106ºC



- Increasing aging temperature and time increases the probability of metastable phase → **Reduced melting point**



- Increasing aging temperature and exposure time → **Larger decrease in the enthalpy of fusion**

Aging evaluation and mechanism understanding

Representative Cases

Prediction of mass loss: Fatty Acids

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Sugar Alcohols

Fatty Acids

Plastic Crystals (solid-solid)

Zeolite NaY

Metal Carbonates

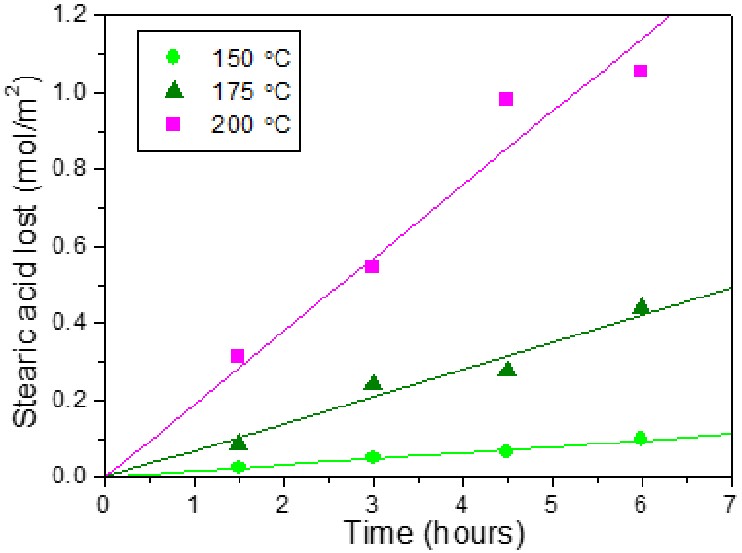
Isothermal tests under stress conditions

- *Temperature well above T_m*
- *Duration: 1 h - 6 h*
- *Open and closed containers*
- *Oven under ambient air atmosphere*
- *Glass bell for capturing/condensing emitted gases*

Degradation observed

1. **Evaporation (physical)**
2. **Colour change (chemical)**

Mass loss monitoring for stearic acid



- Evaporation kinetics by using collision theory approach

$$\ln r = \ln \left[\frac{(p_{eq} - p)}{\sqrt{2\pi MRT}} \right] - \frac{E_{con}}{RT}$$

Lifetime models required to predict PCM long-term behavior

Representative Cases

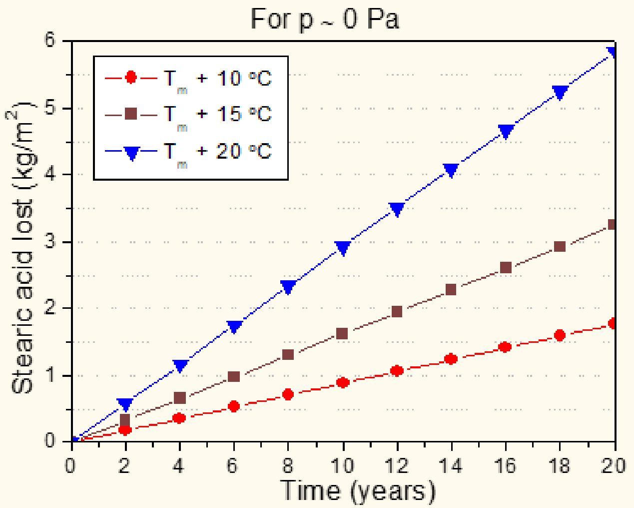
Prediction of mass loss: Fatty Acids

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Prediction of mass loss over time in open systems due to evaporation

- Sugar Alcohols
- **Fatty Acids**
- Plastic Crystals (solid-solid)
- Zeolite NaY
- Metal Carbonates

STEARIC ACID T_m= 69 ºC

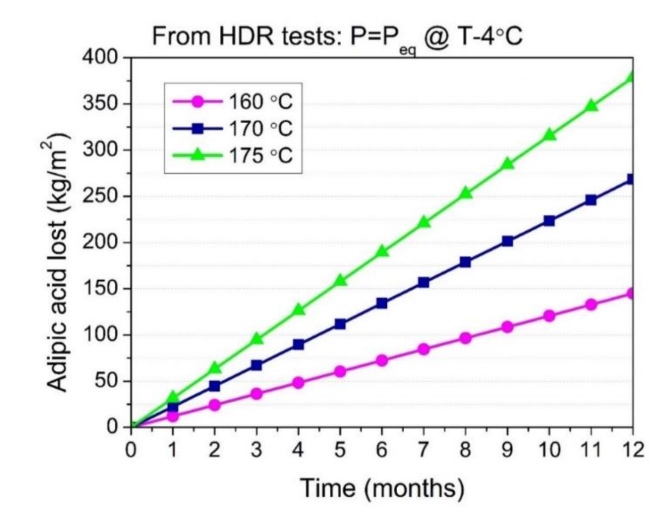


p=0 Pa ➔All evaporated liquid is removed (=the worst situation)

After 20 years only **6 kg of PCM/m²** will be **lost** @ **T_m+20 ºC**

Marginal evaporation is expected under operating conditions

ADIPIC ACID Tm=152 ºC



$p=p_{eq}$ @ T-4ºC ➔Almost all evaporated liquid remains on the surface (= close to equilibrium)

More **than 100 kg of PCM/m²** will be **lost** in **1 year** if adipic acid is kept melted @ T> T_m+8º C

Strong evaporation is expected under operating conditions

TES system configuration and operating conditions can limit/avoid loss of stability

Representative Cases

Prediction of mass loss: Fatty Acids

Sugar Alcohols

Fatty Acids

Plastic Crystals (solid-solid)

Zeolite NaY

Metal Carbonates

Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Project TED2021-131061B-C33 funded by:

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1. *Bayón R, Bonanos A, Rojas E. Assessing the Long-Term Stability of Fatty Acids for Latent Heat Storage by Studying their Thermal Degradation Kinetics. Proceedings Eurosun 2020*
2. *Bayón R., Gismera, V., Rojas. E. 2021.Validation of lauric acid as PCM: study of thermal degradation under quasi-real working conditions. ENERSTOCK 2021. Online Conference. Oral presentation*
3. *Quant, L. Bayón, R., García R. J., Rojas, E. 2022. Kinetic analysis of TGA measurements when evaporation is a degradation process in PCM. Eurosun 2022. Kassel.*
4. *Bayón, R., García R. J., Quant, L., Rojas, E. Study of Thermal Degradation of Adipic Acid as PCM Under Stress Conditions: A Kinetic Analysis, E. 2022. Kinetic analysis of TGA measurements when evaporation is a degradation process in PCM. Eurosun 2022. Kassel.*

Representative Cases

Decomposition/Carbonation reaction

Curtin University

$BaCO_3$ & $BaCO_3{\cdot}M_xO_y$

$$MCO_{3(s)} + \Delta H_r \leftrightarrow MO_{(s)} + CO_{2(g)}$$

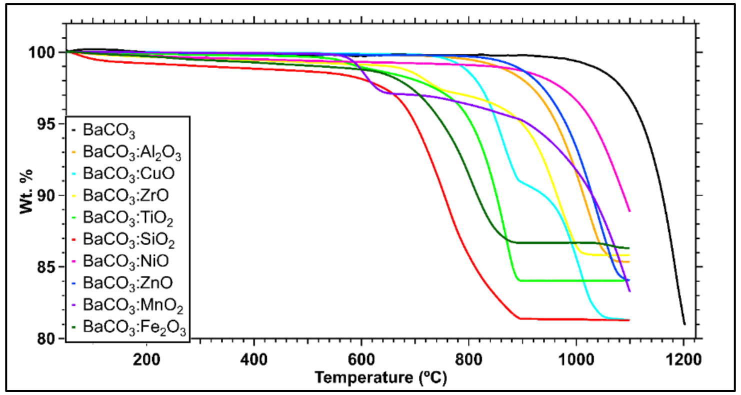
Sugar Alcohols

Plastic Crystals (solid-solid)

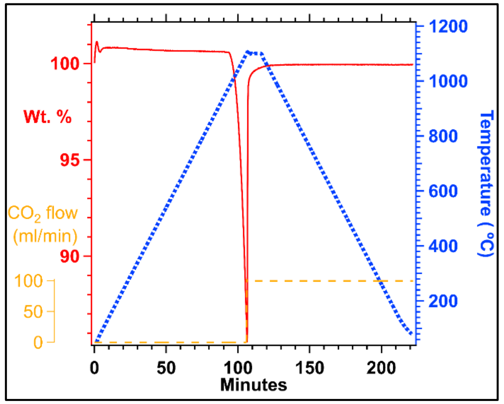
Fatty Acids

Zeolite NaY

Metal Carbonates

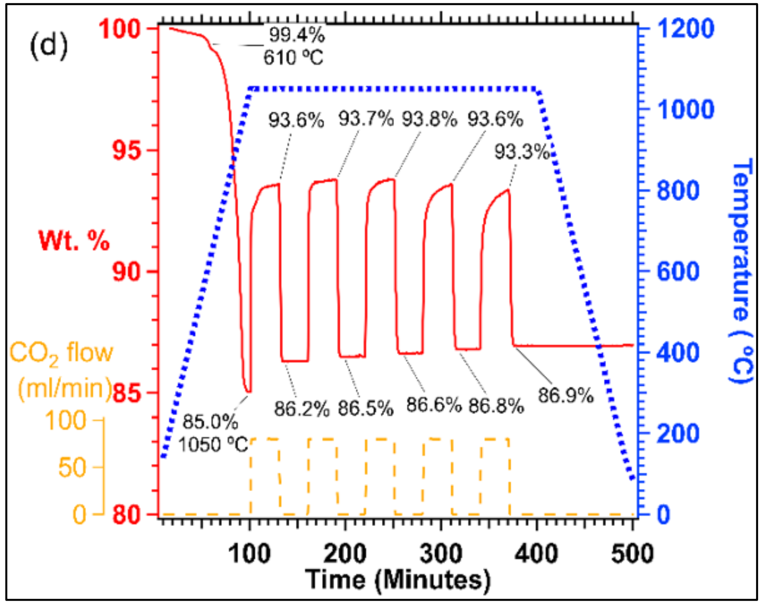


1st. TGA (under argon) for decomposition kinetics and temperatures.



2nd. CO_2 absorption potential (argon then CO_2)

$2BaCO_3{:}TiO_2{:}$(18.6wt.%Ni) (d), heated ($\Delta T/\Delta t$= 10°C·min^{-1}) (blue) in an Al_2O_3 crucible with an intermittent gas flow rate (orange) of CO_2 (0 or 80 mL·min^{-1}) and a constant flow of argon (20 mL·min^{-1}).



3rd. Cycling capacity (variable CO_2 pressure)

Isothermal condition

TGA: Limitation of pressure (1 bar)

Protocol to evaluate cycling capacity of $BaCO_3$ & $BaCO_3{\cdot}M_xO_y$

Representative Cases

Decomposition/Carbonation reaction

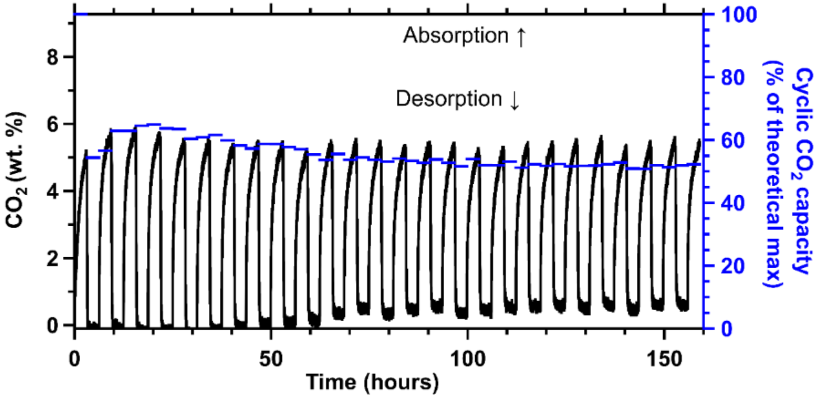
$$MCO_{3(s)} + \Delta H_r \leftrightarrow MO_{(s)} + CO_{2(g)}$$

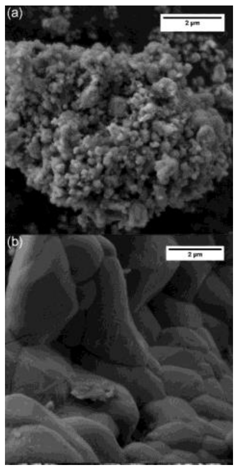
Curtin University

$BaCO_3 \cdot TiO_2$

- Sugar Alcohols
- Plastic Crystals (solid-solid)
- Fatty Acids
- Zeolite NaY
- **Metal Carbonates**

CO_2 Cycling 1085 °C, **0.4 bar des., 2.2 bar abs**.



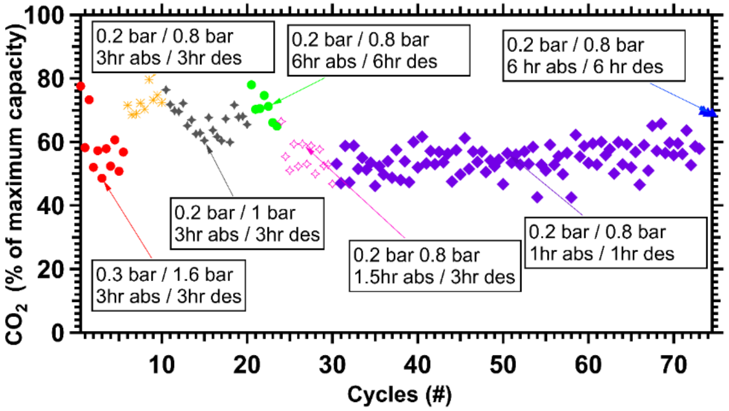


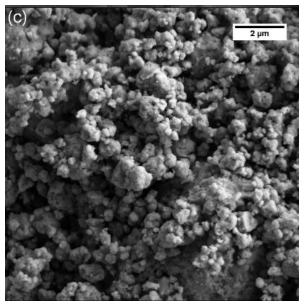
$BaTiO_3$+$BaCO_3$ (1 cycle)

$BaTiO_3$+$BaCO_3$ (50 cycles)

- Good CO_2 cycling capacity retention
- **Slow absorption due to grain growth**

CO_2 Cycling 1072 °C, (Nickel additive)





$BaTiO_3$+$BaCO_3$ +0.02 Ni **(75 cycles)**

- ✓ Good CO_2 cycling capacity retention
- ✓ **Sintering avoided**

75 cycles without sintering when adding Ni. Variable operating conditions in ad hoc device