Thermal Energy Storage Webinar Series

Novel Materials in Thermal Energy Storage for Buildings

Building Technologies Office

https://www.energy.gov/eere/buildings/building-technologies-office

David Nemtzow, Karma Sawyer, Sven Mumme, Nelson James

August 5, 2020

This Webinar is being recorded.

If you do not wish to participate, please exit now.

Building Technologies Office Approach

BTO invests in energy efficiency & related technologies that make homes and buildings more affordable and comfortable, and make the US more sustainable, secure and prosperous. Budget ~US$285M/year; activities include:

R&D

Pre-competitive, early-stage investment in next-generation technologies

Integration

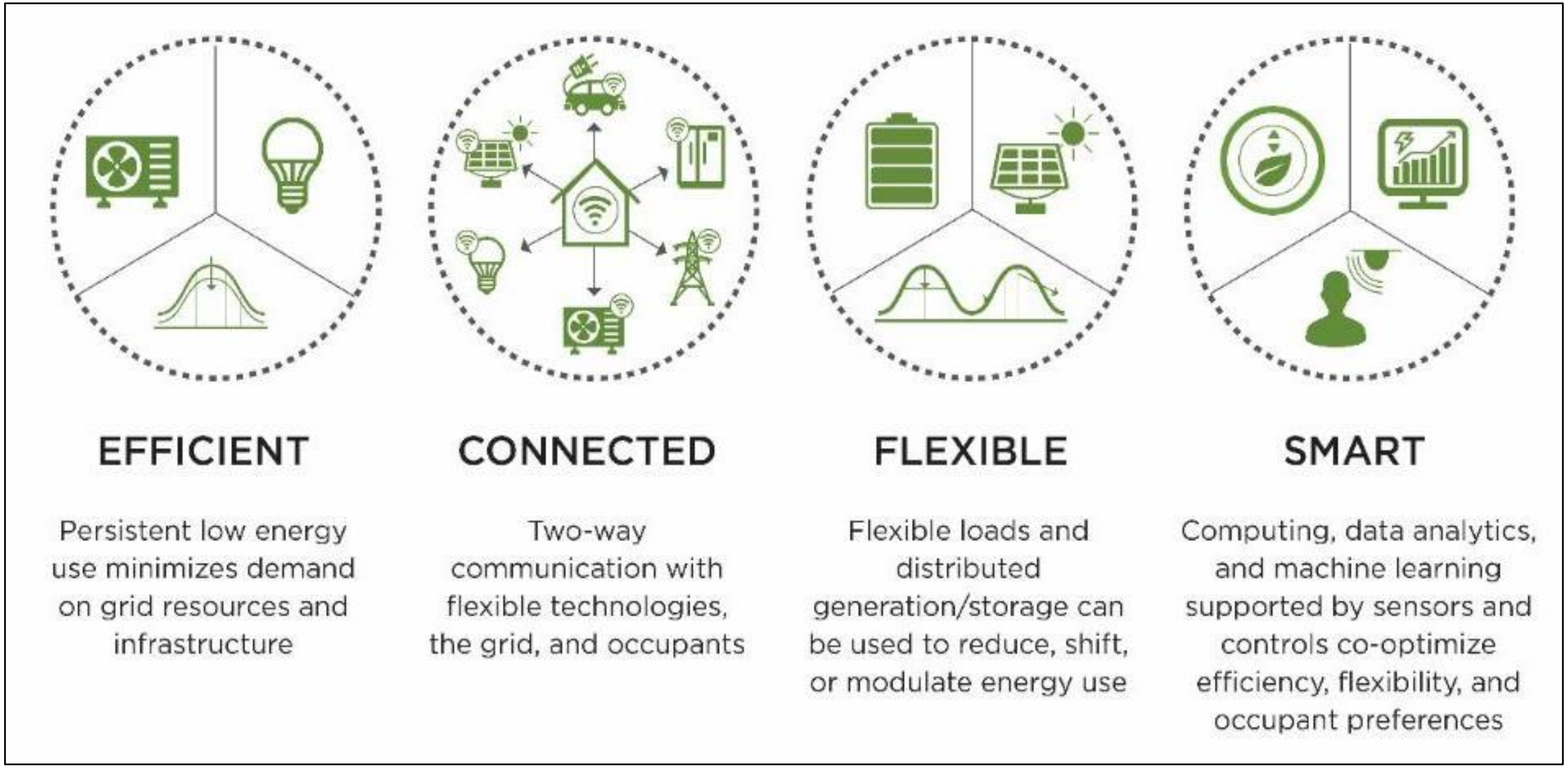
Technology validation, field & lab testing, metrics, market integration

Codes & Standards

Whole building & equipment standards technical analysis, test procedures, regulations

www.energy.gov/eere/buildings

Characteristics of Grid-interactive Efficient Bldgs.



EFFICIENT

Persistent low energy use minimizes demand on grid resources and infrastructure

CONNECTED

Two-way communication with flexible technologies, the grid, and occupants

FLEXIBLE

Flexible loads and distributed generation/storage can be used to reduce, shift, or modulate energy use

SMART

Computing, data analytics, and machine learning supported by sensors and controls co-optimize efficiency, flexibility, and occupant preferences

www.energy.gov/eere/buildings/GEB

Energy Storage Grand Challenge Draft Roadmap

ENERGY STORAGE
GRAND CHALLENGE
U.S. DEPARTMENT OF ENERGY

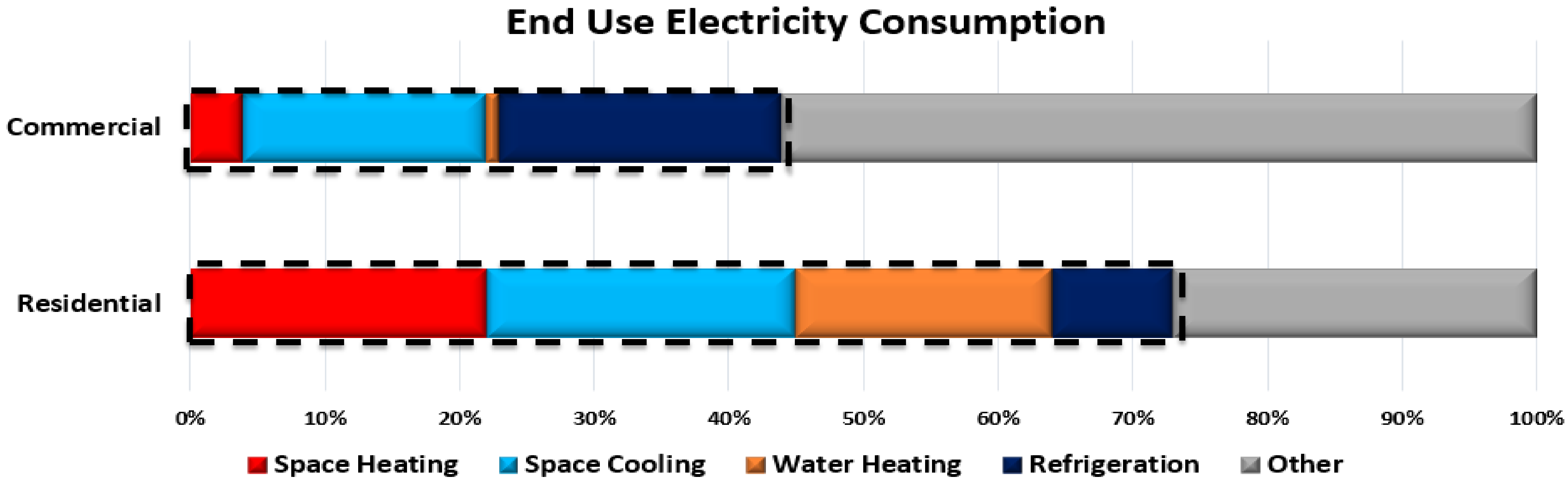
U.S. DEPARTMENT OF
ENERGY

- Technology Development
- Manufacturing and Supply Chain
- Technology Transition
- Policy and Valuation
- Workforce Development

Responses to this RFI will be due **August 31, 2020**

https://www.energy.gov/energy-storage-grand-challenge/downloads/energy-storage-grand-challenge-draft-roadmap

Why Thermal Energy Storage



Adapted from BTO HVAC GEB Technical Report

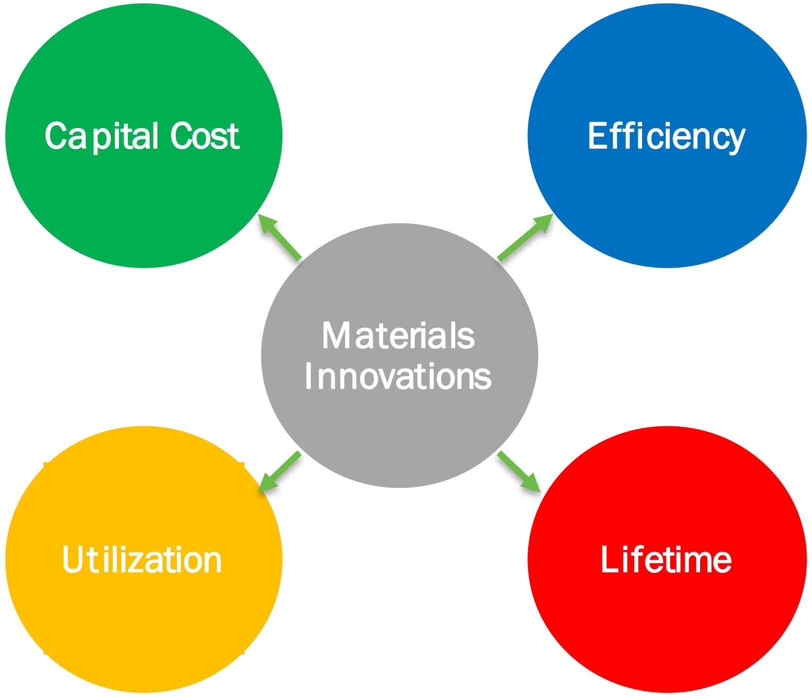
- Significant portion of bldg. loads already thermally based
- Thermal loads are major drivers of system peaks

- Can be a lower cost solution than batteries
- Generally have longer system lifetimes
- Potential to downsize equipment
- Potentially more efficient for thermal loads

Thermal Energy Storage Research Needs

2019 Workshop on Fundamental Needs for Dynamic and Interactive Thermal Storage Solutions for Buildings

- Explored ways to revolutionize thermal energy storage technologies to have more significant impact in the built environment and energy ecosystem
- 11 recommendations provided for future research



Capital Cost

Efficiency

Materials Innovations

Utilization

Lifetime

NREL BERKELEY LAB

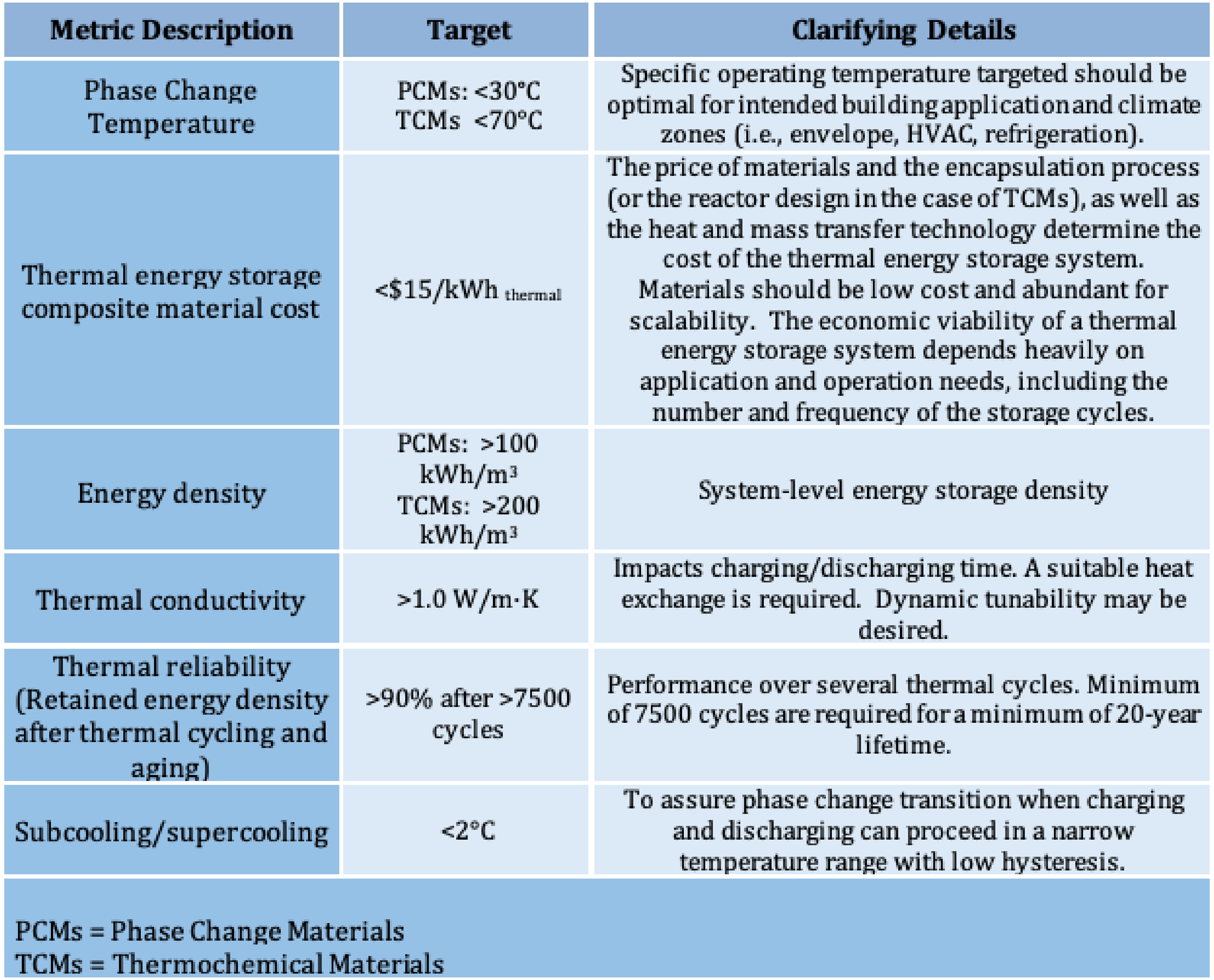
2019 Workshop on Fundamental Needs for Dynamic and Interactive Thermal Storage Solutions for Buildings

Sumanjeet Kaur,[1] Marcus Bianchi,[2] and Nelson James[3]

1 Lawrence Berkeley National Laboratory
2 National Renewable Energy Laboratory
3 Oak Ridge Institute for Science and Education

https://www.nrel.gov/docs/fy20osti/76701.pdf

BTO R&D targets for Next Generation Thermal Storage Materials



Metric Description	Target	Clarifying Details
Phase Change Temperature	PCMs: <30°C TCMs <70°C	Specific operating temperature targeted should be optimal for intended building application and climate zones (i.e., envelope, HVAC, refrigeration).
Thermal energy storage composite material cost	$<\$15/\text{kWh}_{\text{thermal}}$	The price of materials and the encapsulation process (or the reactor design in the case of TCMs), as well as the heat and mass transfer technology determine the cost of the thermal energy storage system. Materials should be low cost and abundant for scalability. The economic viability of a thermal energy storage system depends heavily on application and operation needs, including the number and frequency of the storage cycles.
Energy density	PCMs: >100 kWh/m^3 TCMs: >200 kWh/m^3	System-level energy storage density
Thermal conductivity	>1.0 W/m·K	Impacts charging/discharging time. A suitable heat exchange is required. Dynamic tunability may be desired.
Thermal reliability (Retained energy density after thermal cycling and aging)	>90% after >7500 cycles	Performance over several thermal cycles. Minimum of 7500 cycles are required for a minimum of 20-year lifetime.
Subcooling/supercooling	<2°C	To assure phase change transition when charging and discharging can proceed in a narrow temperature range with low hysteresis.
PCMs = Phase Change Materials TCMs = Thermochemical Materials		

Thermal Energy Storage Webinar Series

- Ice Thermal Energy Storage
  - January 16th, 2020
  - https://www.energy.gov/sites/prod/files/2020/02/f71/bto-IceStorageWebinar-011620.pdf

- Hot Water Thermal Energy Storage
  - March 19th, 2020
  - https://www.energy.gov/sites/prod/files/2020/03/f73/bto-HotWaterWebinar-032420.pdf

- Novel Materials for Thermal Energy Storage
  - August 5th, 2020

Today's Webinar


Kyle Gluesenkamp **Navin Kumar**
Oak Ridge National Laboratory

Patrick Hopkins
University of Virginia

Sumanjeet Kaur
Lawrence Berkeley National Laboratory

Patrick Shamberger
Texas A&M University


Allison Mahvi **Jason Woods**
National Renewable Energy Laboratory

OAK RIDGE
National Laboratory

BTO Thermal Energy Storage Webinar: Salt Hydrate Phase Change Materials

Kyle R. Gluesenkamp, PhD

Navin Kumar, PhD

Oak Ridge National Laboratory

August 5, 2020

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ENERGY

Acknowledgements

Partners

Oak Ridge National Laboratory

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The University of Tennessee Knoxville

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NeoGraf™ Solutions

Funding

U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

Computational Resources

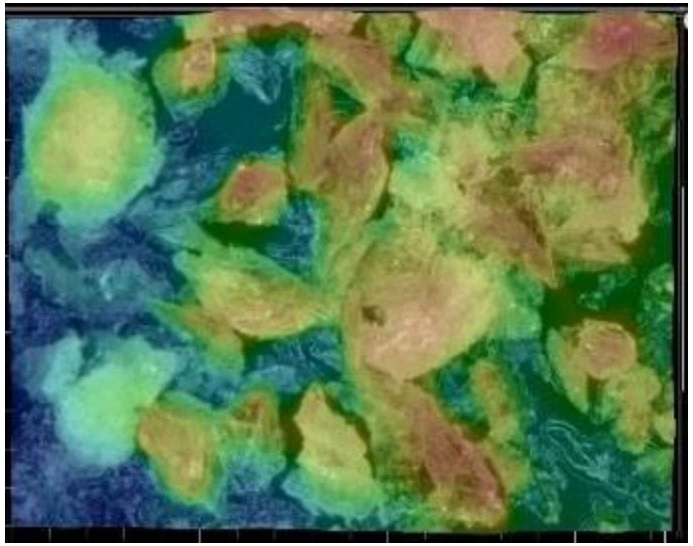
National Center for Computational Sciences

Acknowledgements

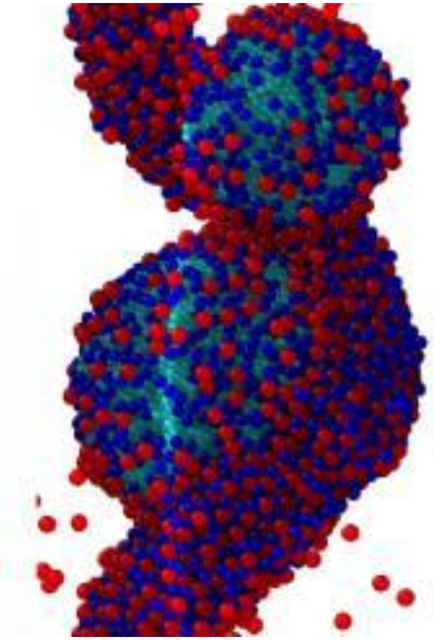
- Funding
  - **Sven Mumme** and **Tony Bouza**: DOE BTO
- Research team members
  - **Yuzhan Li**, ORNL: polymer identification
  - **Jason Hirschey**, Georgia Tech: visualization of materials
  - **Monojoy Goswami**, ORNL: molecular dynamics

Outline

- Review of Salt Hydrates
- Key Challenges
- Current R&D at ORNL



A colormap of sodium sulfate decahydrate crystal size. optical image



Coarse-grain MD model of sodium sulfate decahydrate

Importance of Thermal Energy Storage

Electronics Cooling

Ice Thermal Storage Systems

Cold Storage


https://www.vikingcold.com/

Building Insulation with PCMs

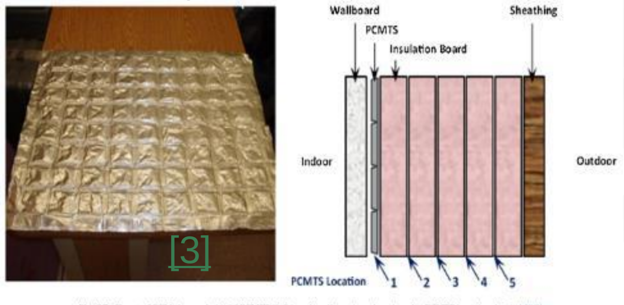


Fig. 37. Sheet of PCM thermal shield PCMTS (left) and wall section showing the PCMTS location (right) [96].

Battery Thermal Management

HVAC Systems

Common PCM Materials:

- Inorganic PCMs
  - ***Salt Hydrates***
  - Ice
  - Salt
  - Metals
- Organic PCMs
  - Paraffin Waxes
  - Fatty Acids
  - Alcohols

[1] https://www.1-act.com/products/pcm-heat-sinks/
[2] https://www.power-grid.com/2017/04/12/ice-energy-nrg-energy-deploy-thermal-energy-storage-in-california/#gref
[3] Souayfane et al. (2016). "PCMs for cooling applications in buildings: a review." *Energy and Buildings* v. 129, 396-431
[4] https://chargedevs.com/features/allcell-technologies%E2%80%99-new-phase-change-thermal-management-material/
[5] https://www.airconco.com/news/roco-personal-robot-air-conditioner/

Introduction to Salt Hydrates as PCM

- Low cost ($/kWh) TES material
- High volumetric energy storage capacity
- Non-flammable
- Majority of salt hydrates are non-toxic

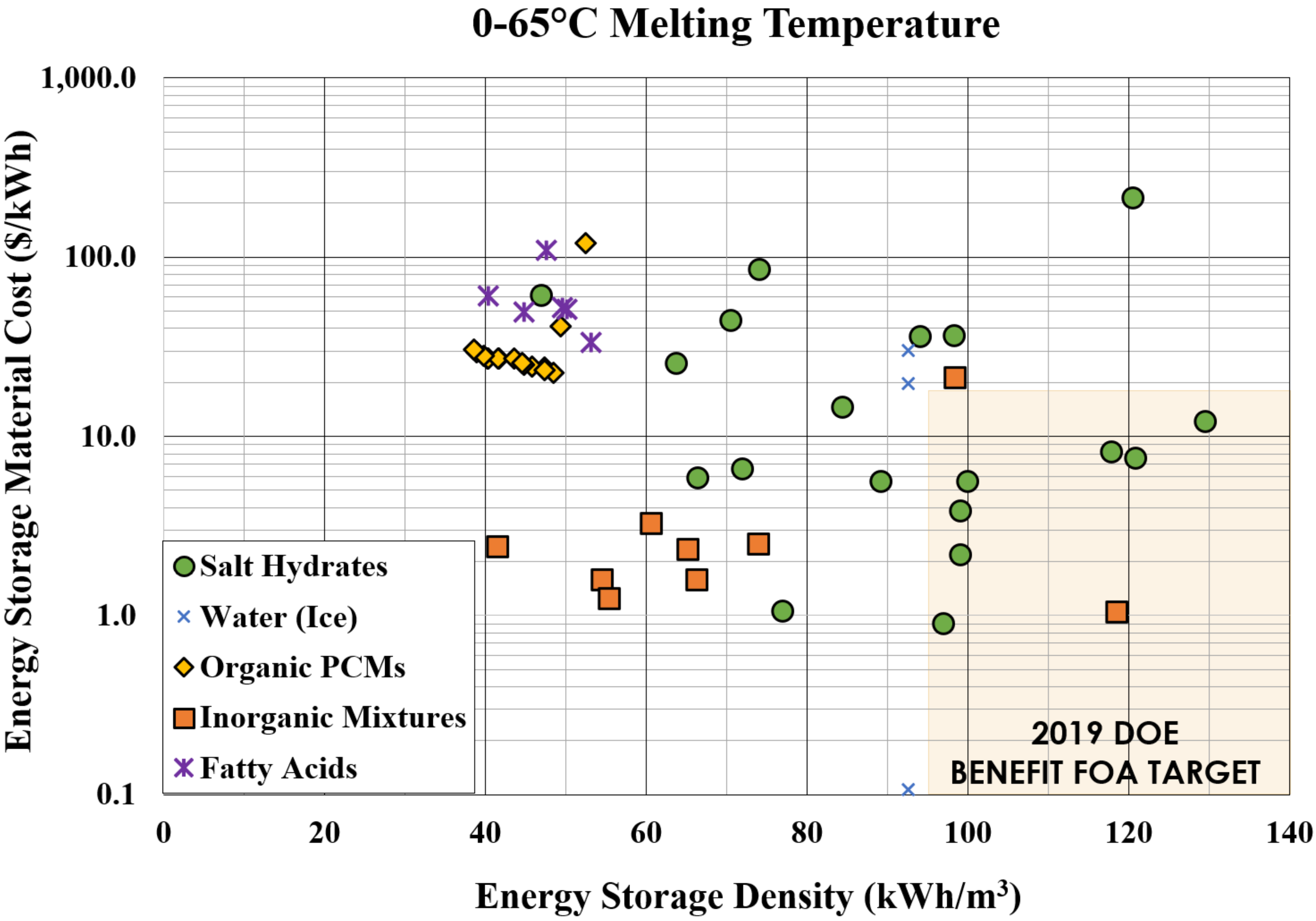
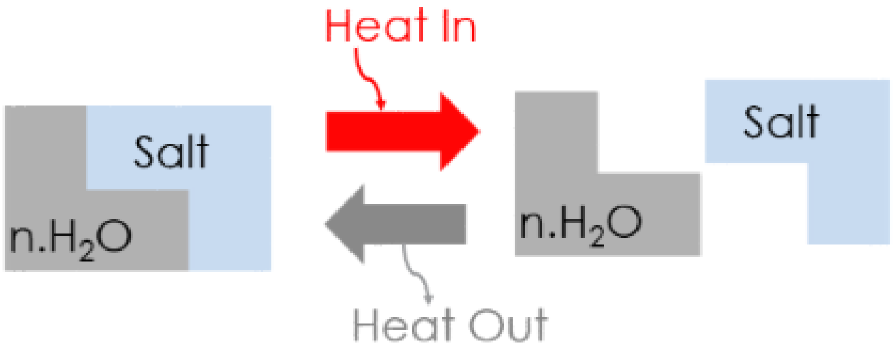


Figure compiled by Hirschey, Kumar, and Gluesenkamp

Introduction to Salt Hydrates as PCM

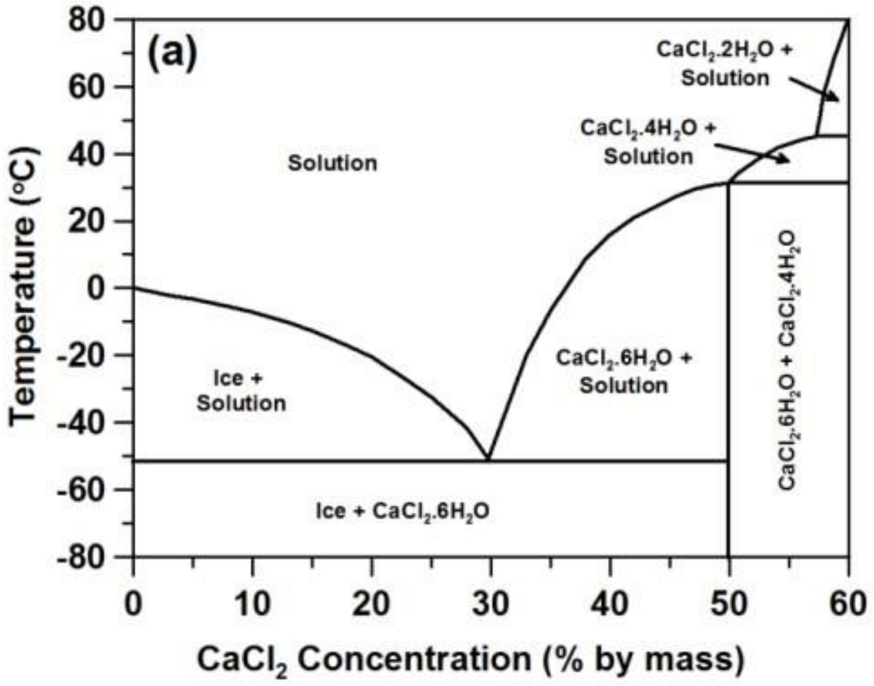


$$salt \cdot nH_2O + Heat \leftrightarrow salt + nH_2O$$

- **Stable crystal structure: water molecules are oriented in a well-defined structure**
  - ❖ Sharp transition temperature
  - ❖ High storage density
- **There are more than 2268 possible salt hydrates combination available for PCMs**

Example:
Calcium Chloride Hexahydrate
($CaCl_2 \cdot 6H_2O$)

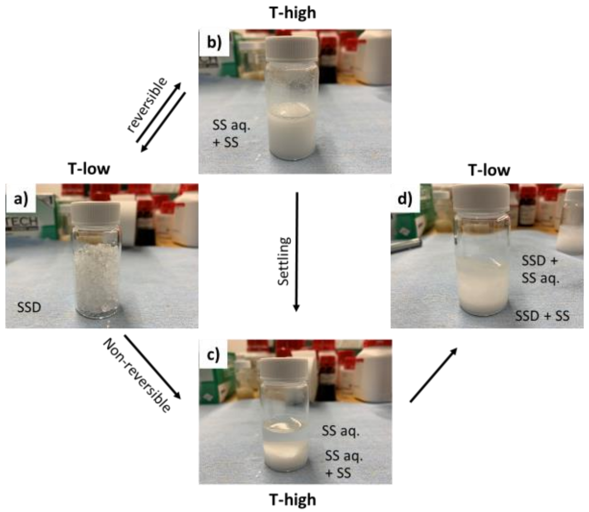
Photo: Yuzhan Li



Phase diagram:
https://engineering.purdue.edu/JTRP/Highlights/cacl2-dihydrate-cacl2-2h2o

Key Technical Challenges with Salt Hydrates

- **Incongruent melting (aka phase segregation)**
  - Many salt hydrates tend to form *anhydrous salt* during melting, which does not re-dissolve
  - Reduces thermal storage capacity with repeated freeze/thaw cycles
- **Supercooling**
  - Large degree of supercooling is common with salt hydrates
  - Inconsistent thermal performance: large ΔT and rapid heat release on freezing
- **Limited options of phase change temperatures**
  - Inorganic chemistry offers discrete options
- **Corrosion and chemical stability**
- **Thermal conductivity**



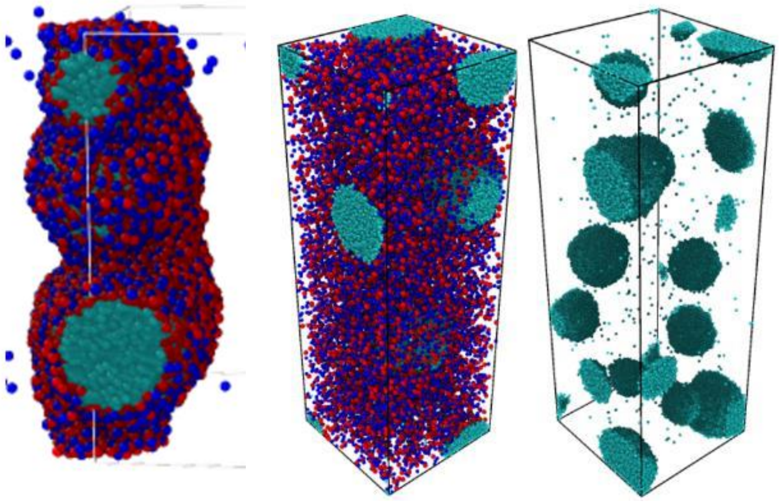
Incongruent melting illustrated

Supercooling illustrated

State of the Art: Reducing Phase Segregation

- **Many “thickening agents” have been employed**
  - Early research: Telkes 1976: thixotropic clay mixture with $Na_2SO_4 \cdot 10H_2O$
  - Other thickeners including diatomaceous earth, sawdust, peat moss, starch and various polymers and gels
- **Excess water, to promote re-dissolution of anhydrous salt**
  - Effective in some systems, but depends on concentrations at phase transitions
- **Many of these work well in the lab with short, repeated freeze thaw cycles but have not been robust in the field**
  - Research by Marks indicated that settling of precipitate still takes place over extended periods
  - Slow testing cycles needed in addition to numerous repeated cycles

Coarse-grain molecular dynamics simulations at ORNL were used to explore impact of viscosity



Results:

- **Reduction in phase segregation is proportional to viscosity.**

State of the Art: Reducing Phase Segregation

- **Since 2010, various “encapsulation” techniques have been developed for salt hydrate PCMs**
  - **Core-Shell** techniques includes in-site, interfacial, emulsion polymerization techniques
  - **Shape Stabilized** techniques includes direct integration into a shape-stabilized material like graphite or metal foam

- **Encapsulation is promising in:**
  - Reducing phase segregation
  - Reducing the reactivity of the salt hydrate with the outside environment

Core-Shell Encapsulation

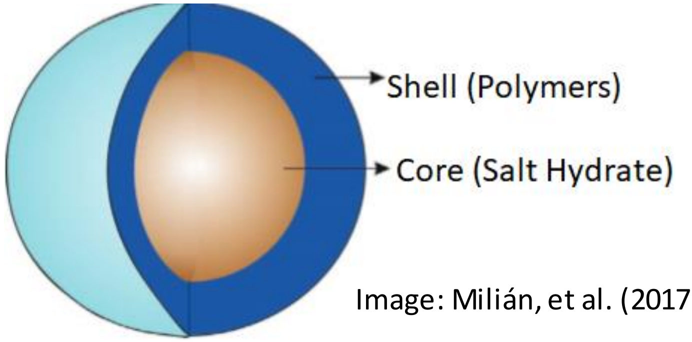


Image: Milián, et al. (2017)

Shape-Stabilized Encapsulation

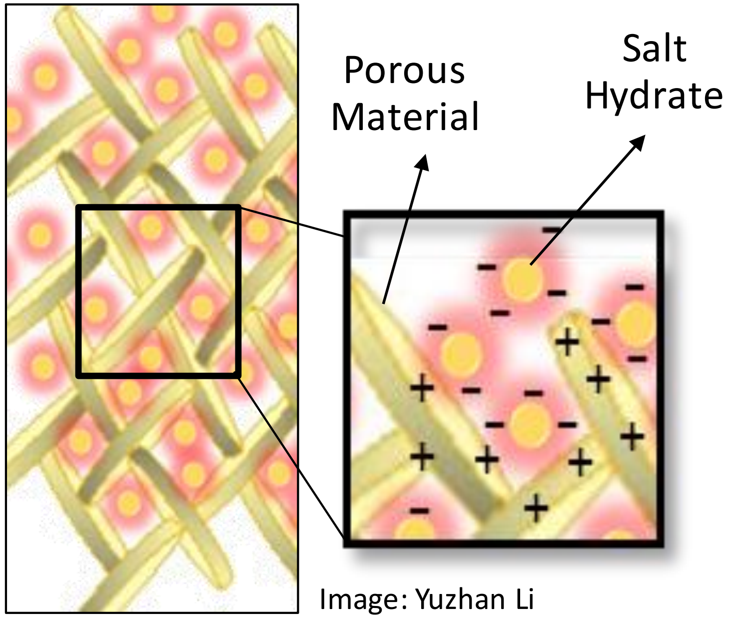


Image: Yuzhan Li

Y. E. Milián, A. Gutiérrez, M. Grágeda, and S. Ushak, “A review on encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties,” *Renew. Sustain. Energy Rev.*, vol. 73, no. December 2016, pp. 983–999, 2017.

Current Success with Encapsulation Technique

Shell-Core Encapsulation

	Shell material	Scale	Core: Shell	T_m (°C)	Latent Heat (J/g)	Reduction in Latent Heat (%)	Number of Cycles
Sodium sulfate decahydrate	SiO_2 + PTMS + ODTMS + Al_2O_3	Nano	2:8	32	58	77	100
	SiO_2 + TEOS+ MODS + PAOS	Micro	1:9	27.3	38.6	84	100
	TEOS + 3 aminopropyltriethoxysilane	Nano	1:1	-	181	29	100
Sodium monohydrogen phosphate dodecahydrate	MMA and Urea	Micro		51.5	143	46	-
	SiO_2 + TEOS+ MODS + PAOS	Micro	1:9	36.6	69.3	74	-

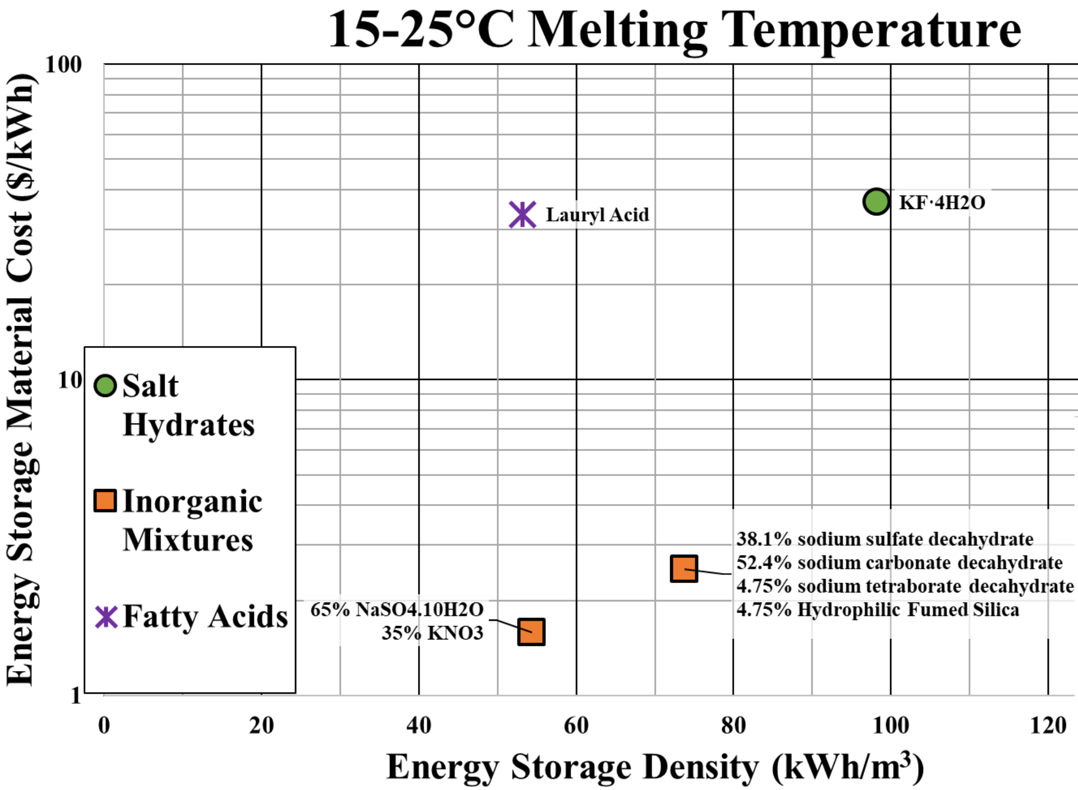
Shape Stabilized Encapsulation

	Supporting	Material Concentration (wt %)	T_m (°C)	Latent Heat (J/g)	Reduction in Latent Heat (%)	Number of Cycles
Calcium chloride hexahydrate	Expanded Graphite	20	31.2	147	23.17	50
		10	36.7	161	15.67	
		40	31.3	145	24	
Sodium sulfate decahydrate	SiO_2	30	32.7	68.5	69.8	100
Lithium nitrate trihydrate	PVA_{87} and PVA_{89}	15	29.9	215	25	-

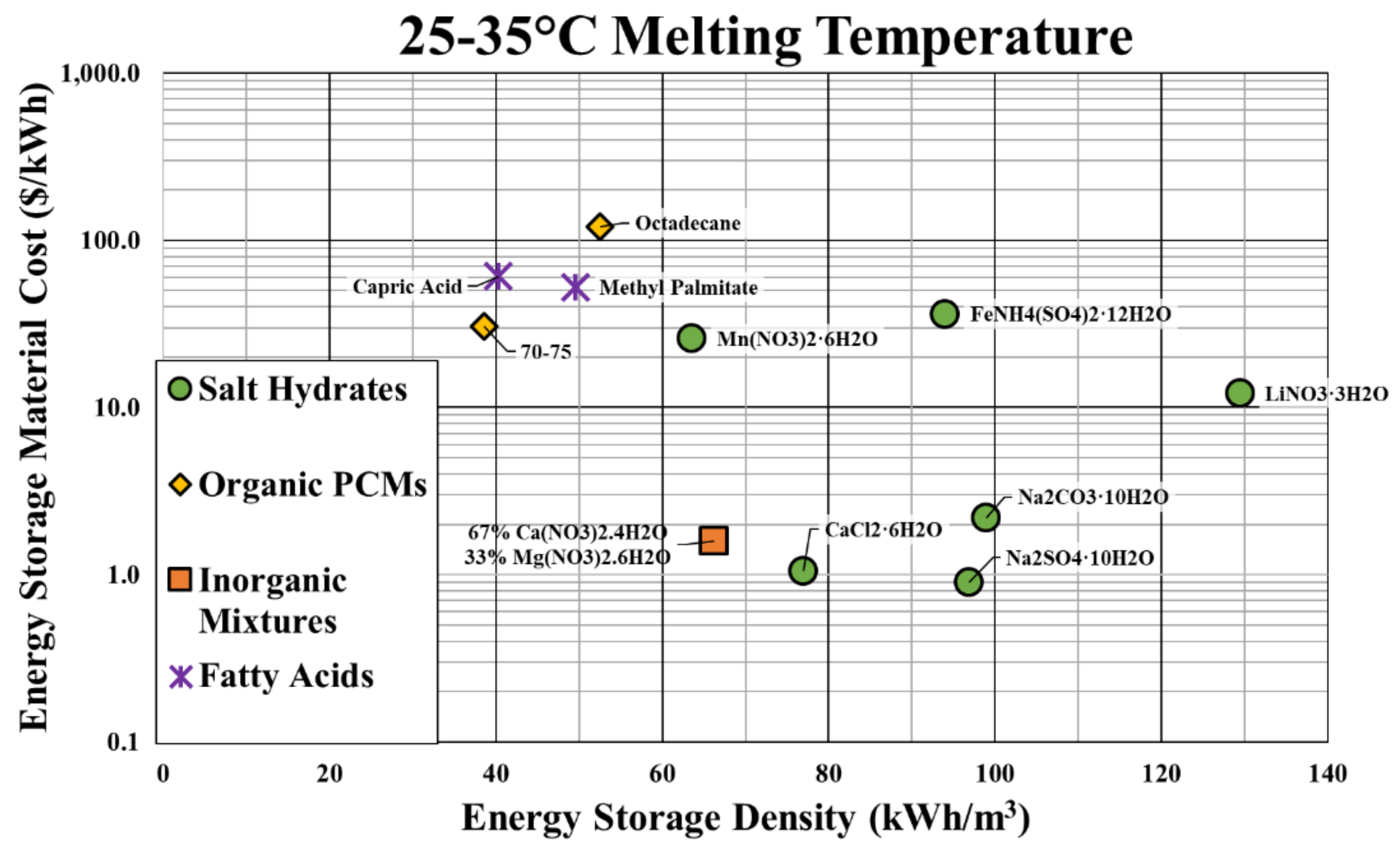
- **Many of encapsulation techniques are**
  - Expensive
  - Low encapsulation yield
  - High encapsulation breakage – Volume expansion
  - Increase in supercooling without nucleators
- **Future research**
  - New low-cost naturally occurring shell materials
  - Fast, cheap and high encapsulation yield technique

Table adapted from: Milián, Y. E., Gutiérrez, A., Grágeda, M., & Ushak, S. (2017). A review on encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties. *Renewable and Sustainable Energy Reviews*, 73, 983–999. https://doi.org/10.1016/j.rser.2017.01.159

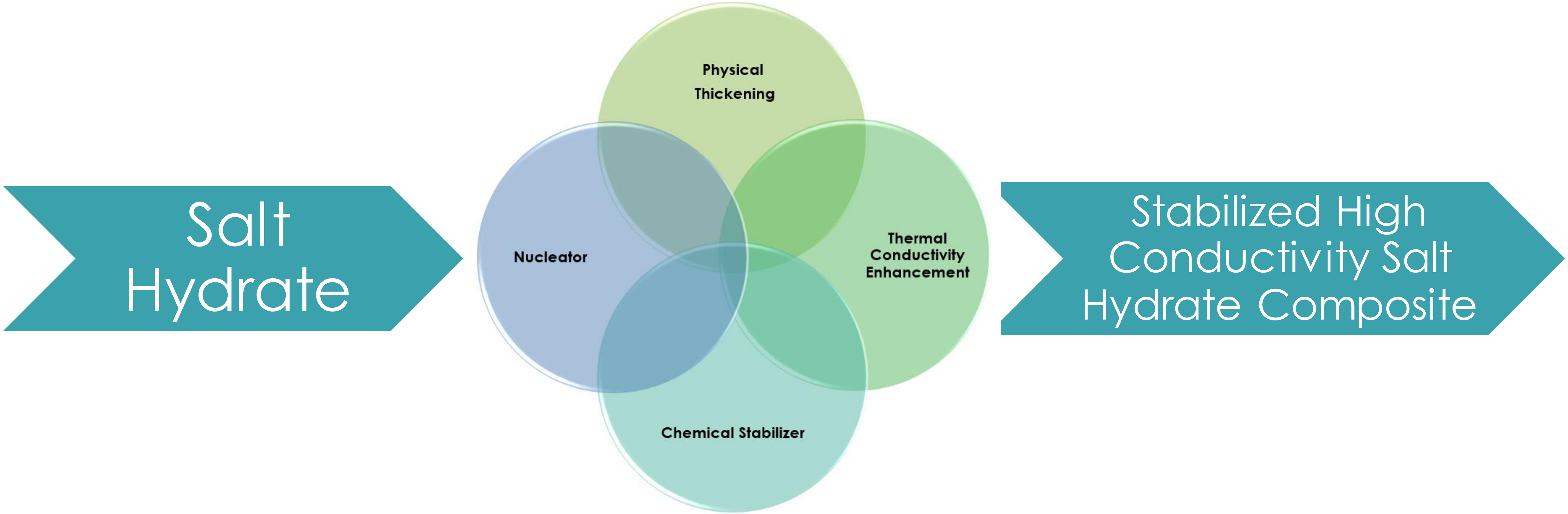
Challenges with Salt Hydrate: Phase Change Temperature



- Limited choices of phase change temperatures
- Requires new techniques to modify the phase change temperature of available salts



ORNL's Stabilization Approach 1: Additives


Salt Hydrate

Physical Thickening

Nucleator

Thermal Conductivity Enhancement

Chemical Stabilizer

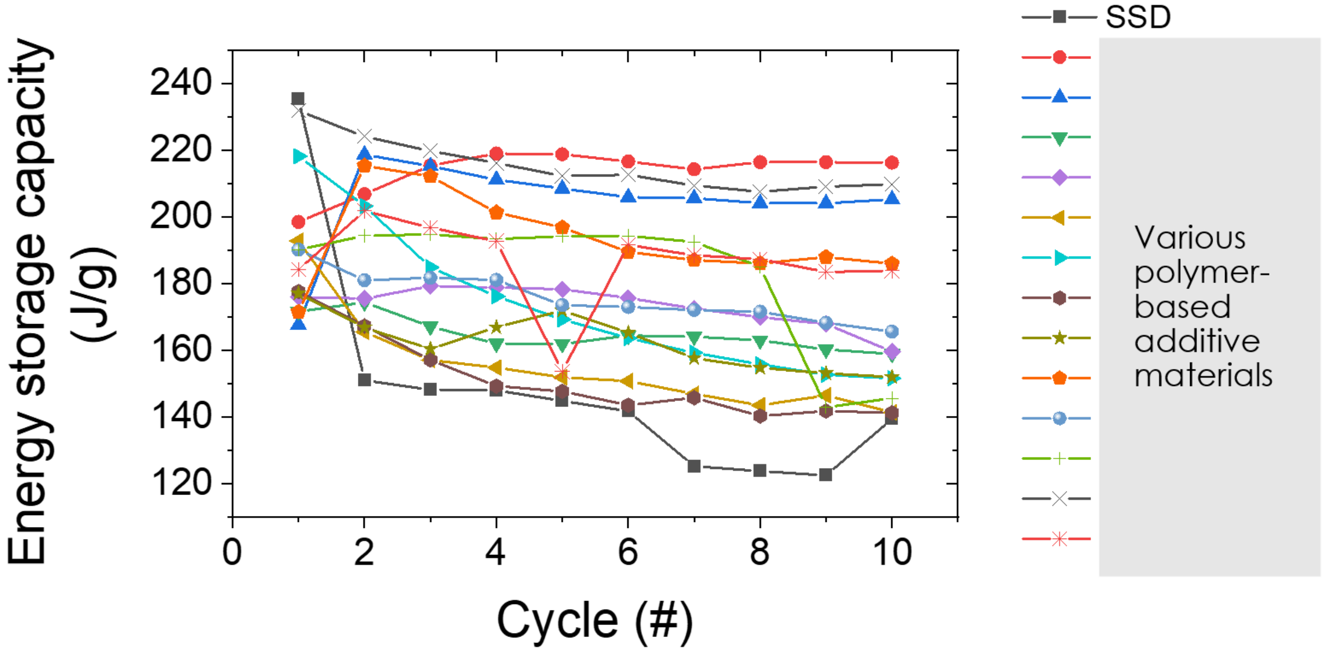
Stabilized High Conductivity Salt Hydrate Composite

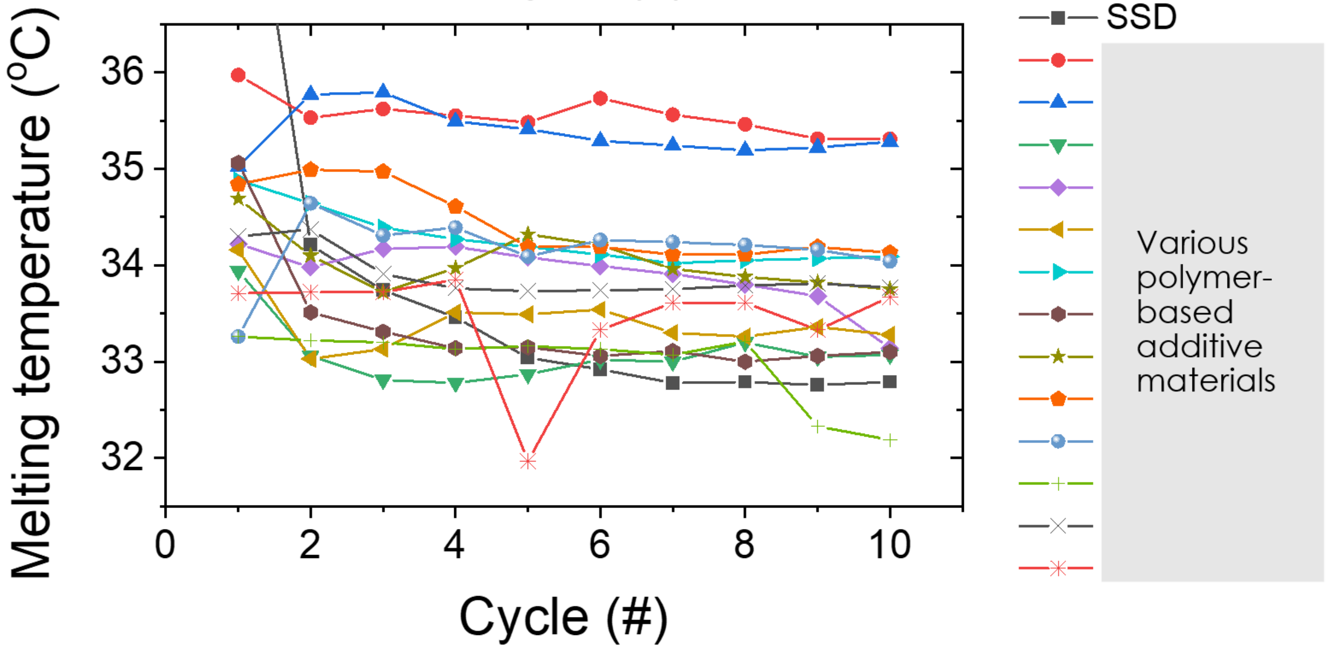
- The ideal stabilization material will provide chemical stabilization, physical thickening, nucleation promotion, and thermal conductivity enhancement.

- Likely, more than one material will be needed to fulfill all four targets.

ORNL Stabilization Approach 1: Additives

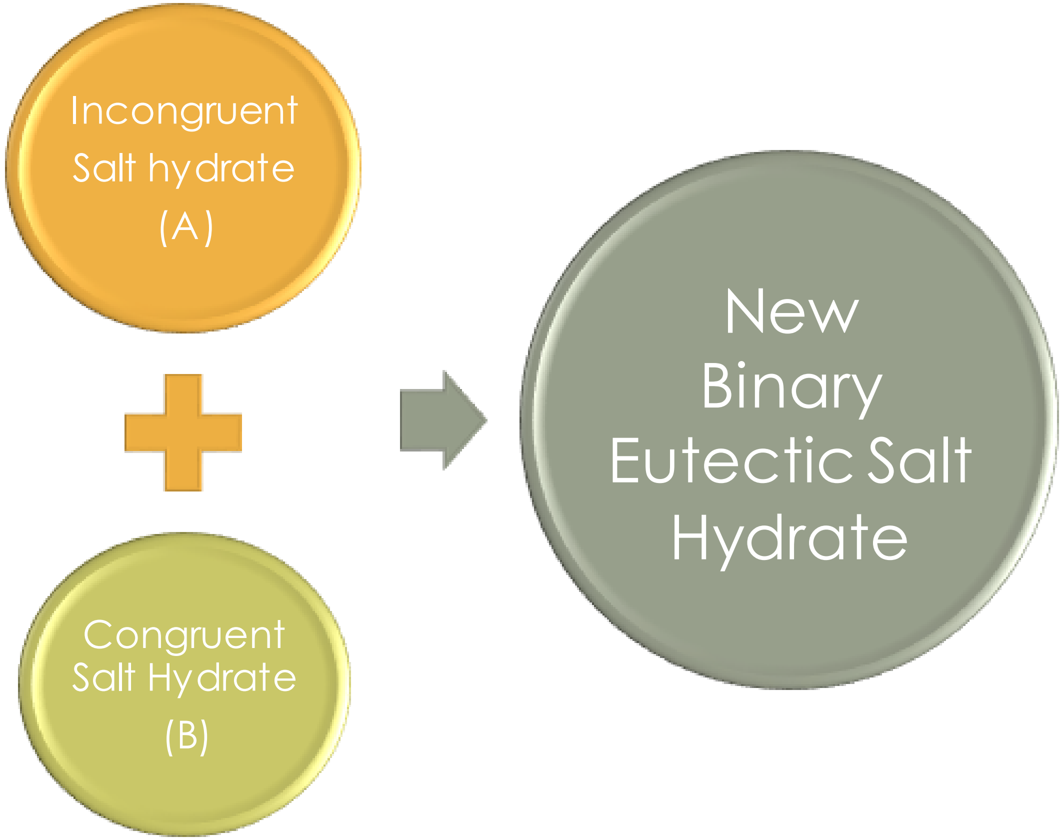
- Implemented our strategy on sodium sulfate decahydrate
- Tried over 14 polymer - based materials to provide *chemical* and *physical* stability
- Learned that polyelectrolytes with specific ions exhibited good stabilizing effect
- Achieved a composite with 150 J/g of storage capacity over 150 cycles
- Reduced supercooling to less than 3°C
- Achieved a projected material cost of **$5.80/kWh**





ORNL's Approach 2: Phase Diagram Modifications

- Salt hydrate eutectics to avoid precipitation of anhydrous salt
- Reduce the phase change temperature
- Redraw the phase diagram
- Potential for invention of new salt hydrates based on eutectic models
- New eutectic could be incorporated with any high thermal conductivity material
- ORNL team successfully demonstrated an incongruently melting salt hydrate as a congruent eutectic
  - Energy Storage capacity of 215 J/g over 50 cycles
  - Lowered the phase change temperature by 3-5°C

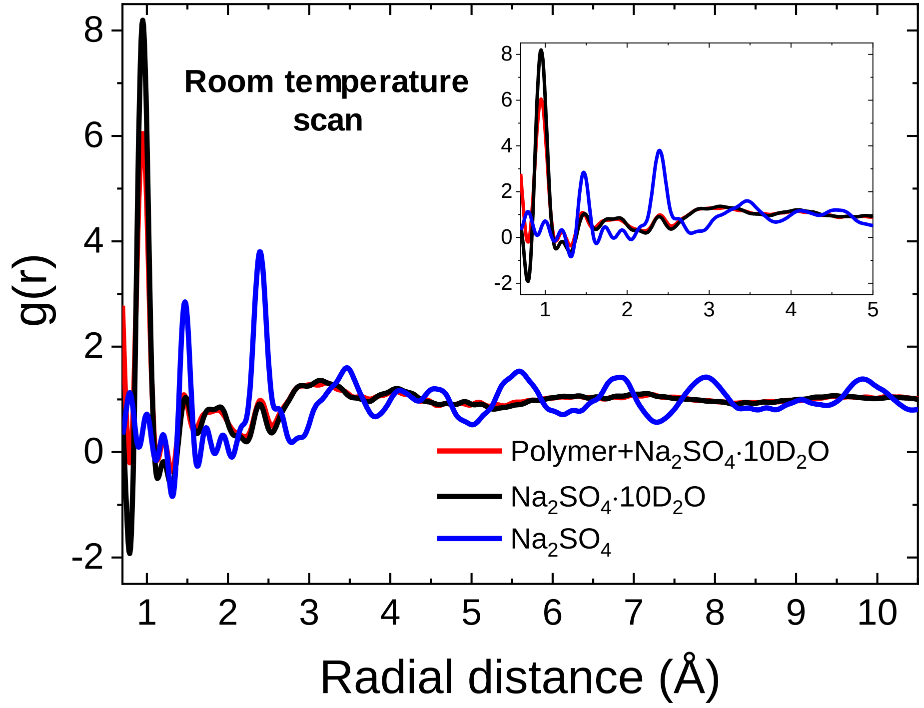


Advanced Characterization of Salt Hydrate PCM Composites

- **ORNL's Spallation Neutron Source**
  - Total scattering using Nanoscale-Ordered Materials Diffractometer (NOMAD)
  - Enabling structural characterization of samples ranging from liquids, polymers, and nanocrystalline materials to long-range-ordered crystals.
  - In-situ heating/cooling capabilities
- **Challenges**
  - Mixed inorganic and organic materials
  - Structure across many length scales
- **Preliminary Results**
  - Sodium sulfate (Na_2SO_4)
  - Deuterated sodium sulfate decahydrate ($Na_2SO_4 \cdot 10D_2O$)
  - Polymer-modified $Na_2SO_4 \cdot 10D_2O$
  - Thermally cycled between 19 to 80 °C

Spallation Neutron Source at ORNL

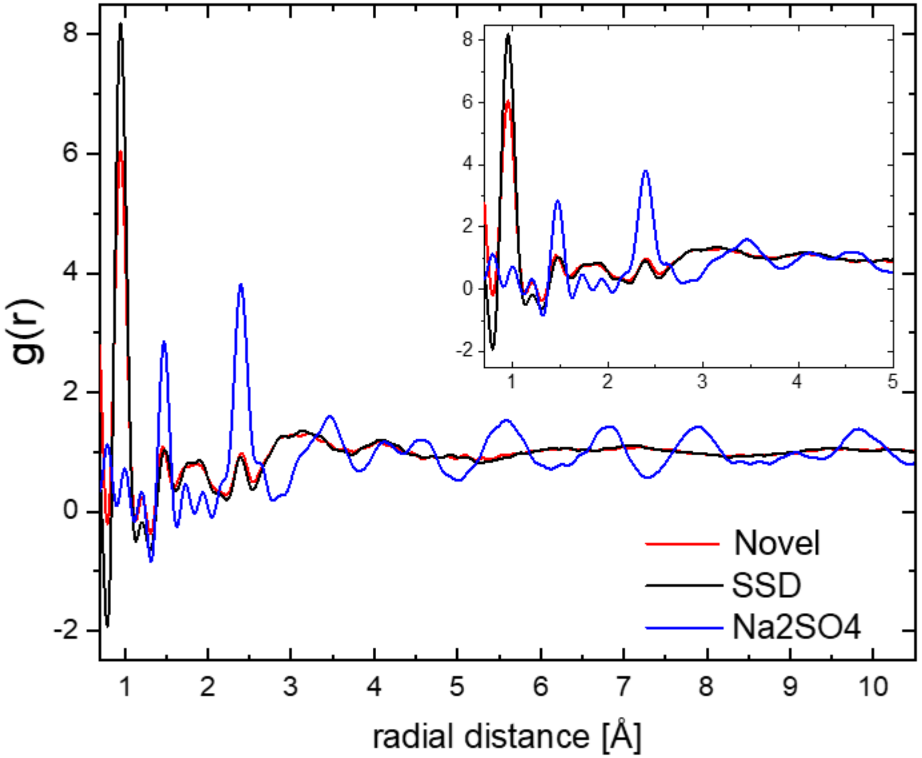
NOMAD beamline (as seen from the sample position)



Change of short-range (atomic bonding) and long-range order (crystalline structure) of the material are tracked during thermal cycling to investigate stability

Advanced Characterization of Salt Hydrate PCM Composites

- **ANL's Advanced Photon Source (APS)**
- **Experimental Results**
  - Sodium sulfate (Na_2SO_4)
  - Sodium sulfate decahydrate
  - Graphite
  - Composite of SSD with graphite (as-prepared)
  - Composite of SSD with graphite (thermally cycled)
  - Composite of SSD with polymer (as-prepared)
- **Utilization of Total Scattering Characterization**
  - Understand the fundamental issues with salt hydrates
  - Improving the salt hydrates performance based on the fundamental understanding
  - Designing of new salt hydrate materials



Conclusions

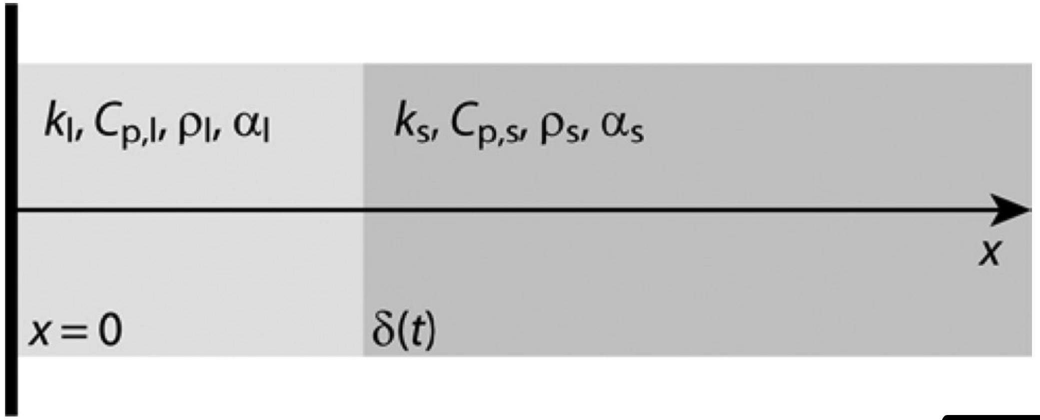
- Salt hydrates are among the most promising PCMs due to:
  - low cost
  - high energy density
- Key challenges are:
  - achieving cycling stability (avoiding phase segregation),
  - limiting supercooling,
  - developing new temperature ranges
- ORNL is advancing the state of the art with:
  - physical+chemical stabilization
  - new eutectics
  - insights through new fundamental characterization techniques

UVA | SCHOOL *of* ENGINEERING & APPLIED SCIENCE

Bio-based phase change materials (PCMs) for Thermal Energy Storage

Patrick E. Hopkins
Professor, University of Virginia
phopkins@virginia.edu
https://patrickehopkins.com

A typical PCM "figure of merit"



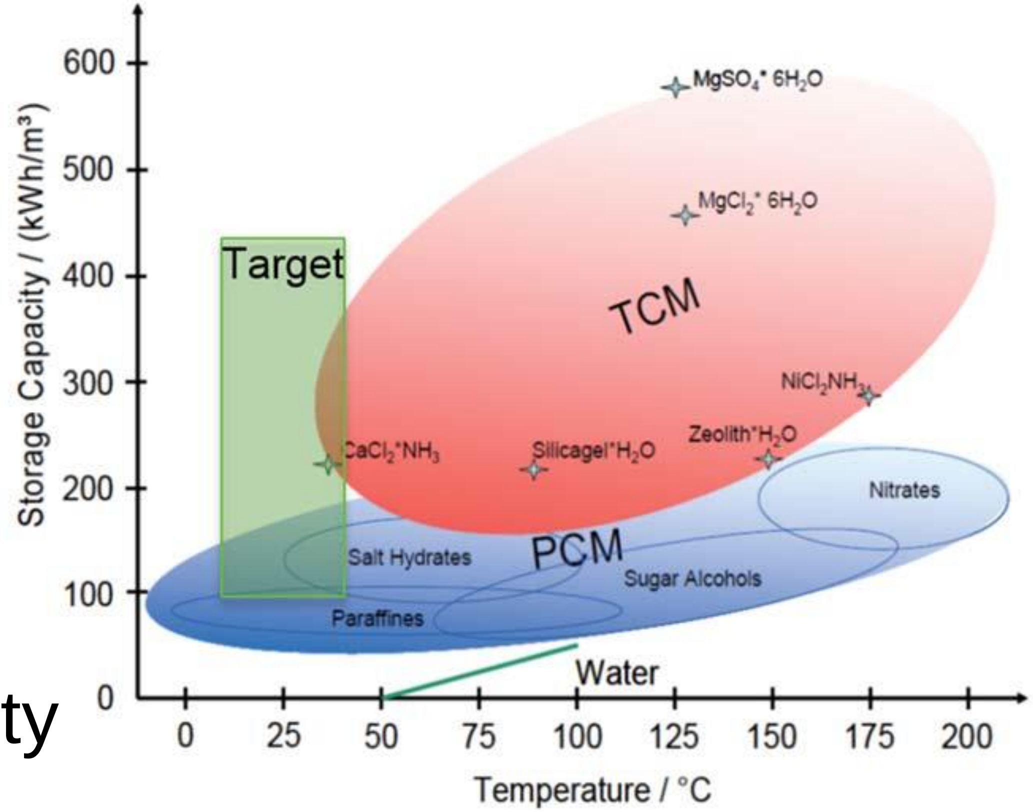
$$\mathrm{FOM} \propto E = \sqrt{\kappa C}$$

Thermal effusivity

Thermal conductivity

Heat capacity

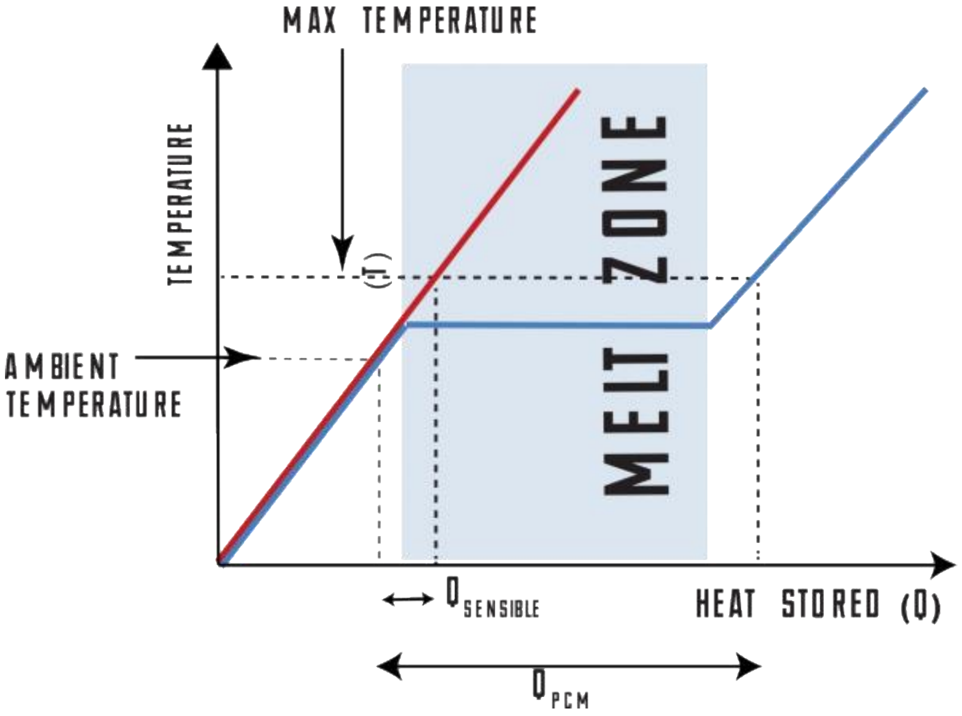
BTO targets



Int. J. Heat Mass Trans. **43**, 2245 (2000)

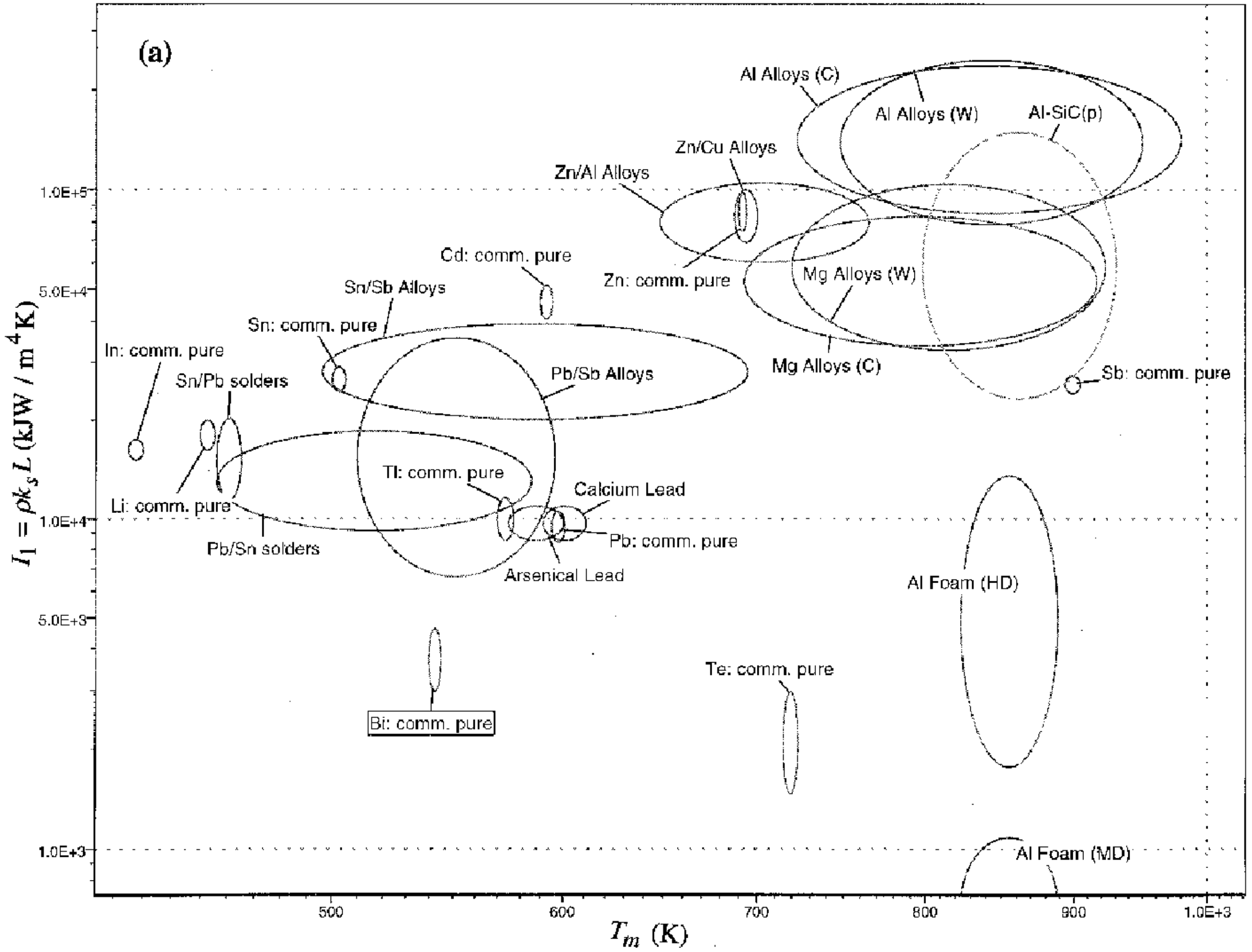
J. Heat Trans. **138,** 024502 (2015)

PCMs can have large changes in *C* (*from L*) across T_m



Advanced Cooling Technologies website

https://www.1-act.com/products/pcm-heat-sinks/

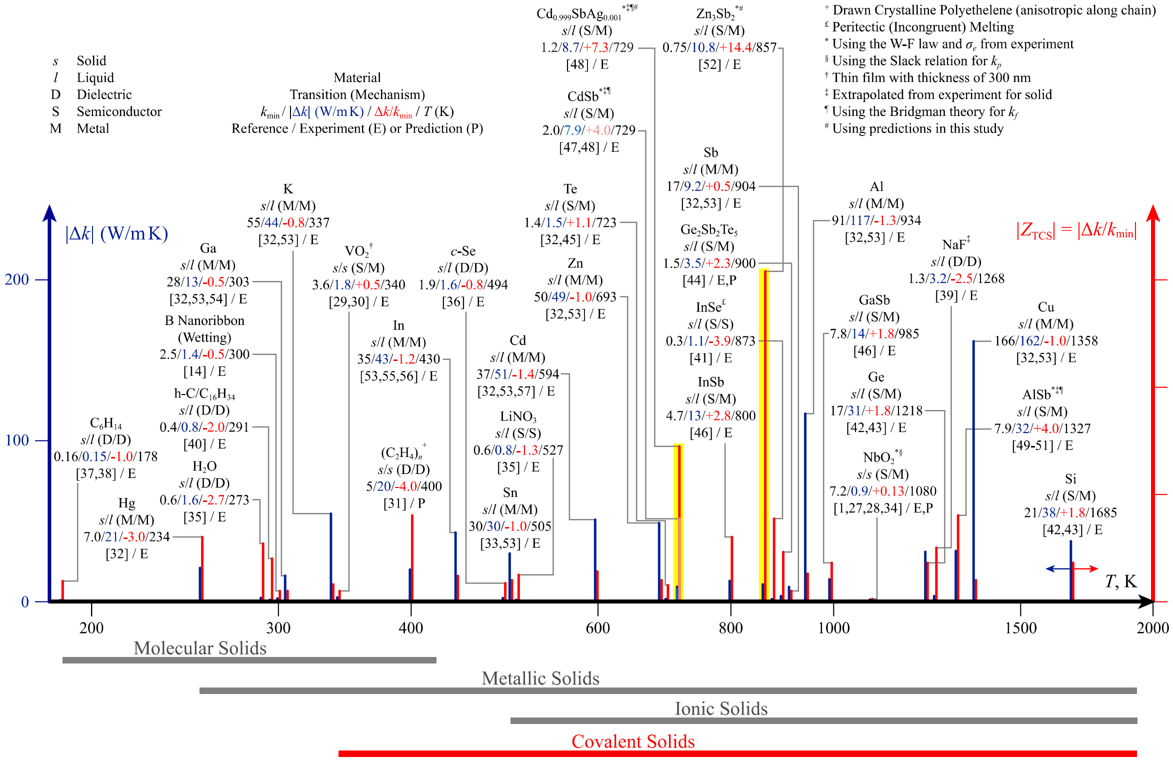


Int. J. Heat Mass Trans. **43**, 2245 (2000)

But can we also change κ?
The thermal conductivity switch

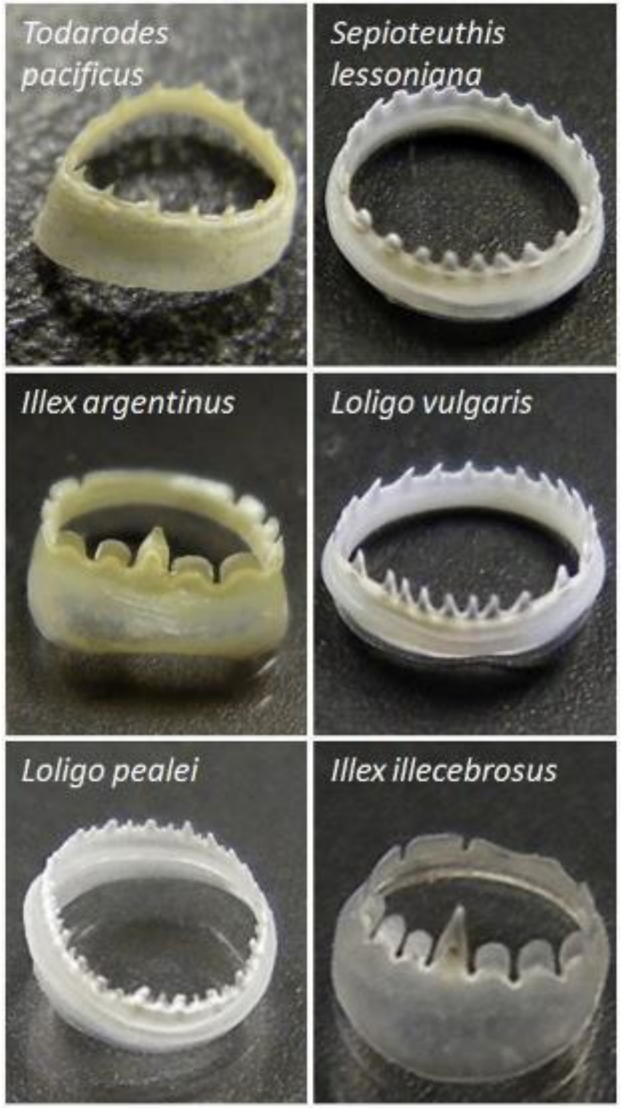
- Charging/discharging rate and heat flux in/out based on thermal conductivity
- Switchable thermal conductivity based on storage or charge
- Common for melting of inorganics

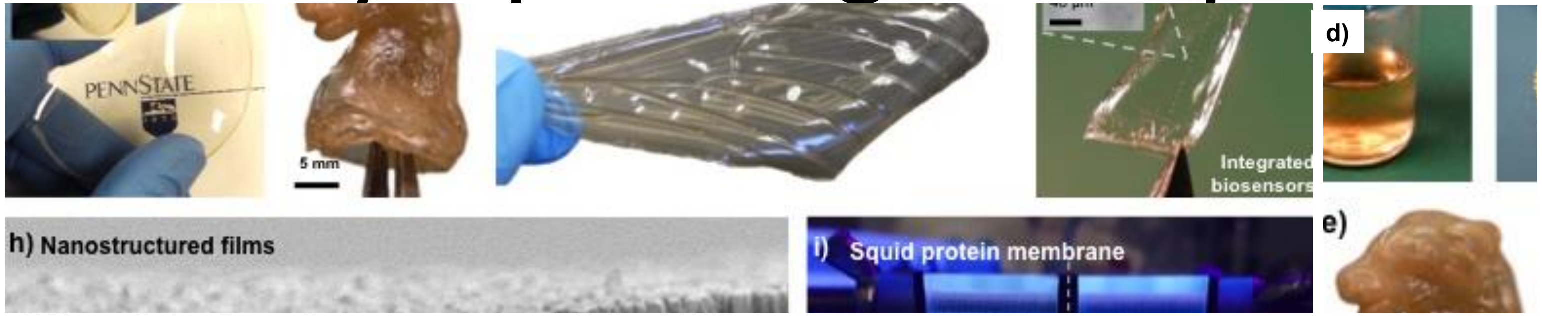
$$\mathrm{FOM} \propto E = \sqrt{\kappa C}$$

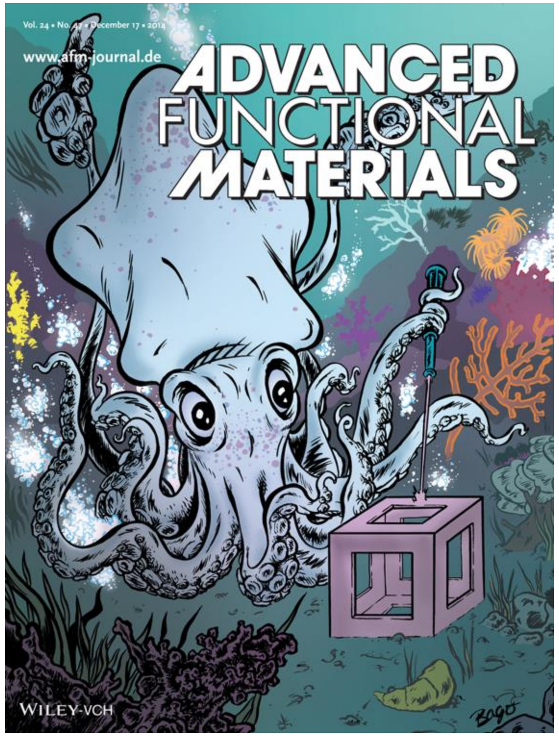


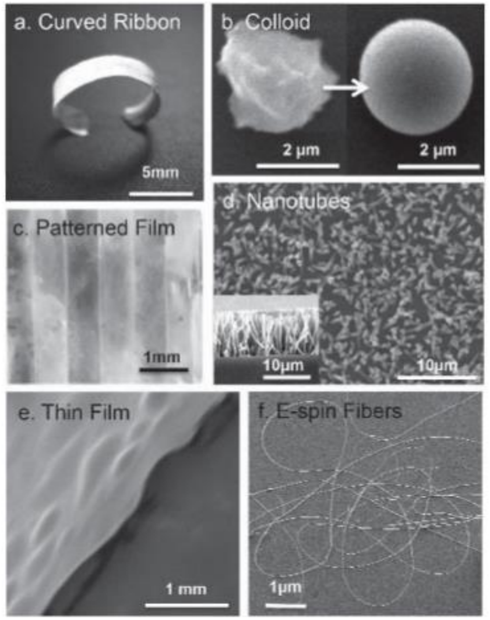
Phys. Rev. B **94**, 155203 (2016)

Bio-based PCM derived by squid ring teeth protein







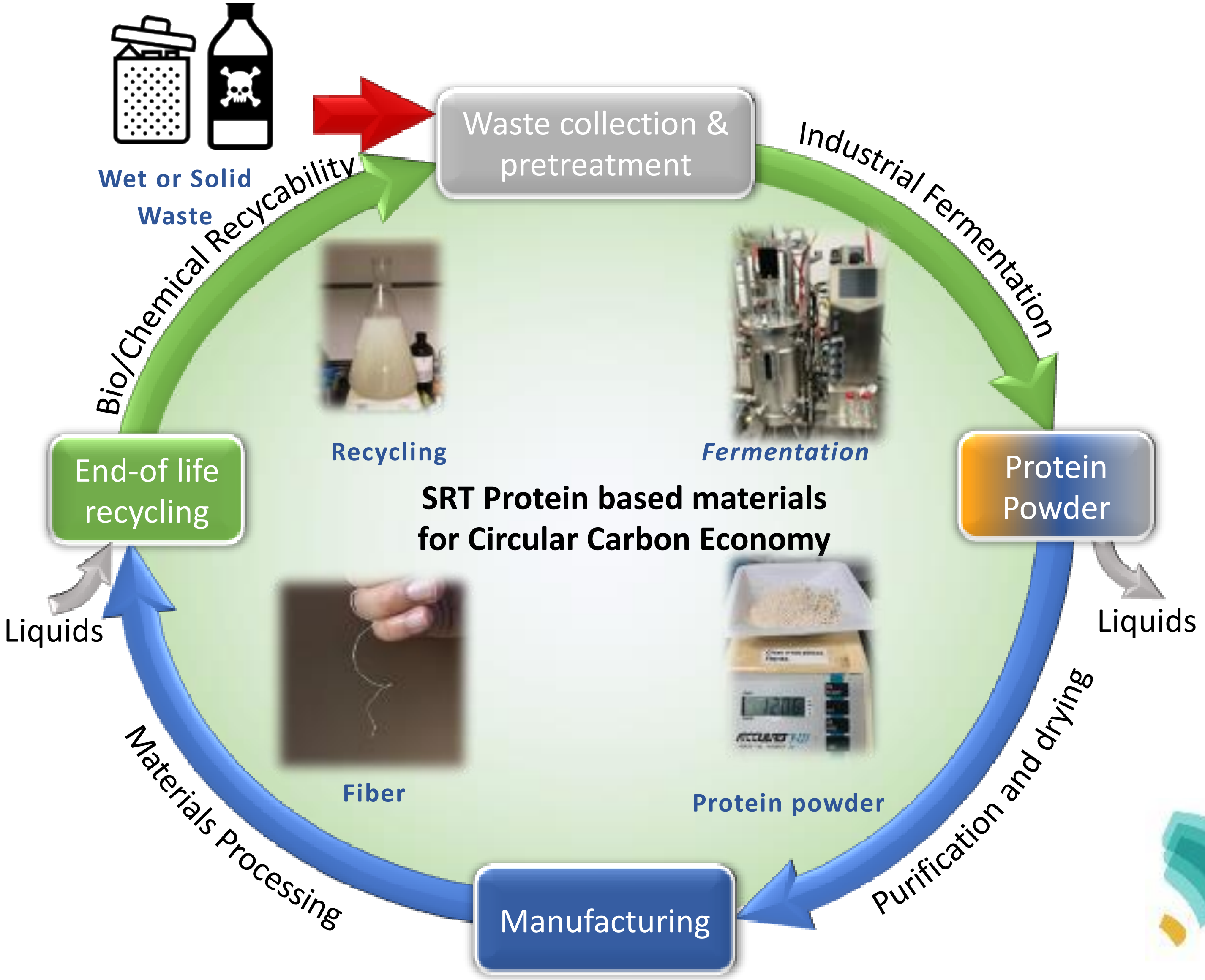


TANDEM REPEAT

Jung *et al*., *PNAS* **113**, 6478 (2016)

Pena-Francesch *et al*., *Advanced Functional Materials* **24**, 7401 (2014)

Bio-based PCM derived by squid ring teeth protein



Wet or Solid Waste

Waste collection & pretreatment

Industrial Fermentation

Protein Powder

Liquids

Purification and drying

Manufacturing

Materials Processing

Liquids

End-of life recycling

Bio/Chemical Recyclability

Recycling

Fermentation

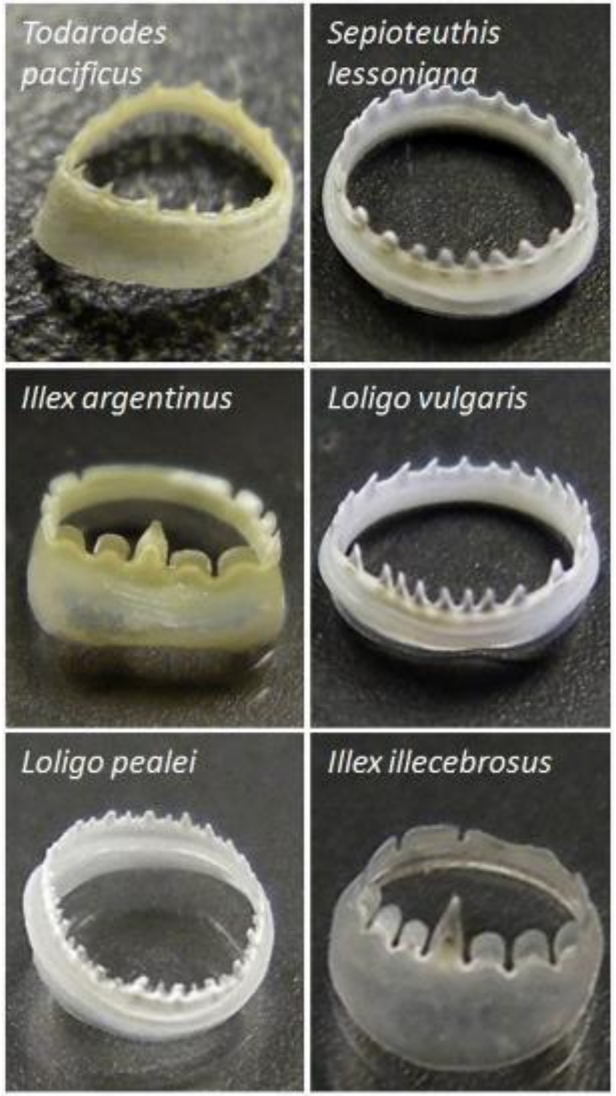
SRT Protein based materials for Circular Carbon Economy

Fiber

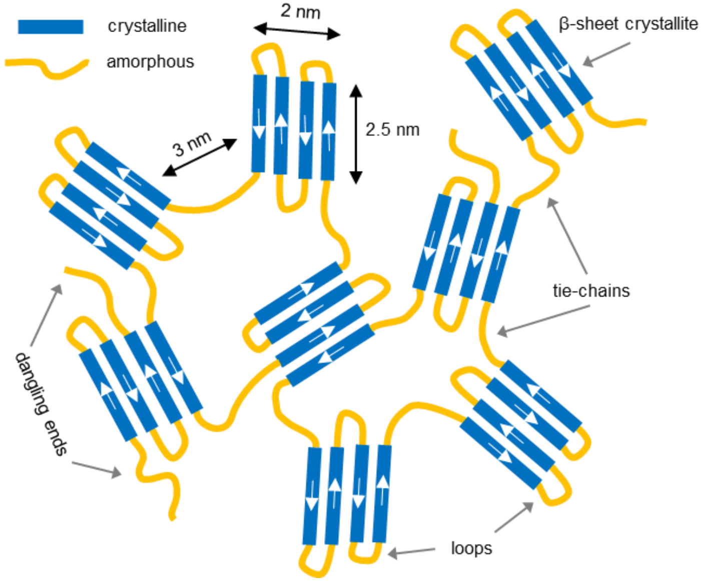
Protein powder

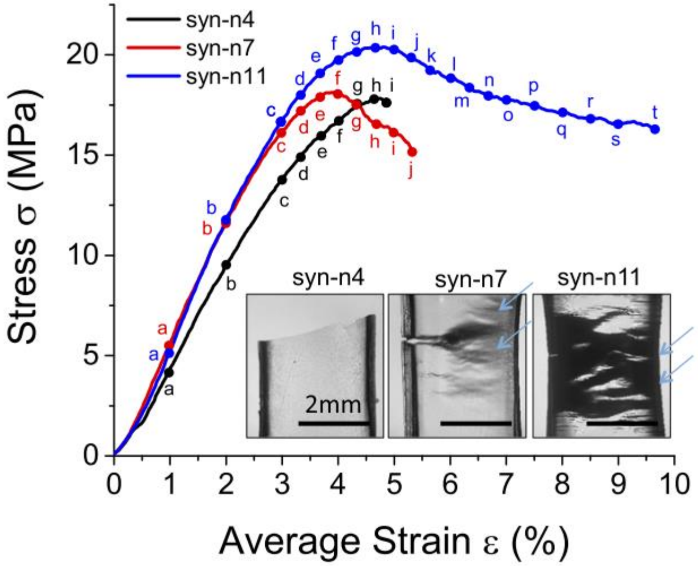
TANDEM REPEAT

Bio-based PCM derived by squid ring teeth protein



DURABLE: High strength protein due to semi crystalline (beta sheets) hydrogen bonded network



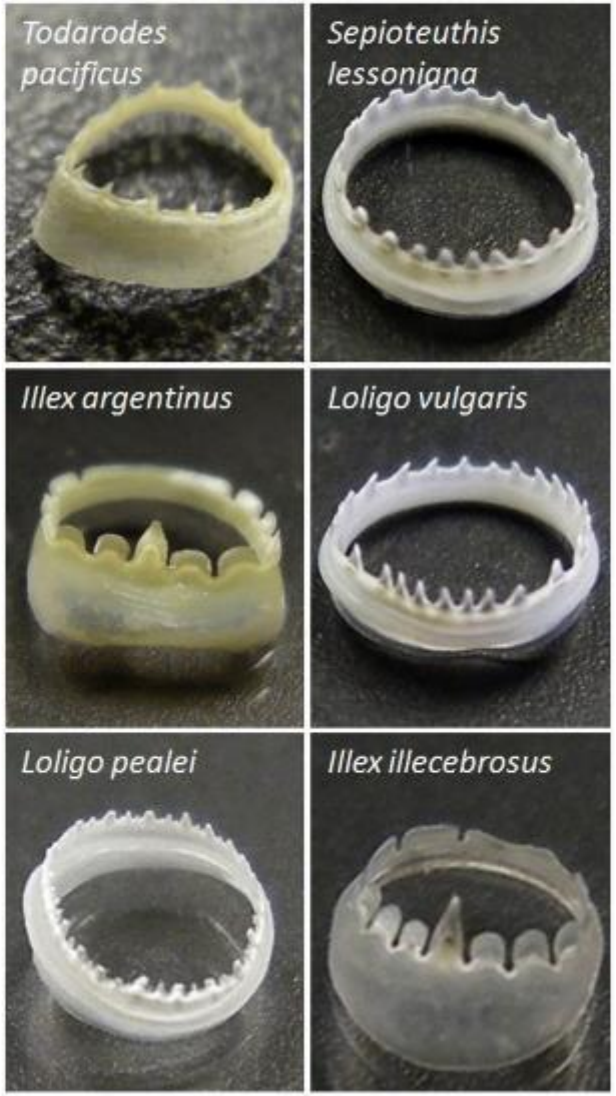


TANDEM REPEAT

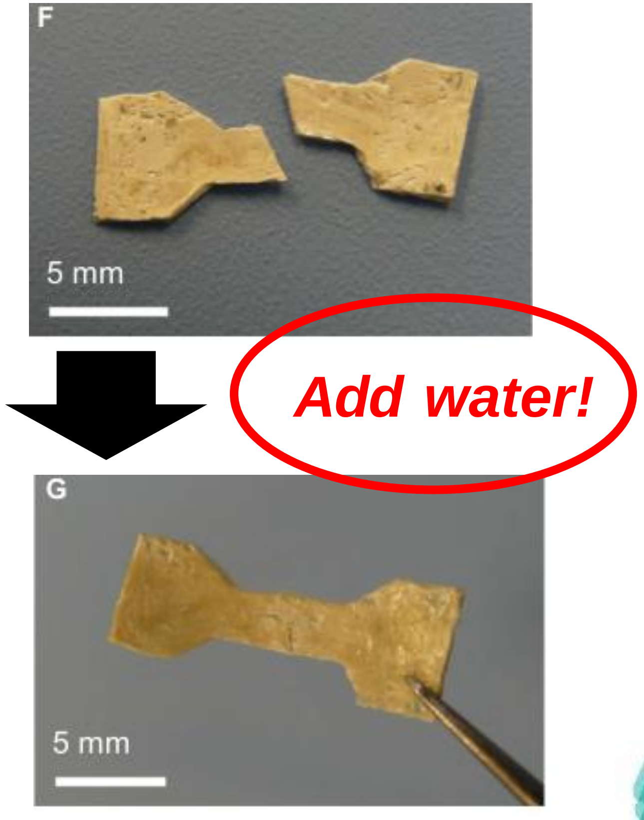
Jung *et al.*, *PNAS* **113**, 6478 (2016)

Pena-Francesch *et al.*, *Advanced Functional Materials* **24**, 7401 (2014)

Bio-based PCM derived by squid ring teeth protein



Self healing when hydrated
(with a little bit of heat)



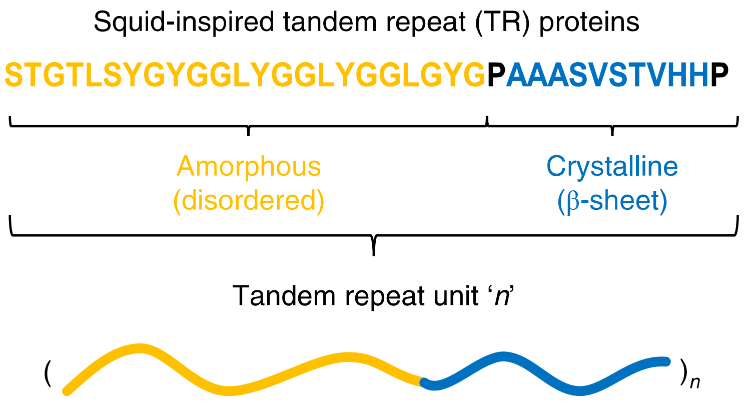
TANDEM
REPEAT

Jung *et al.*, *PNAS* **113**, 6478 (2016)

Pena-Francesch *et al.*, *Advanced Functional Materials* **24**, 7401 (2014)

Bio-based PCM derived by squid ring teeth protein

Molecular structure of each tandem repeat dictates properties of SRT,
including thermal properties!



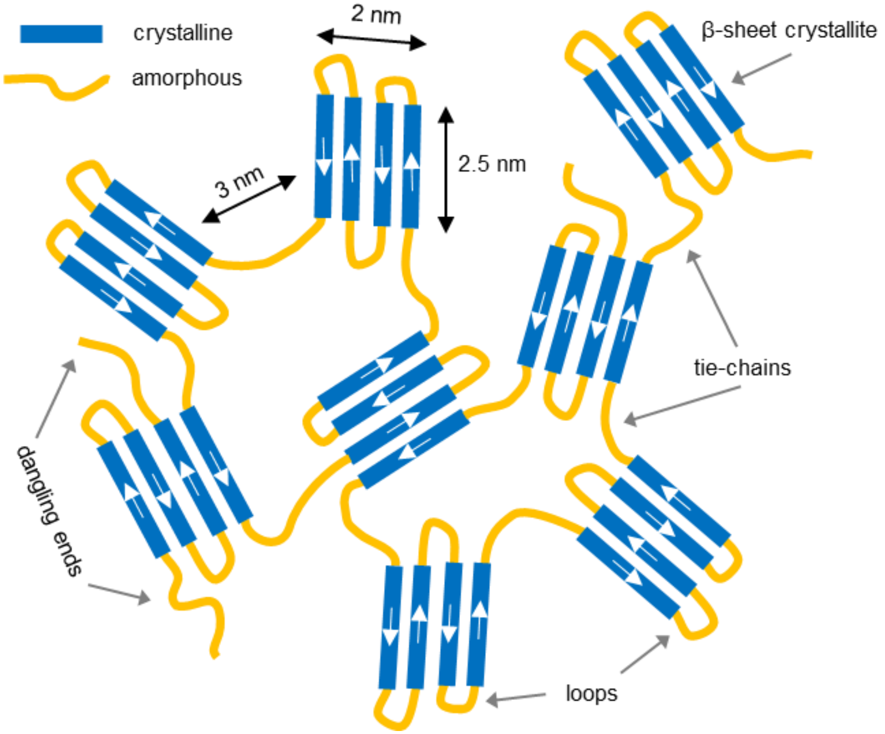
Squid-inspired tandem repeat (TR) proteins

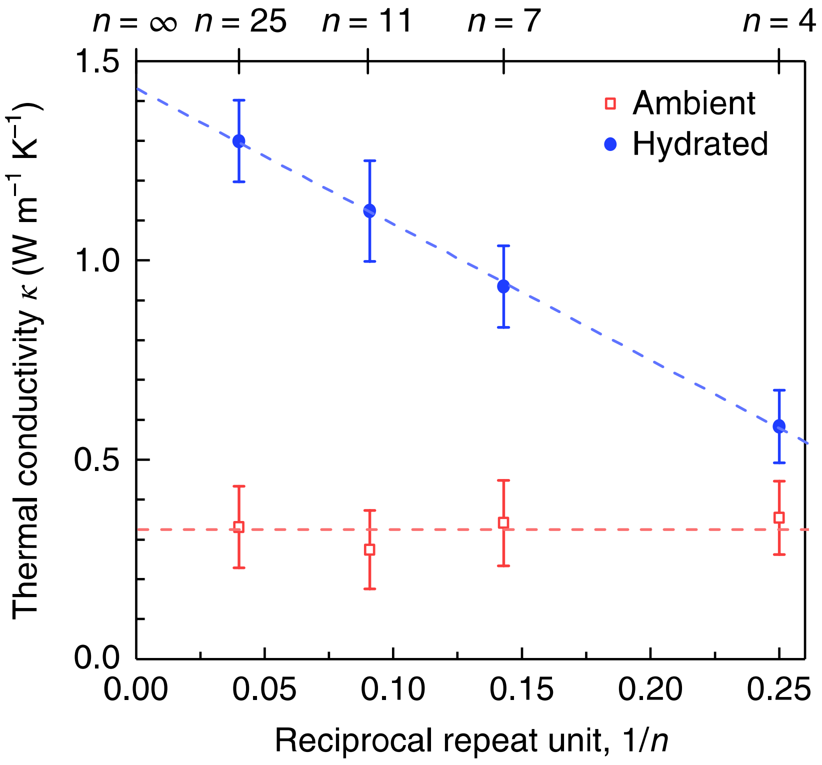
STGTLSYGYGGLYGGLYGGLGYGPAAASVSTVHHP

Amorphous (disordered)

Crystalline (β-sheet)

Tandem repeat unit ‘*n*’

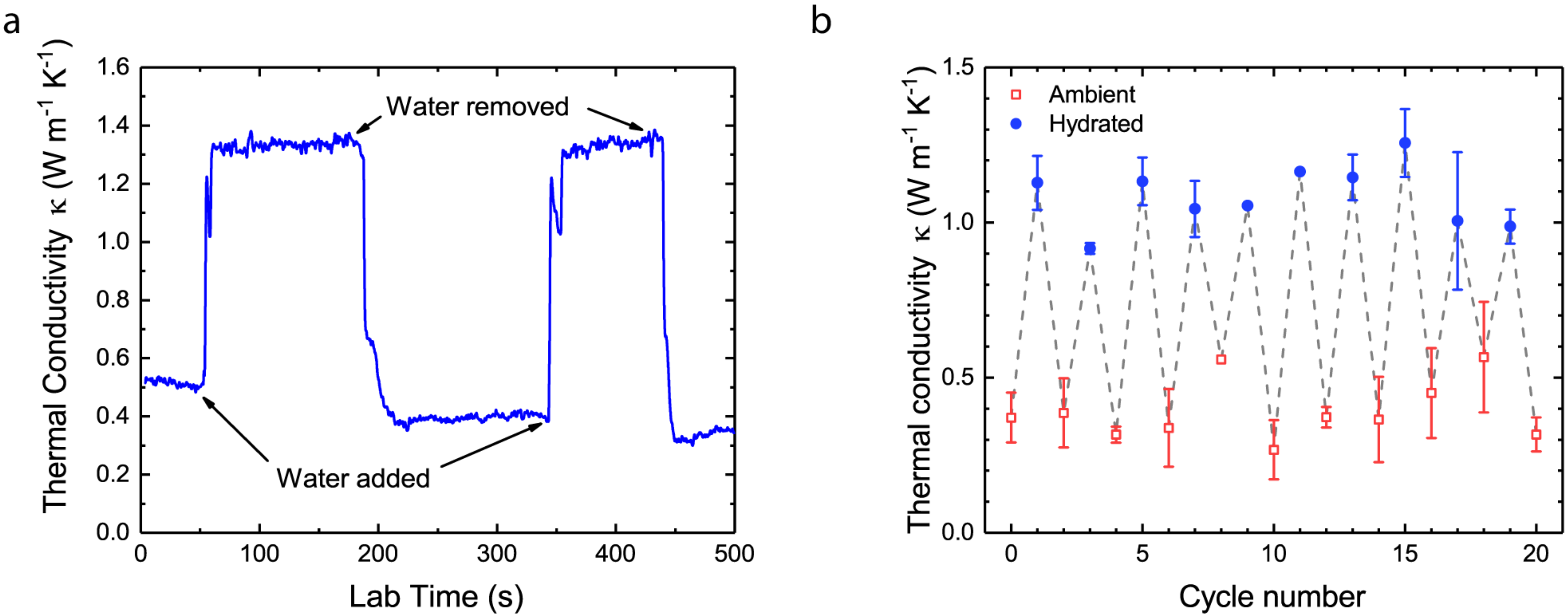




Tomko *et al. Nature Nanotechnology* **13**, 959 (2018)

Bio-based PCM derived by squid ring teeth protein

Thermal conductivity switching: Plasticizer increases thermal conductivity “on demand”



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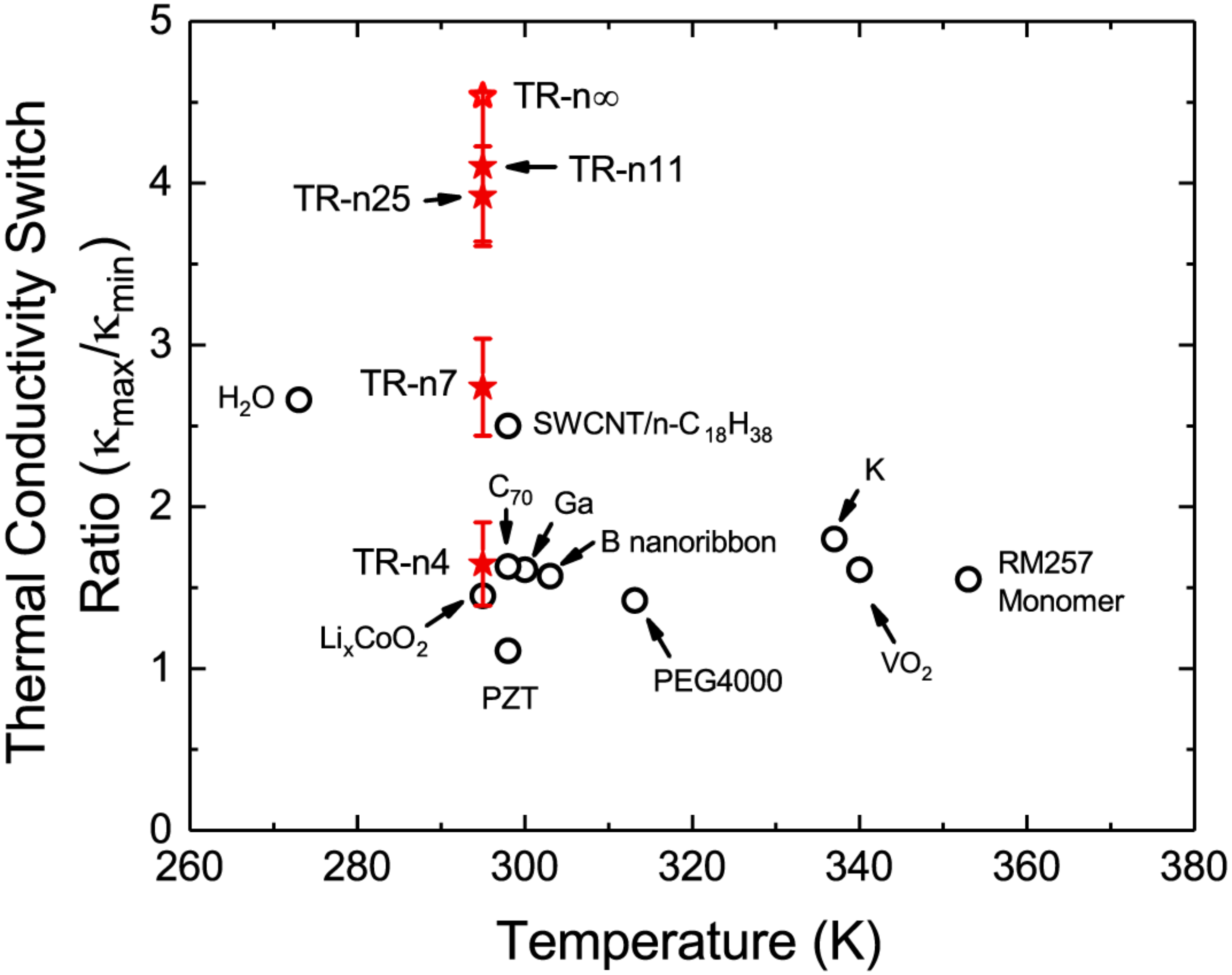
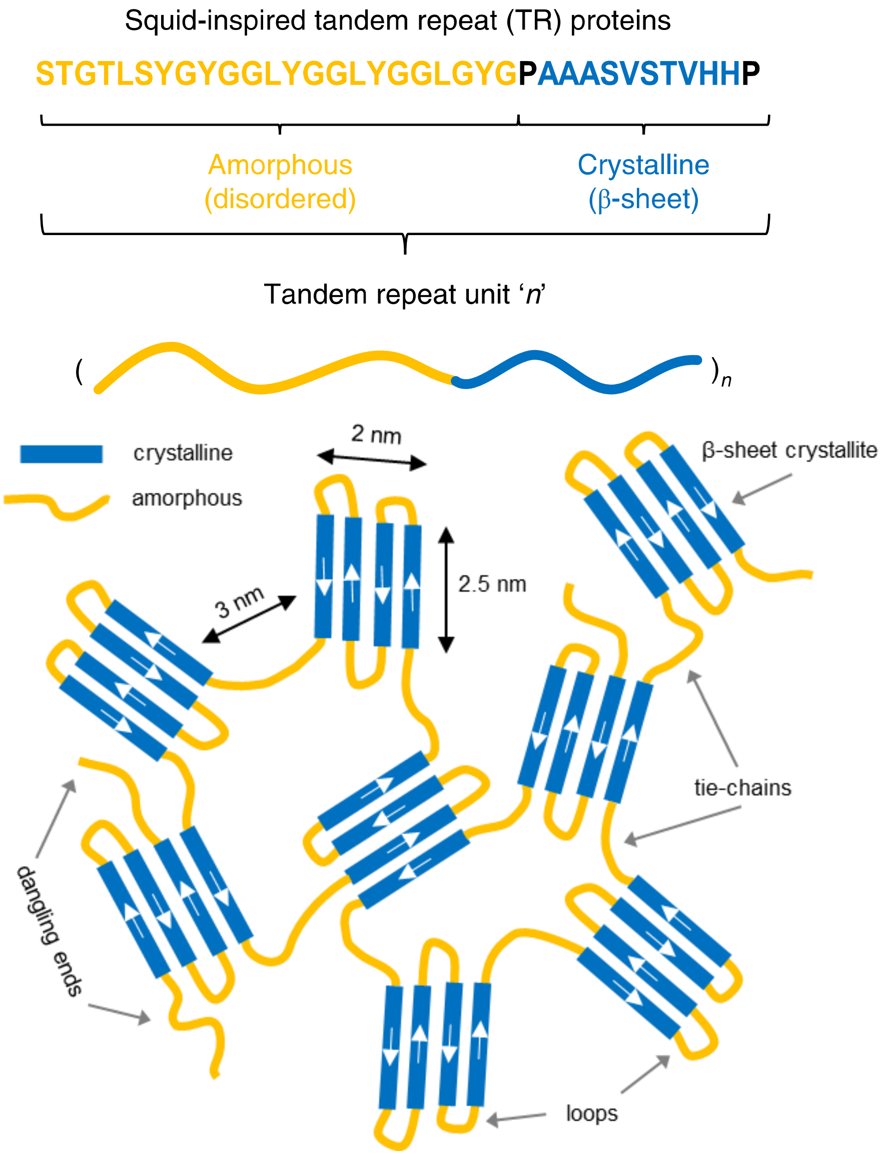
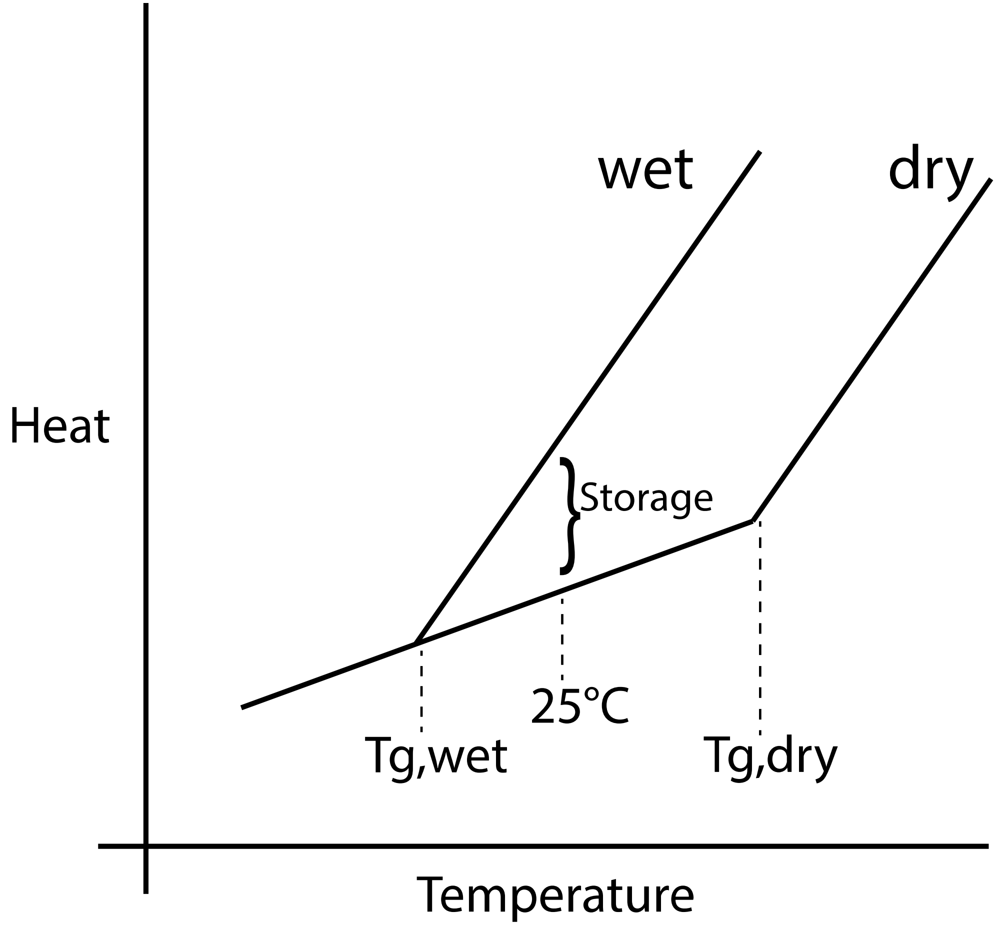




Tomko *et al.* *Nature Nanotechnology* **13**, 959 (2018)

Bio-based PCM derived by squid ring teeth protein

Plasticizing squid ring teeth (SRT) for on-demand, room temperature energy storage: modulating the glass transition temperature



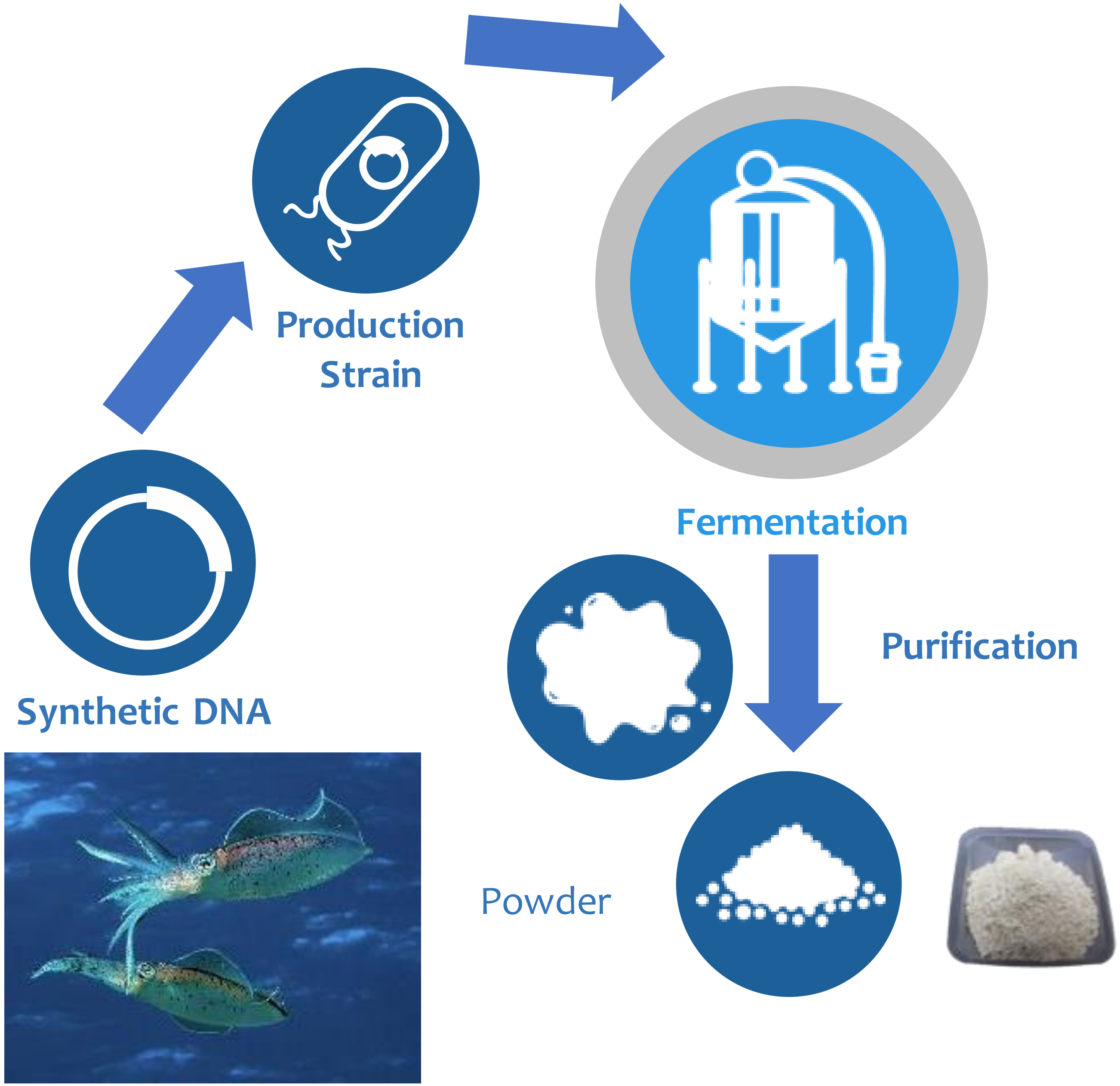
Tomko *et al.* *Nature Nanotechnology* **13**, 959 (2018)

Manufacturing bio-based SRT PCM

Tandem Repeat is creating
Bioderived
Tunable
Customizable
Self-healing
protein material inspired by squid structural proteins

TANDEM
REPEAT

www.tandemrepeat.com



Synthetic DNA

Production Strain

Fermentation

Purification

Powder

*Bio-based phase change materials based on SRT for thermal energy storage

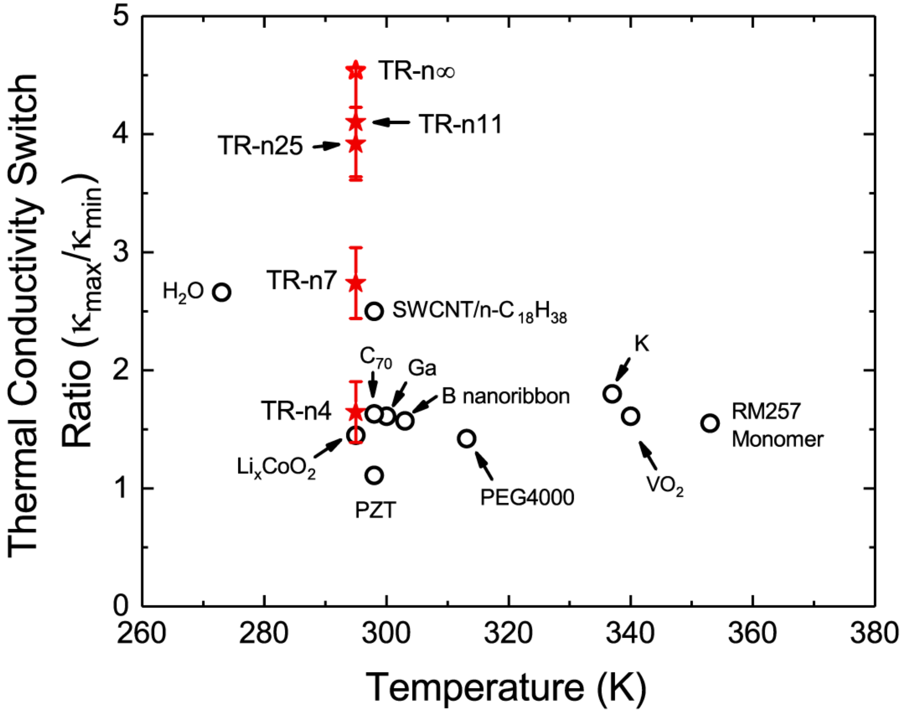
*Team of UVA, Ga Tech and Tandem Repeat currently investigating as part of DOE BTO BENEFIT program

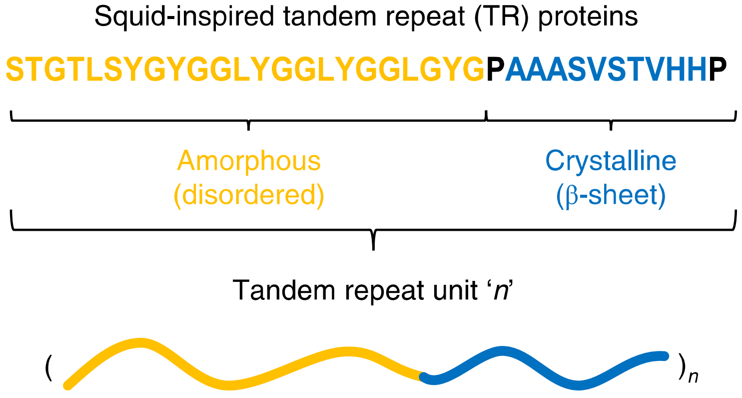
UNIVERSITY of VIRGINIA

SCHOOL of ENGINEERING
& APPLIED SCIENCE

TANDEM
REPEAT

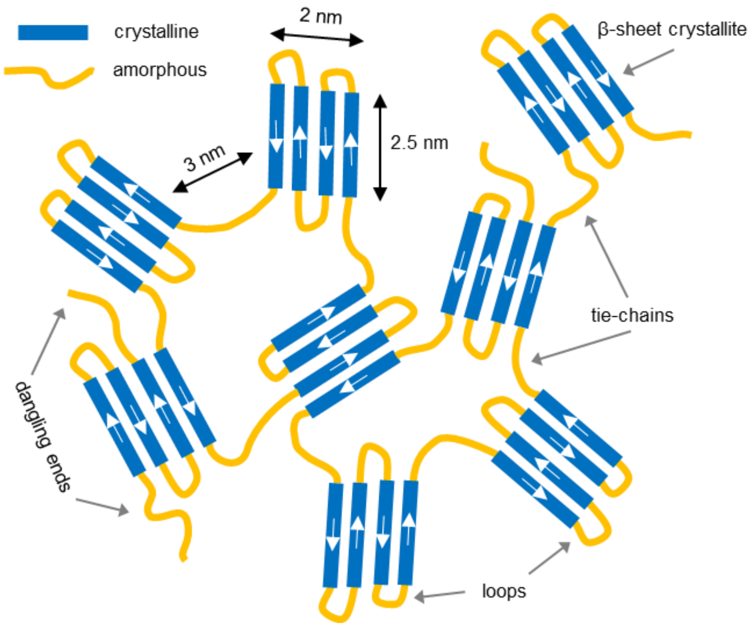
Georgia
Tech





Squid-inspired tandem repeat (TR) proteins

STGTLSYGYGGLYGGLYGGLGYG**P**AAASVSTVHH**P**



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TANDEM REPEAT

SCHOOL *of* ENGINEERING & APPLIED SCIENCE

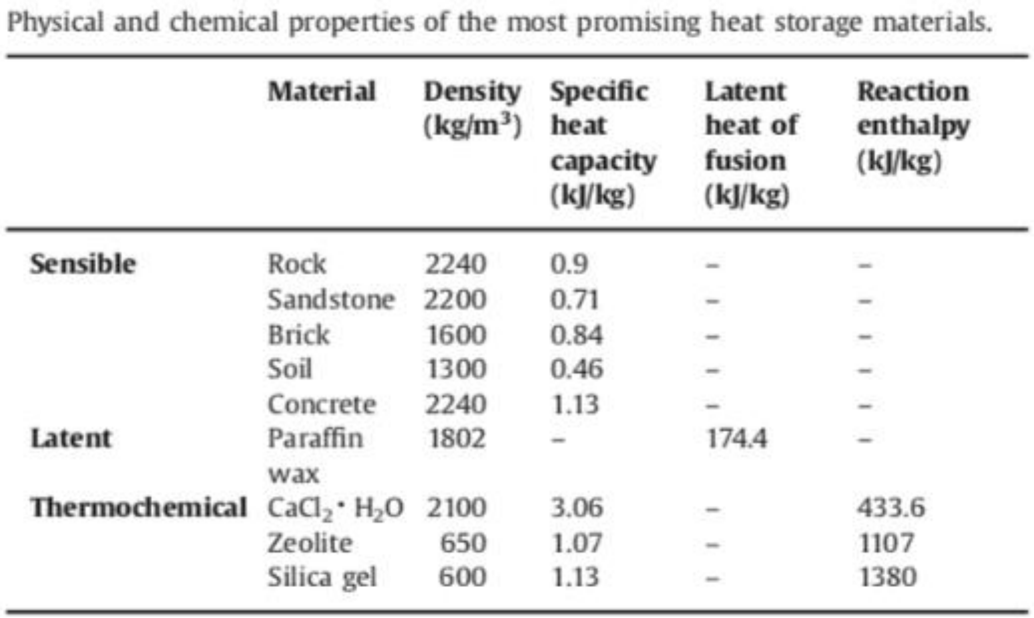
Georgia Tech

Thermochemical Energy Storage Materials

Sumanjeet Kaur

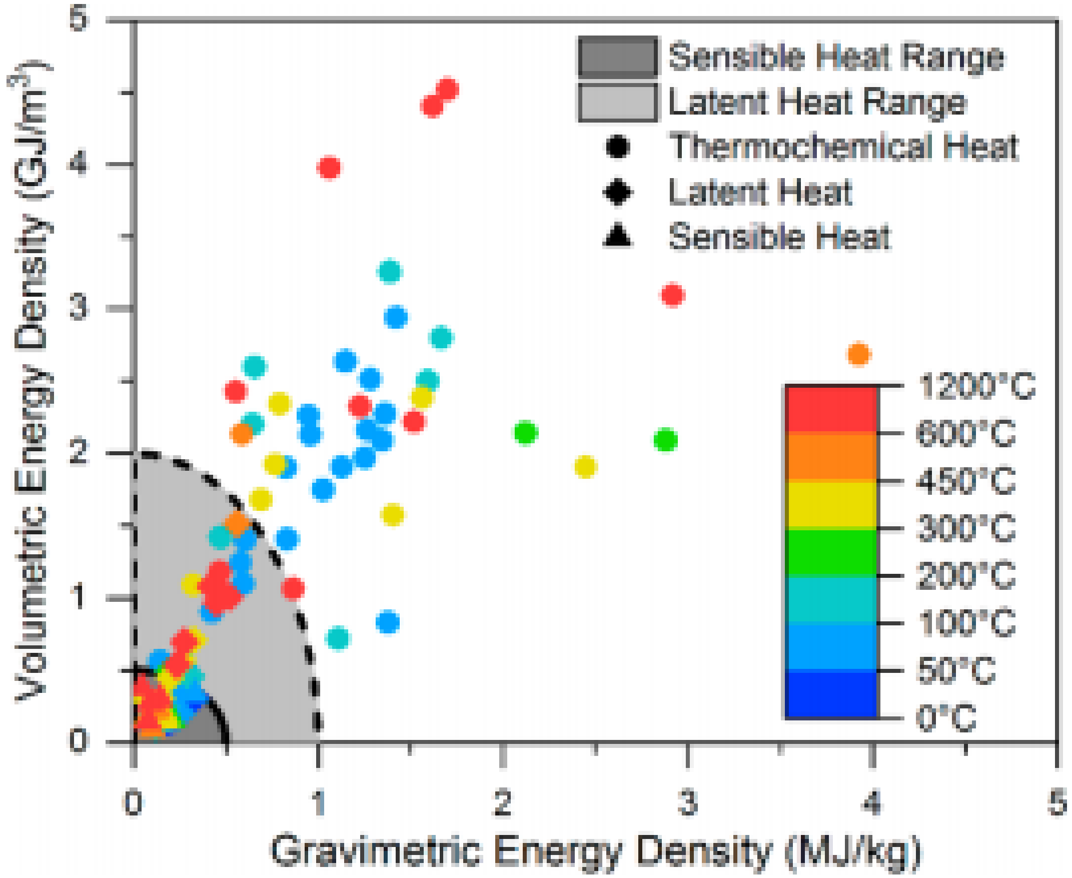
Thermal Energy Storage Materials

- ➢ Sensible heat
- ➢ Latent heat
- ➢ Thermochemical heat



Physical and chemical properties of the most promising heat storage materials.

	Material	Density (kg/m³)	Specific heat capacity (kJ/kg)	Latent heat of fusion (kJ/kg)	Reaction enthalpy (kJ/kg)
Sensible	Rock	2240	0.9	–	–
	Sandstone	2200	0.71	–	–
	Brick	1600	0.84	–	–
	Soil	1300	0.46	–	–
	Concrete	2240	1.13	–	–
Latent	Paraffin wax	1802	–	174.4	–
Thermochemical	$CaCl_2 \cdot H_2O$	2100	3.06	–	433.6
	Zeolite	650	1.07	–	1107
	Silica gel	600	1.13	–	1380

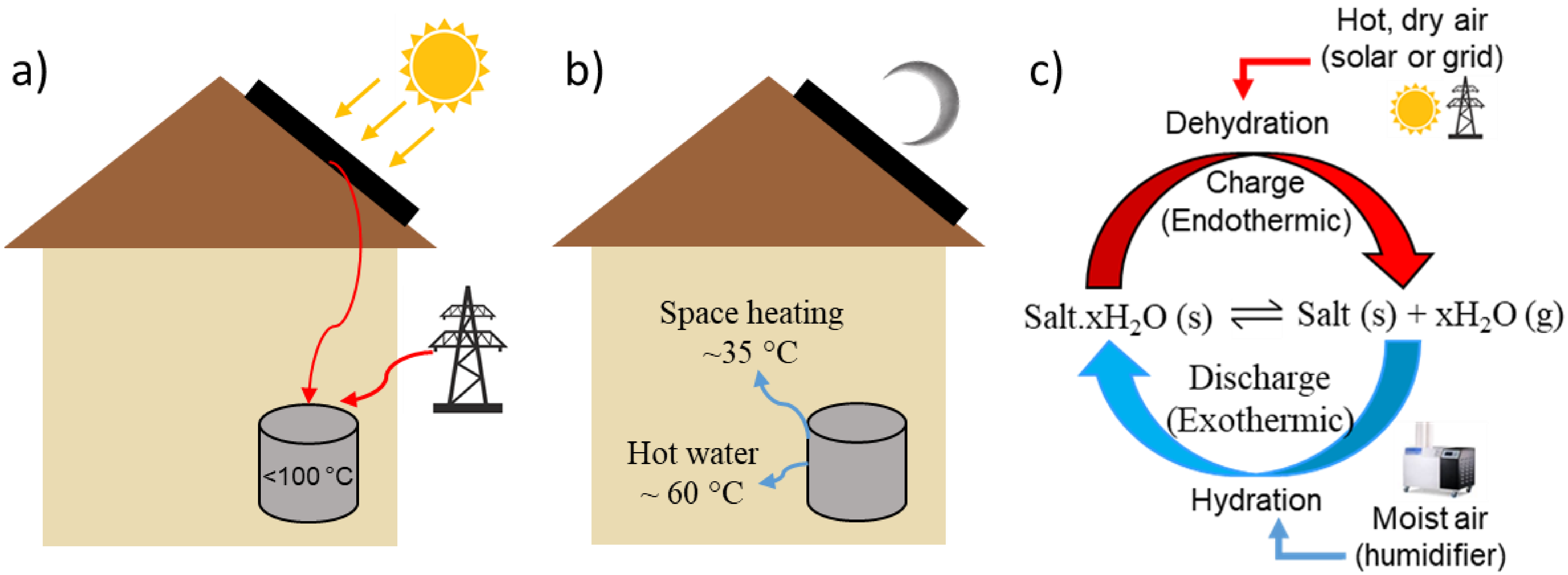


DOI: 10.1021/acs.chemmater.7b05230

Thermochemical materials (TCMs)

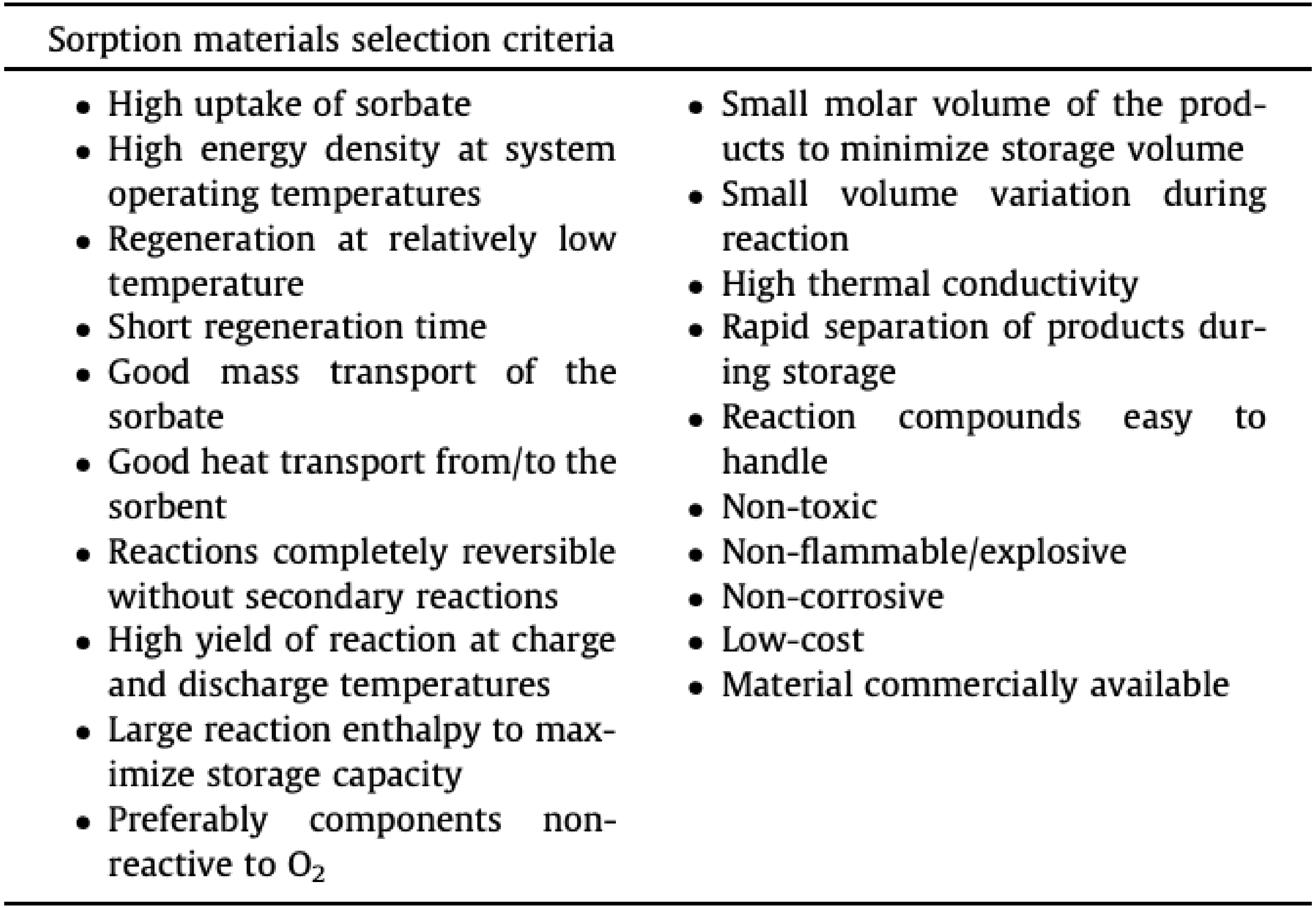
- TCMs have a fundamental advantage of significantly higher theoretical energy densities (200 to 600 kWh/m^3) than PCMs (50 - 150 kWh/m^3) because the energy is stored in reversible reactions.
- Depending upon the type of reaction, TCMs can be divided broadly into two categories: a**b**sorption materials (salt hydrates) or a**d**sorption (zeolites or silica gel).
- In a**b**sorption TCMs energy is stored or released by reversible solid-gas reaction (chemisorption) which involves breaking and restoring of strong bonds (such as covalent bonds) between the constituents throughout the bulk of the material, whereas in a**d**sorption TCMs the reversible reaction is based on weak van der Waals interactions between solid and gas (physiosorption) and is limited to the surface of the solid.
- Example of salt hydrates such as $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, and $CaCl_2 \cdot 6H_2O$. They charge and discharge by undergoing reversible dehydration and hydration reactions.

Thermochemical as energy storage



a) TCMs can be charged using solar energy or grid electricity. b) Energy stored in TCM can be discharged at desired T for thermal end-uses. c) Reversible solid-gas reactions (salt hydrate) in an open system.

Thermochemical Materials for Buildings



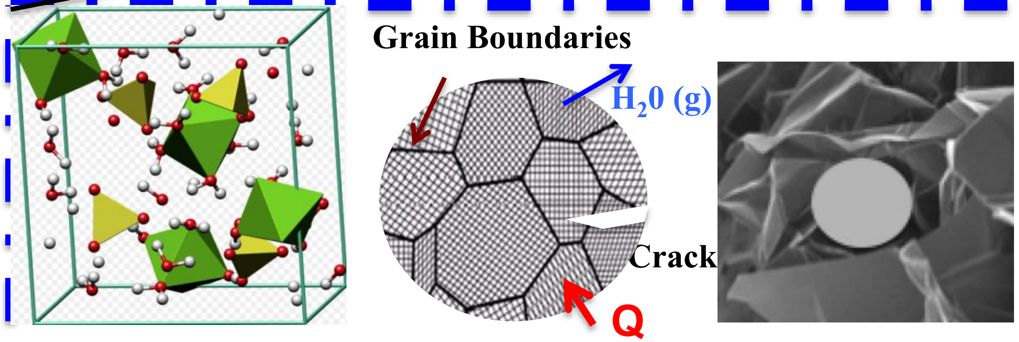
Sorption materials selection criteria

- High uptake of sorbate
- High energy density at system operating temperatures
- Regeneration at relatively low temperature
- Short regeneration time
- Good mass transport of the sorbate
- Good heat transport from/to the sorbent
- Reactions completely reversible without secondary reactions
- High yield of reaction at charge and discharge temperatures
- Large reaction enthalpy to maximize storage capacity
- Preferably components non-reactive to O_2
- Small molar volume of the products to minimize storage volume
- Small volume variation during reaction
- High thermal conductivity
- Rapid separation of products during storage
- Reaction compounds easy to handle
- Non-toxic
- Non-flammable/explosive
- Non-corrosive
- Low-cost
- Material commercially available

http://dx.doi.org/10.1016/j.apenergy.2016.12.148

Challenges: Molecular, Particle and Composite Level

Material Level



Molecular level
defines max theoretical energy density and stability zones of various phases.

Challenge:
-unstable phases under operating conditions

Particle Level
defines heat/mass transport, and structural stability of the salt particle.

Challenge:
- pulverization, melting, agglomeration, deliquescence,

Composite level
define salt loading, % porosity, heat/ mass transport and structural stability under cycling.

Challenge:
-low energy density, poor mechanical strength, poor multi-cycle efficiency

At the *__material level__**, the greatest challenge is the* ***stability of the salt hydrate****.*

- *structural and volumetric changes*
- *slow reaction kinetics,*
- *high hygroscopicity of salt hydrates under operating conditions*

Challenges

- Structural changes, for example, from crystalline to amorphous reduce the water capacity of the hydrate and the salt energy density.
- Similarly, large volume changes during hydration and dehydration could lead to crack formation
- Heat and Mass Flux :

  During the dehydration step, higher heat flux could result in incongruent melting of salt hydrate if the heat transport at material level happens faster than the mass transport (i.e. if water vapor cannot escape quickly enough from the material).

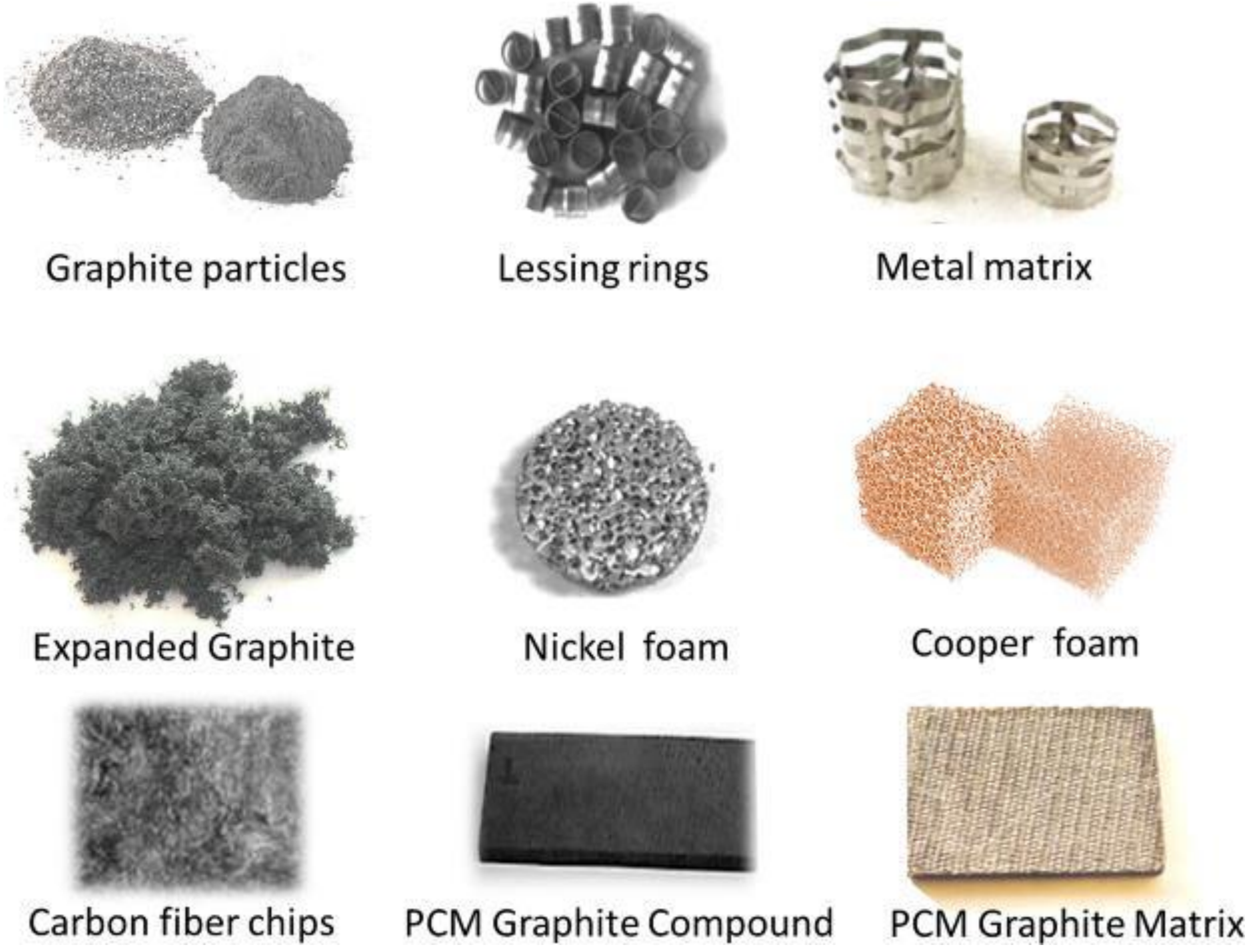
  Since this is a solid-gas reaction, the formation of any liquid phase of the salt (melting/deliquescence) is undesirable as it leads to salt leakage and agglomeration, structural modifications, and renders the material inactive.

Challenges-Composite

Like phase change materials, researchers are exploring salt hydrates impregnation into a host matrix (composite TCMs) to improve heat and mass transport and prevent agglomeration of the salt.

Challenges:

- ➢ Lower energy density
- ➢ Low mechanical strength (disintegration of the composite)
- ➢ Poor multi-cycle efficiency



Commonly added materials to phase change materials (PCMs). https://doi.org/10.1002/est2.127

Challenges (Reactor Level)

<u>At the reactor level</u> the major challenges are ***poor mass and thermal transport and structural integrity in a packed bed of particles***.

- Material-level problems are exacerbated when salt hydrates or composite TCMs are compacted as packed beds in a thermochemical reactor as non-uniformity in the packed beds becomes a major hindrance to the both mass and heat transport.
- Sub-optimal design of the packed bed reactor can also lead to non-uniform heat and mass transport (chemical reaction) which in turn leads to localized hotspots on the particle, creating additional mechanical stress and meta-stable/unstable phases.

Possible Solutions

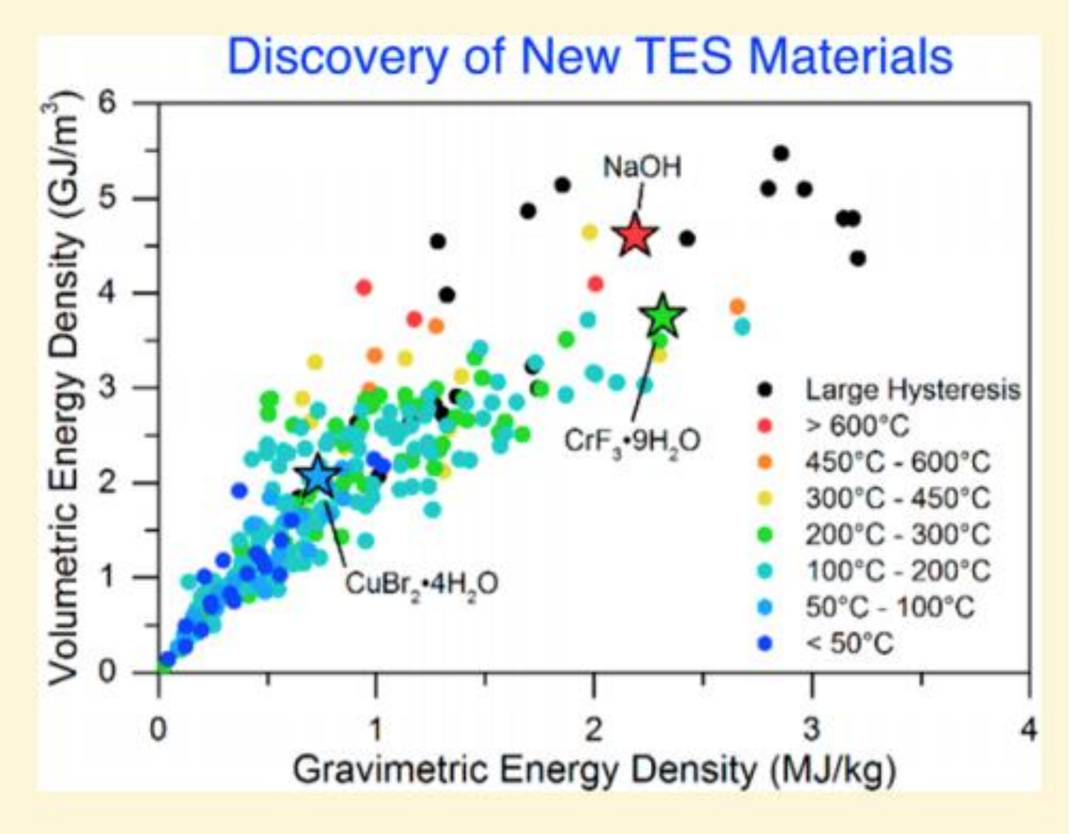
A) Perform simultaneous optimization of chemical, mechanical, and thermal (***CMT***) behavior of TCMs using multi-scale (materials to reactor) modeling and experimentation to achieve specific goals:

1. high reactor-level energy density
2. high cyclic efficiency
3. thermal conductivity >1 W/m-K

B) Material discovery for new TCM.

265 hydration reactions were characterized by high throughput DFT calculations.

- Several new high-energy density reactions
- Reactions for low, medium and high T



DOI: 10.1021/acs.chemmater.7b05230

MATERIALS SCIENCE & ENGINEERING
TEXAS A&M UNIVERSITY

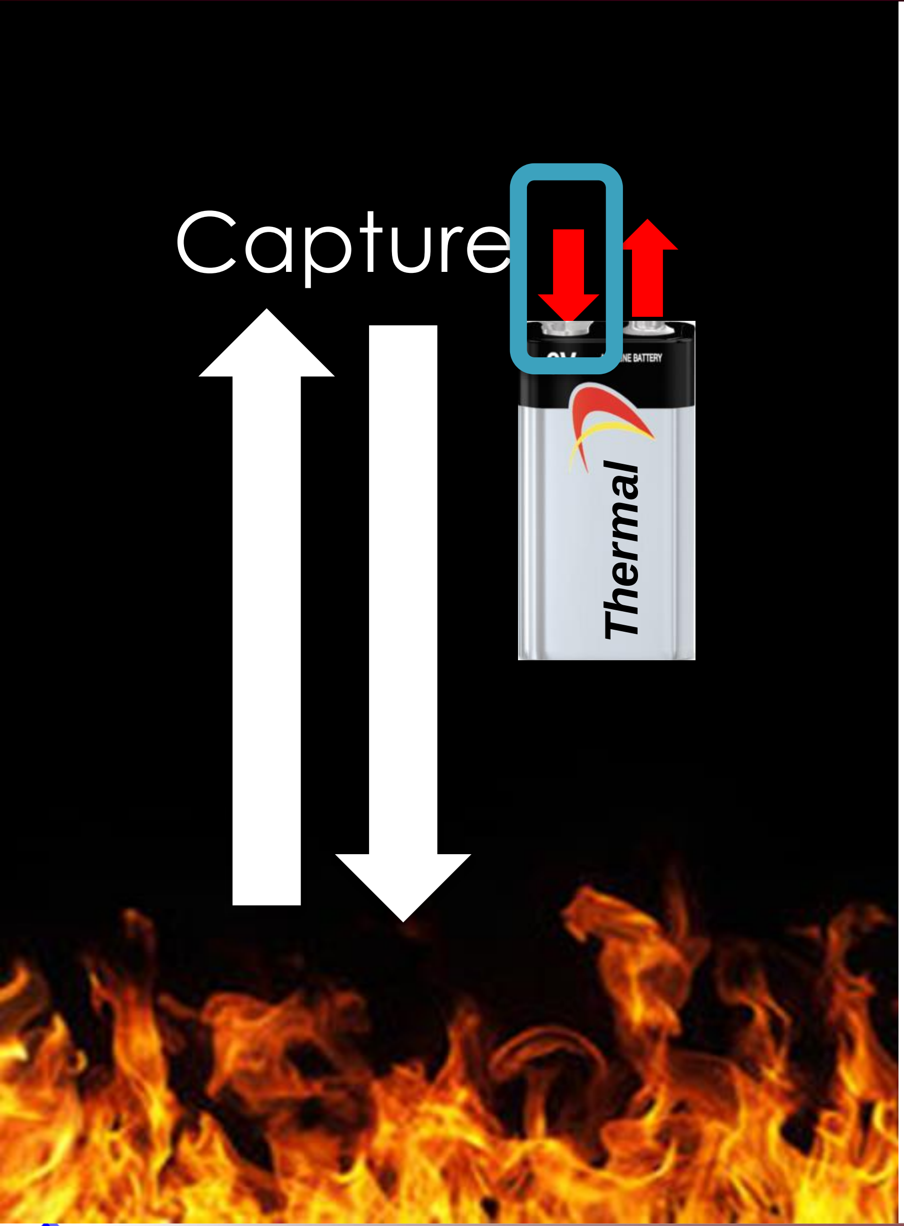
Design of Engineered Thermal Energy Storage Materials

P.J. Shamberger [1]

[1] *Dept. of Materials Science and Eng.*, Texas A&M University, College Station, TX, USA.

PHATE

The Rate Problem: How quickly can a material "store" heat?

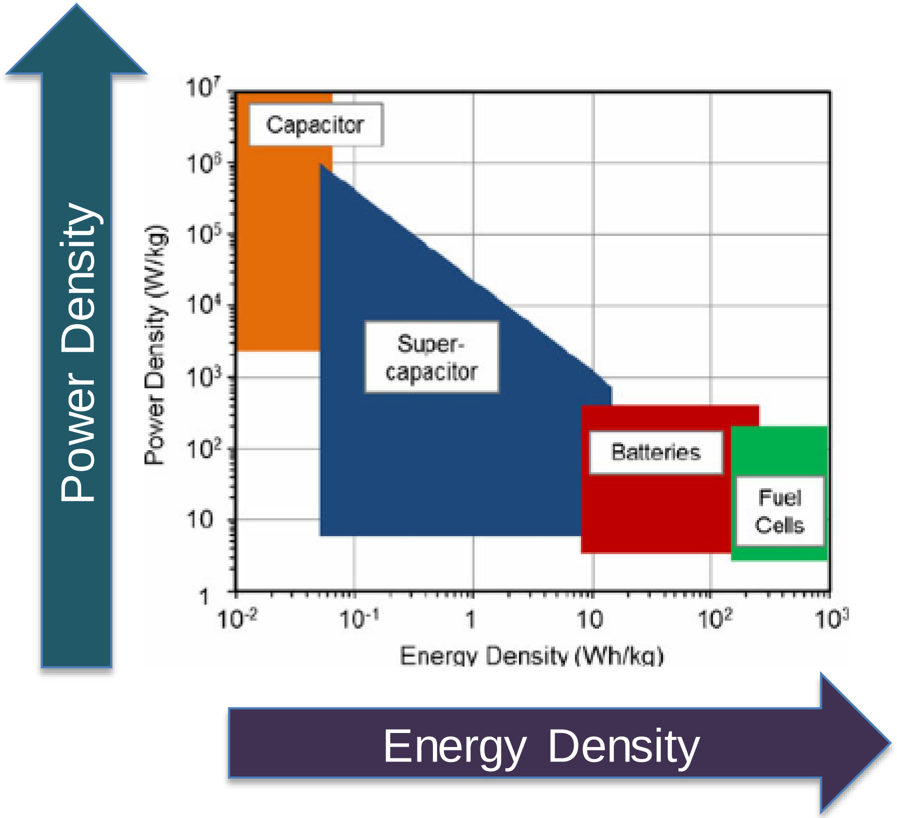


Analog:

How much power can your battery absorb/release?

Development of Cooling Power Figure of Merit

Electrical



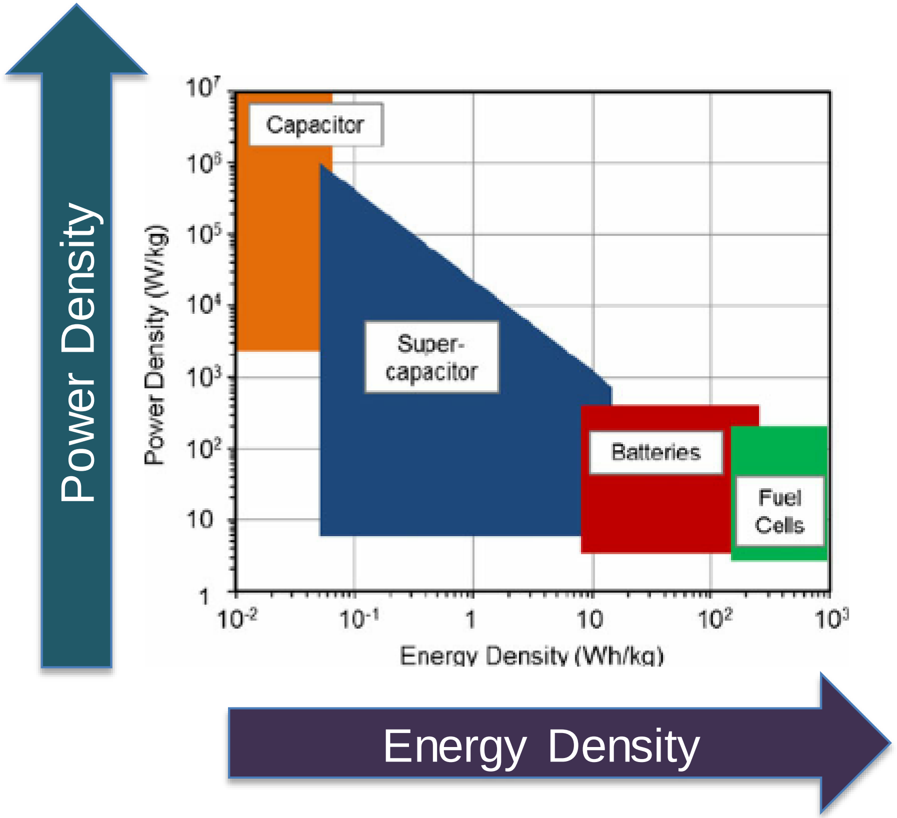
Thermal

?

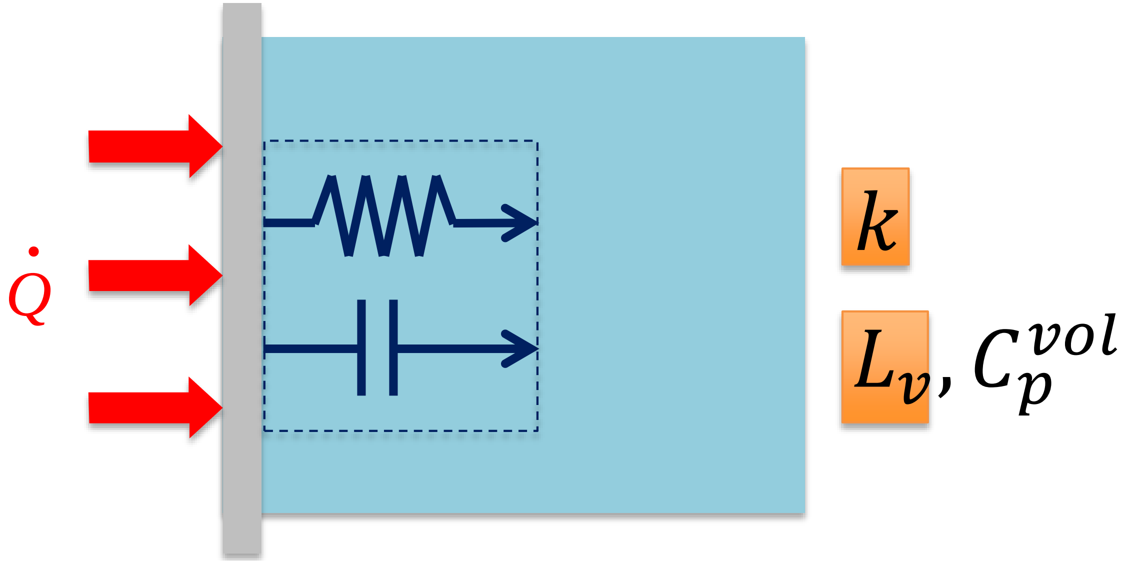
- How do we understand these tradeoffs for thermal energy storage?
- What is **the optimal material** for a particular application?

Development of Cooling Power Figure of Merit

Electrical



Thermal

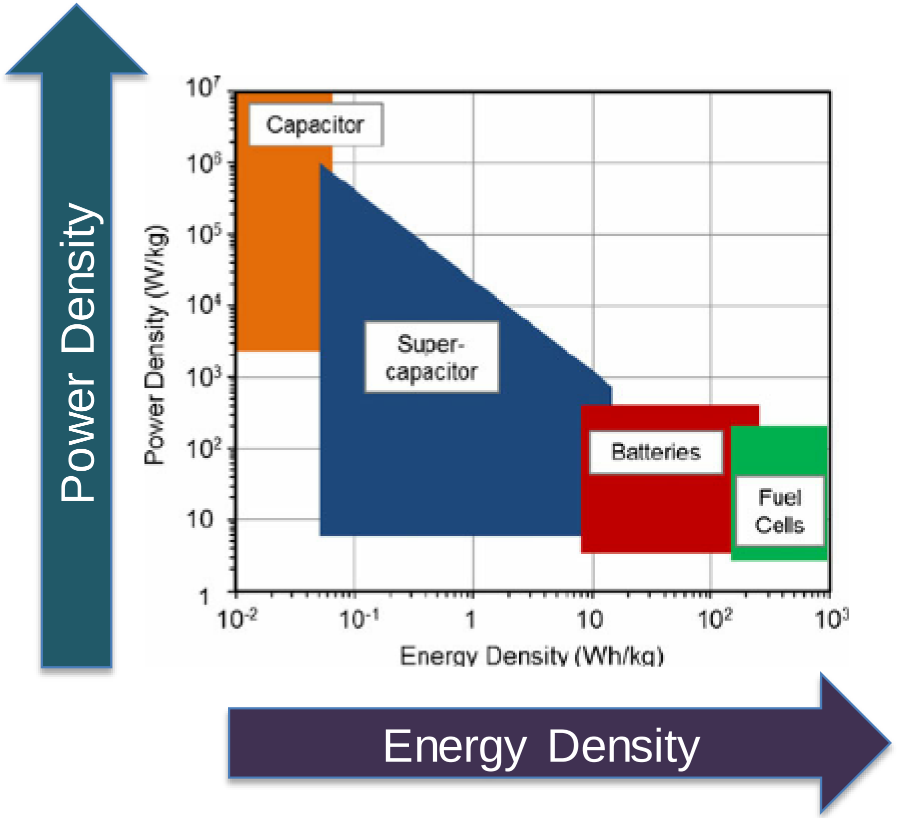


- Evaluate at the material level

Shamberger, P. J. (2016). Cooling capacity figure of merit for phase change materials. *Journal of Heat Transfer*, *138*(2).

Development of Cooling Power Figure of Merit

Electrical



Thermal

- Constant T B.C. (exact Neumann solution)

$$q''(0,t) = \frac{(T_\mathrm{w} - T_\mathrm{m})}{\sqrt{t}} \cdot \frac{1}{\sqrt{\pi}\ \mathrm{erf}(\lambda)} \cdot \frac{k_\mathrm{l}}{\sqrt{\alpha_\mathrm{l}}}$$

$$\eta_q \sim \frac{k_l}{\sqrt{\alpha_l}\sqrt{St_l}} = \sqrt{k_l \rho_l L_w} = \sqrt{k_l L_v}$$

P.J. Shamberger, Cooling capacity figure of merit for phase change materials. *Journal of Heat Transfer*, *138*(2), (2016) 024502.

- Constant q" B.C. (quasi-steady state appx.)

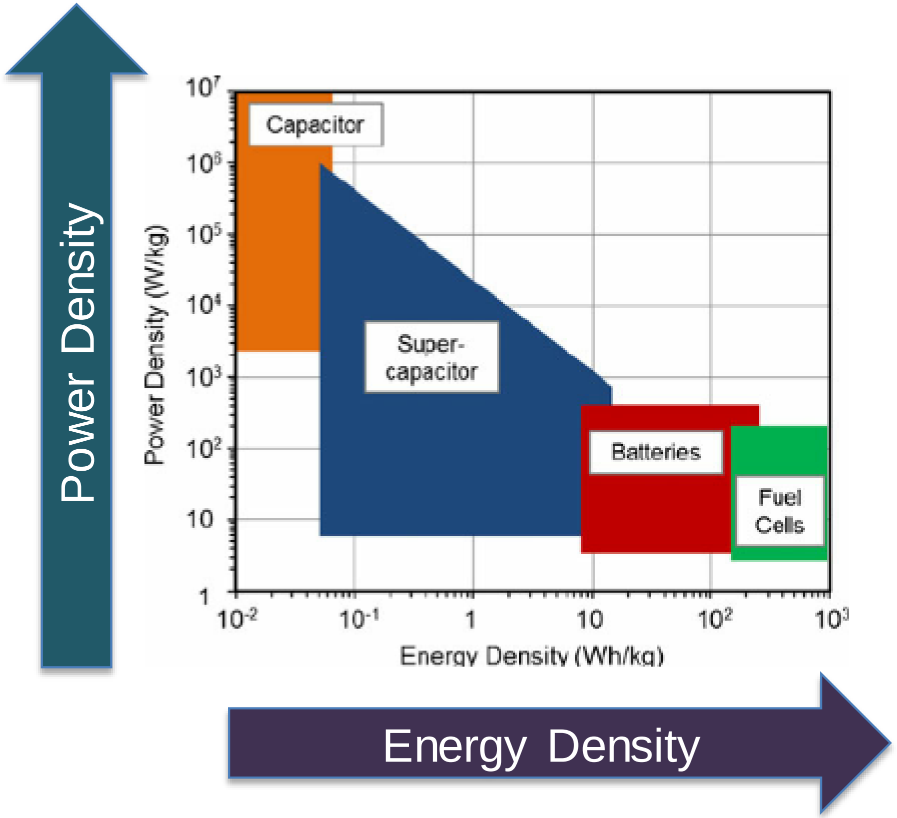
$$T_\mathrm{l}(x,t) = T_\mathrm{m} - \frac{q_0''}{k_\mathrm{l}}\left\{x - \frac{q_0'' t}{L_\mathrm{v}}\right\},\ x \le \delta(t),$$

$$\Delta T(t) = \frac{(q_0'')^2}{k_\mathrm{l} L_\mathrm{v}} t.$$

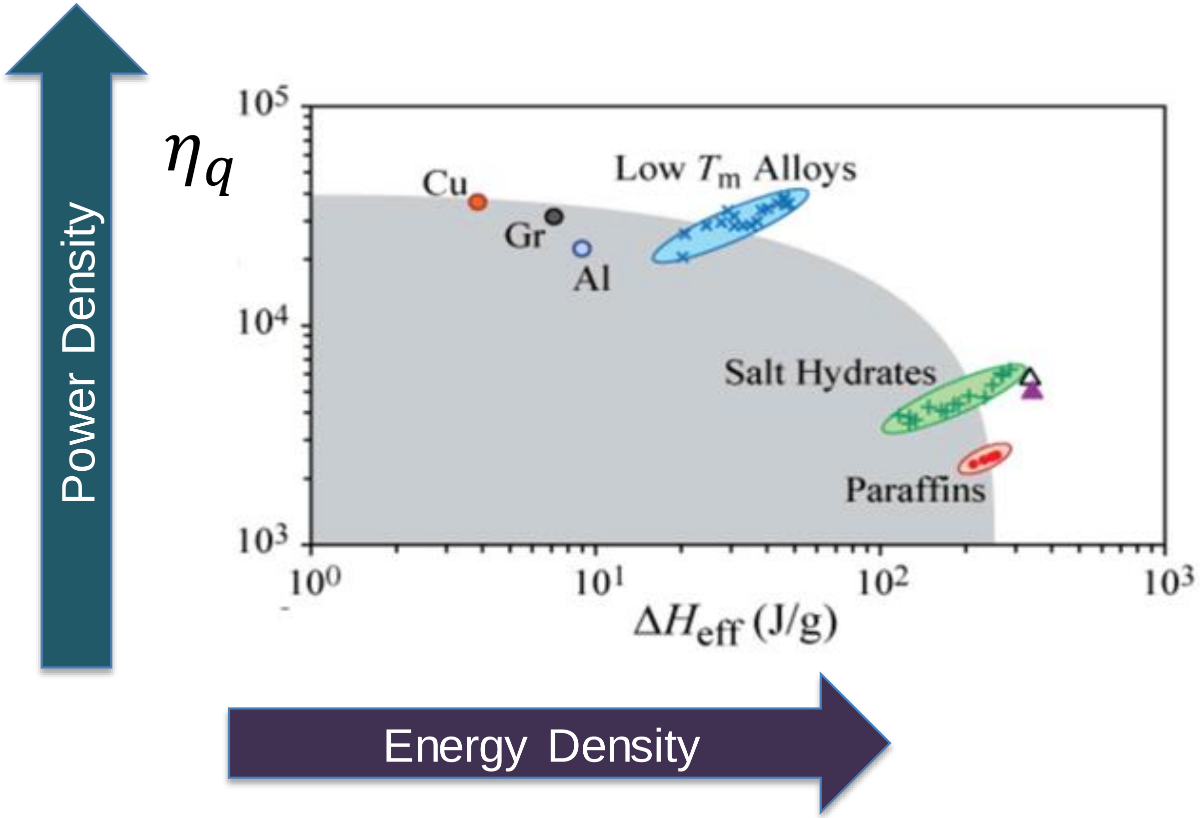
T. Lu, Thermal management of high power electronics with phase change cooling, *Int. J. Heat Mass Trans*. 43 (2000) 2245–2256.

Development of Cooling Power Figure of Merit

Electrical



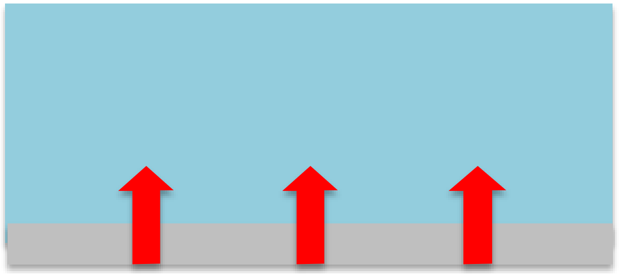
Thermal

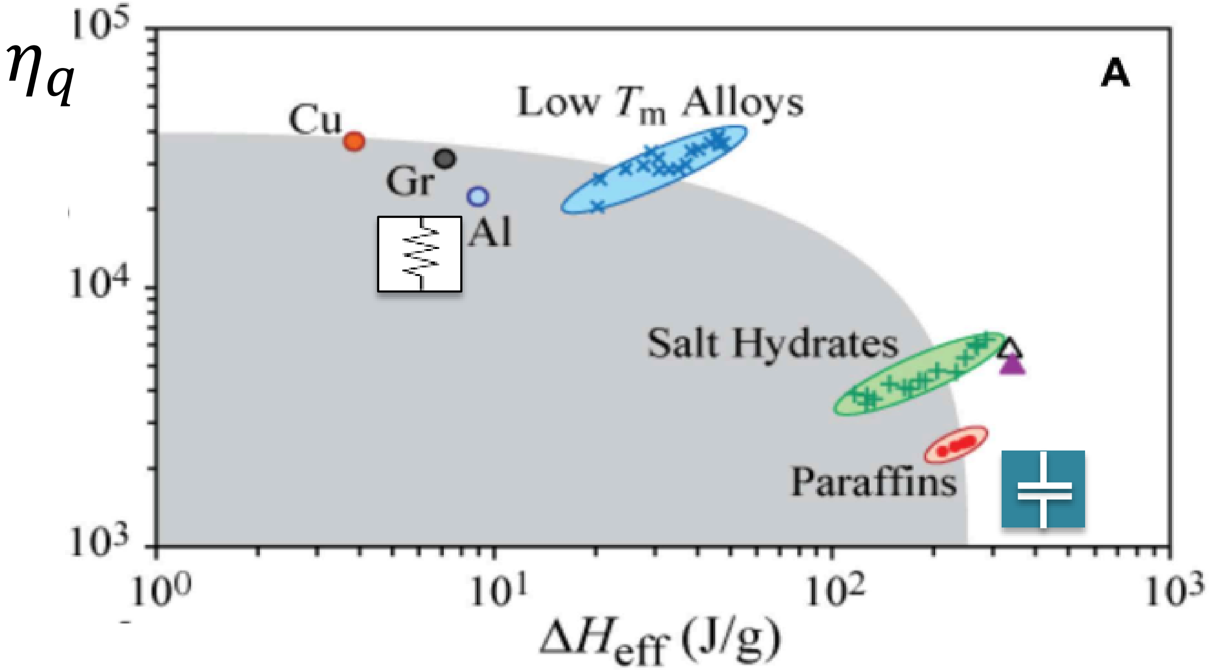


- Under limiting conditions, η_q is proportional to a material's ability to absorb heat.

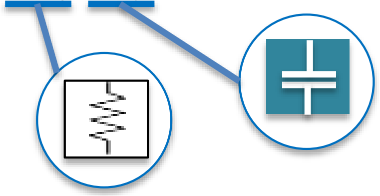
K. Yazawa, P.J. Shamberger, T. Fisher., *Frontiers in Mech. Eng.*, **5**, 29 (2019). doi: 10.3389/fmech.2019.00029

Design of Homogeneous Composites from Figures of Merit





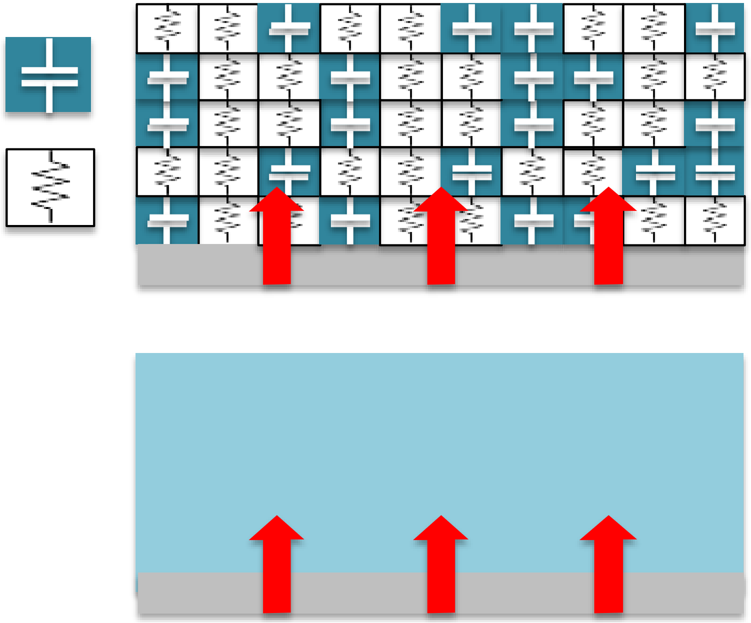
$$\eta_q \sim \sqrt{\underline{k_l}\,\underline{L_v}}$$

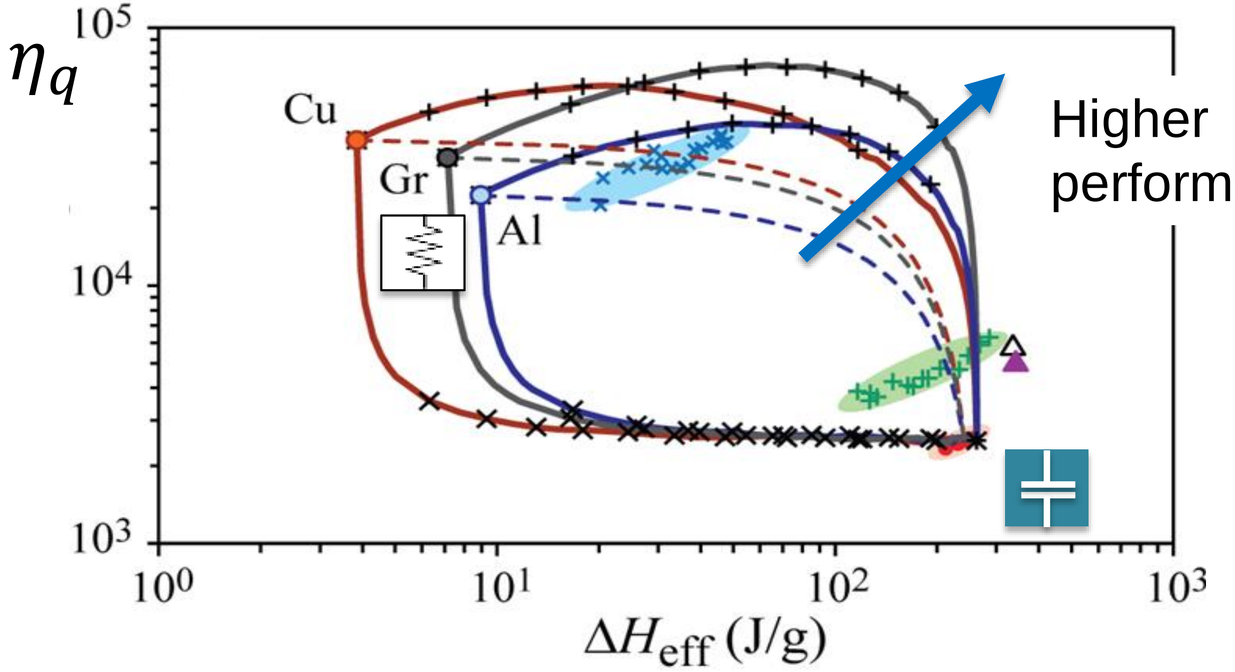


P.J. Shamberger, *J. of Heat Transfer*, **138**(2), 024502 1-7 (2016). doi: 10.1115/1.4031252

K. Yazawa, P.J. Shamberger, T. Fisher., *Frontiers in Mech. Eng.*, **5**, 29 (2019). doi: 10.3389/fmech.2019.00029

Design of Homogeneous Composites from Figures of Merit



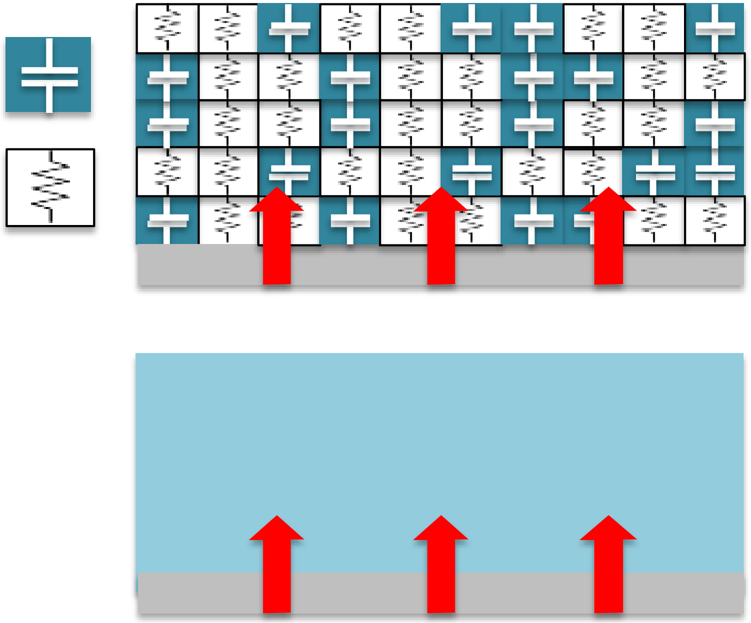


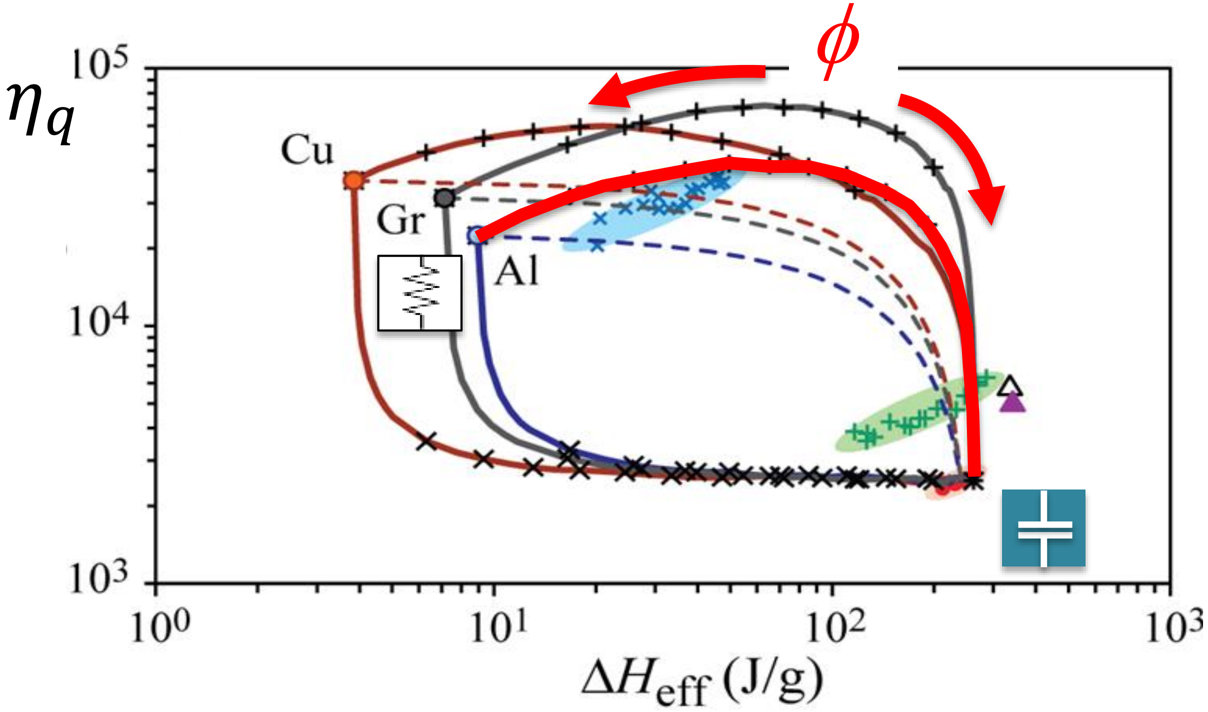
Higher performance

- Treat these systems as homogeneous composites (with effective properties)
- Generally can out-perform single-phase systems.

P.J. Shamberger, T. Fisher., *Int. J. Heat Mass Transfer*, ***117***, 1205-1215 (2018).

Design of Homogeneous Composites from Figures of Merit





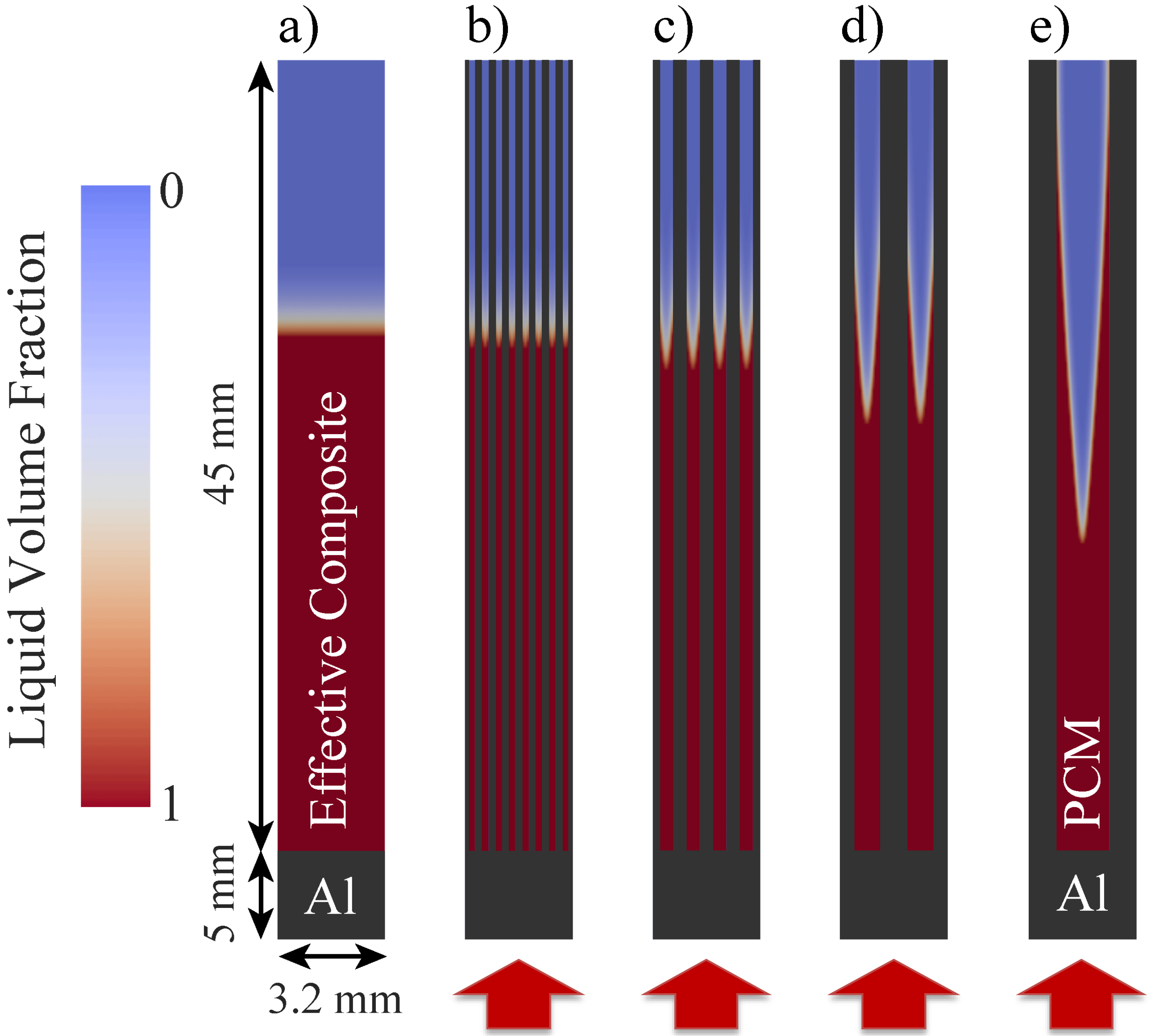
- Interrogate trade-offs & materials design space.

P.J. Shamberger, T. Fisher., *Int. J. Heat Mass Transfer*, ***117***, 1205-1215 (2018).

1. Treating lamellar composites as a homogeneous medium
   - **When** can this approximation be applied?
   - **How well** does it work?

2. ‘Optimal’ composites (beyond η_q)

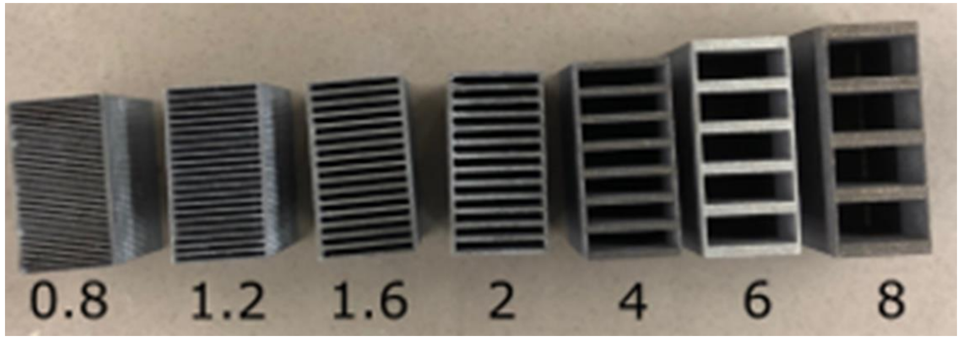
Critical lengthscale.



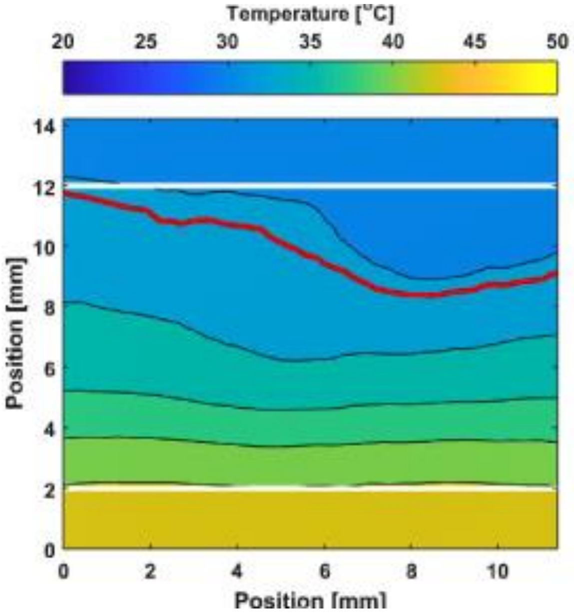
Consequence: below a critical thickness *f*(*t*, *L*), system can be treated as a composite material with effective properties.

A. Hoe*, M. Deckard*, A. Tamraparni, A. Elwany, J. Felts, P.J. Shamberger. Conductive heat transfer in lamellar phase change material composites, Applied Thermal Engineering 178 (2020) 115553.

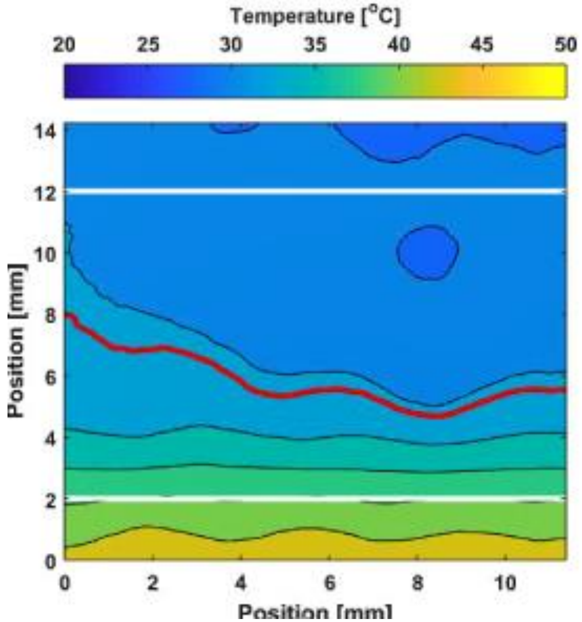
Effect of pitch on temperature distribution



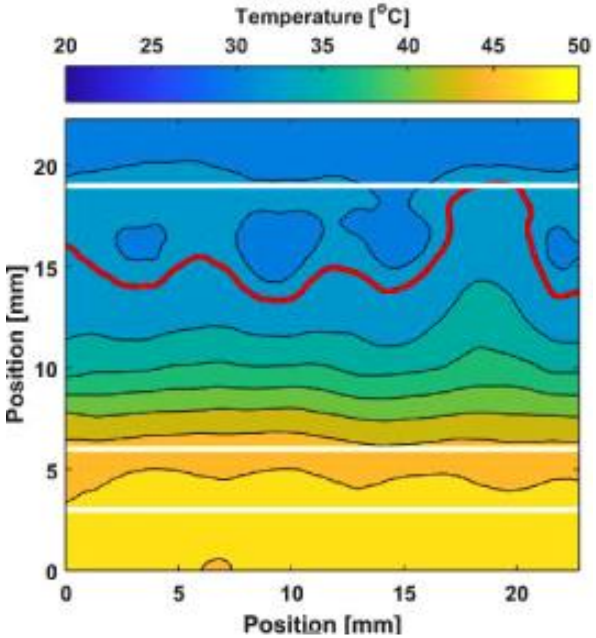
2 mm



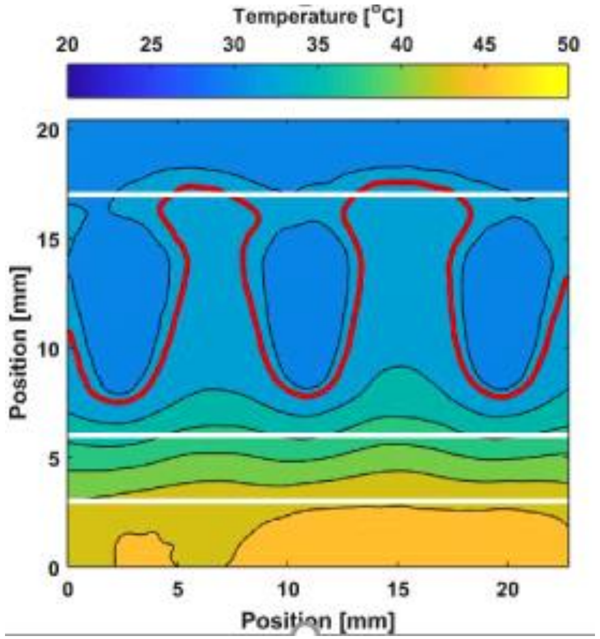
4 mm



6 mm

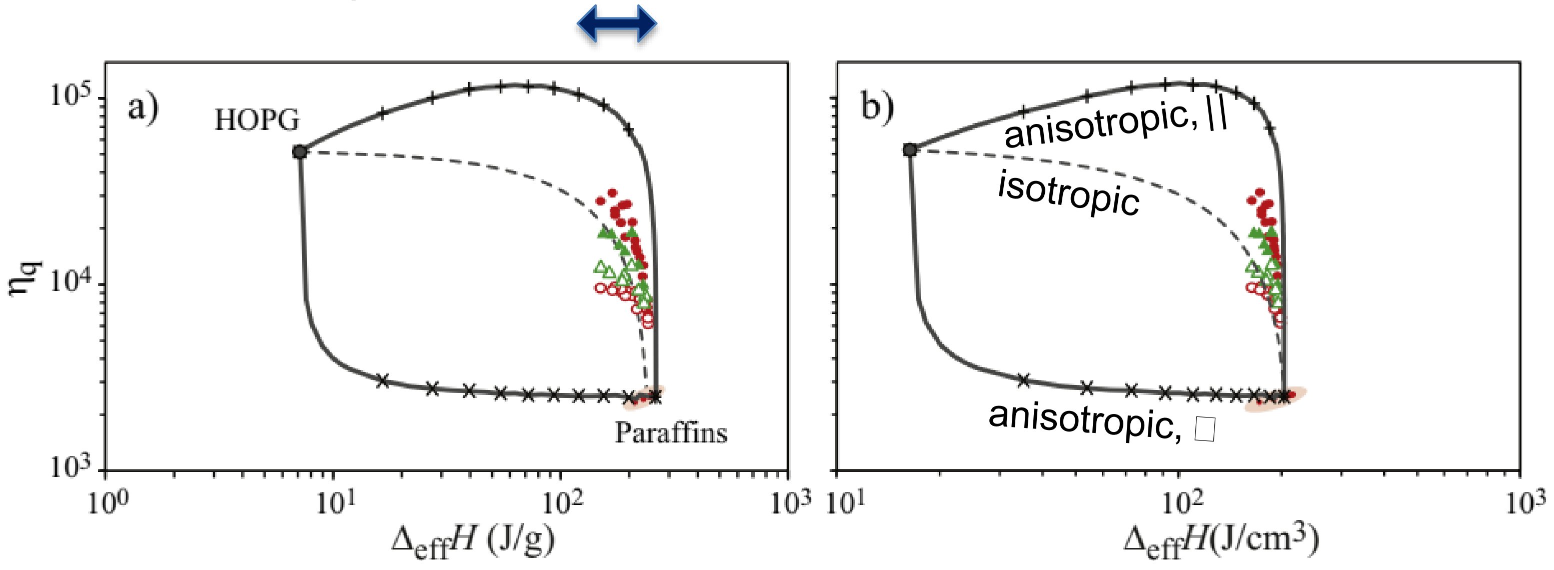


8 mm

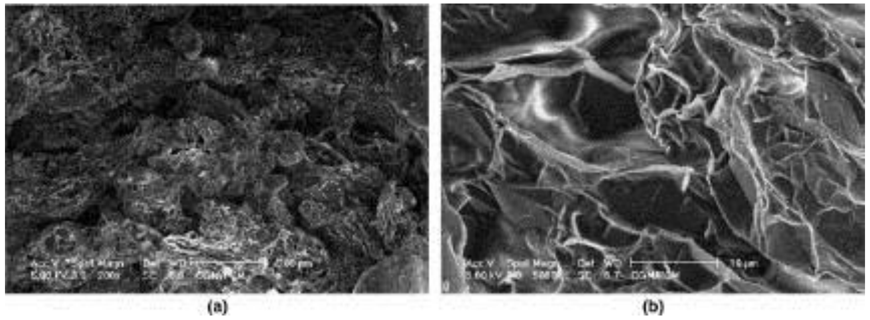


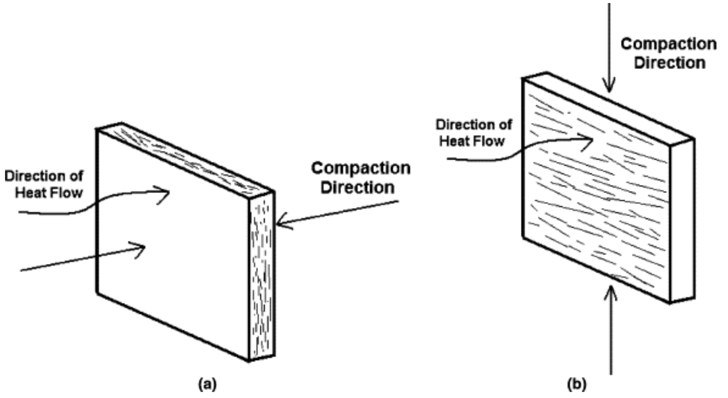
PCM intercalated Foams/Compressed graphite (CENG)

- ϕ controlled by compression.



Paraffin + CENG





Shamberger, P. J., & Fisher, T. S. (2018). Cooling power and characteristic times of composite heatsinks and insulants. *International Journal of Heat and Mass Transfer*, *117*, 1205-1215.

X. Py, R. Olives, S. Mauran. 44 (2001) 2727–2737.
A. Mills, M. Farid, J. Selman, S. Al-Hallaj, Appl. Therm. Eng. 26 (2006) 1652–1661.

1. Treating lamellar composites as a homogeneous medium

2. ‘Optimal’ composites (beyond η_q)
    - Application to heat extraction from a tube
    - What does the **optimal** composite look like?
    - (it depends. On t, ΔT, r_0, …)

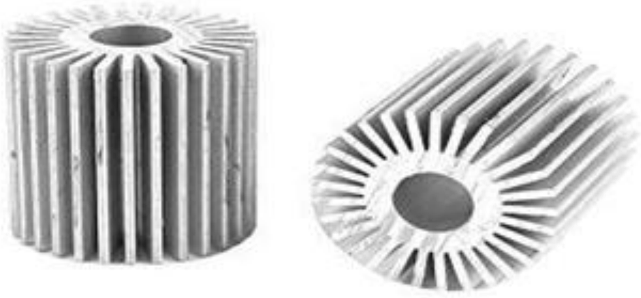
Application of Reduced Order models to TES Design

1 DOF

Performance Curves (single DOF)

multiple DOF

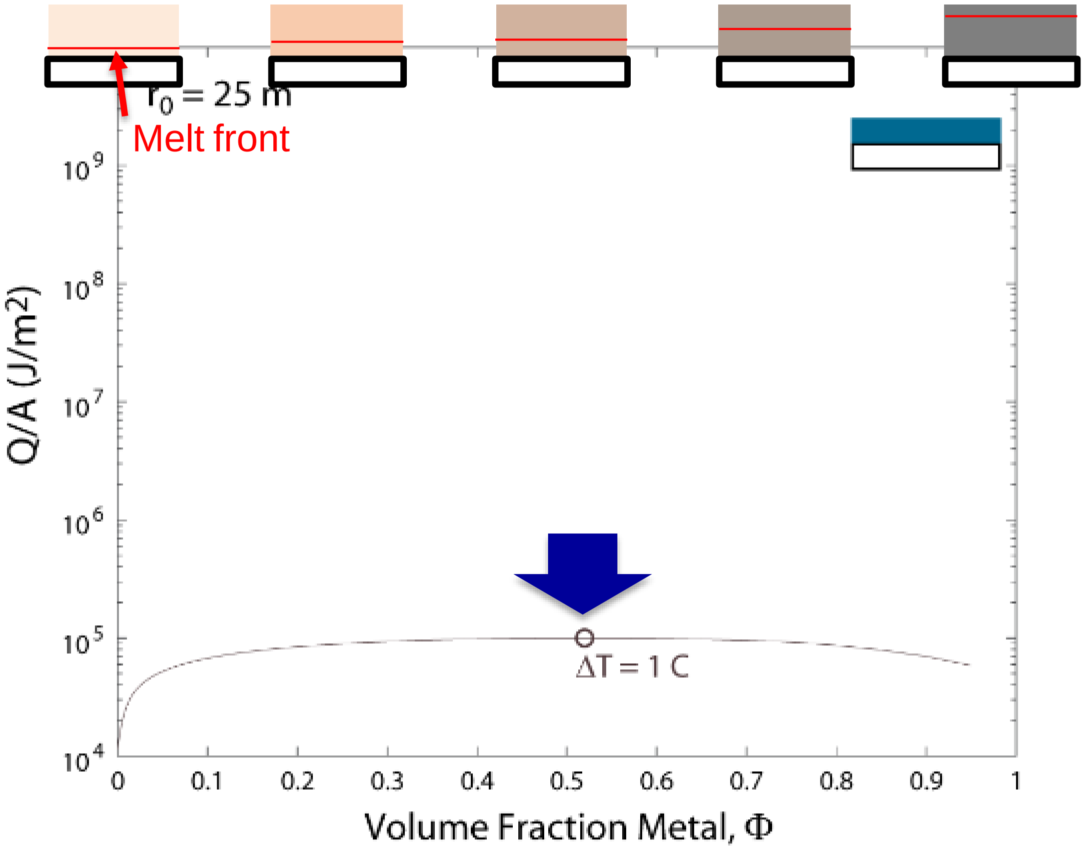
Efficient Optimal Design Approach (multiple DOF)



A. Hoe*, A. Easley, M. Deckard*, J. Felts, P.J. Shamberger, 19th IEEE Intersoc. Conf. on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm, 2020).

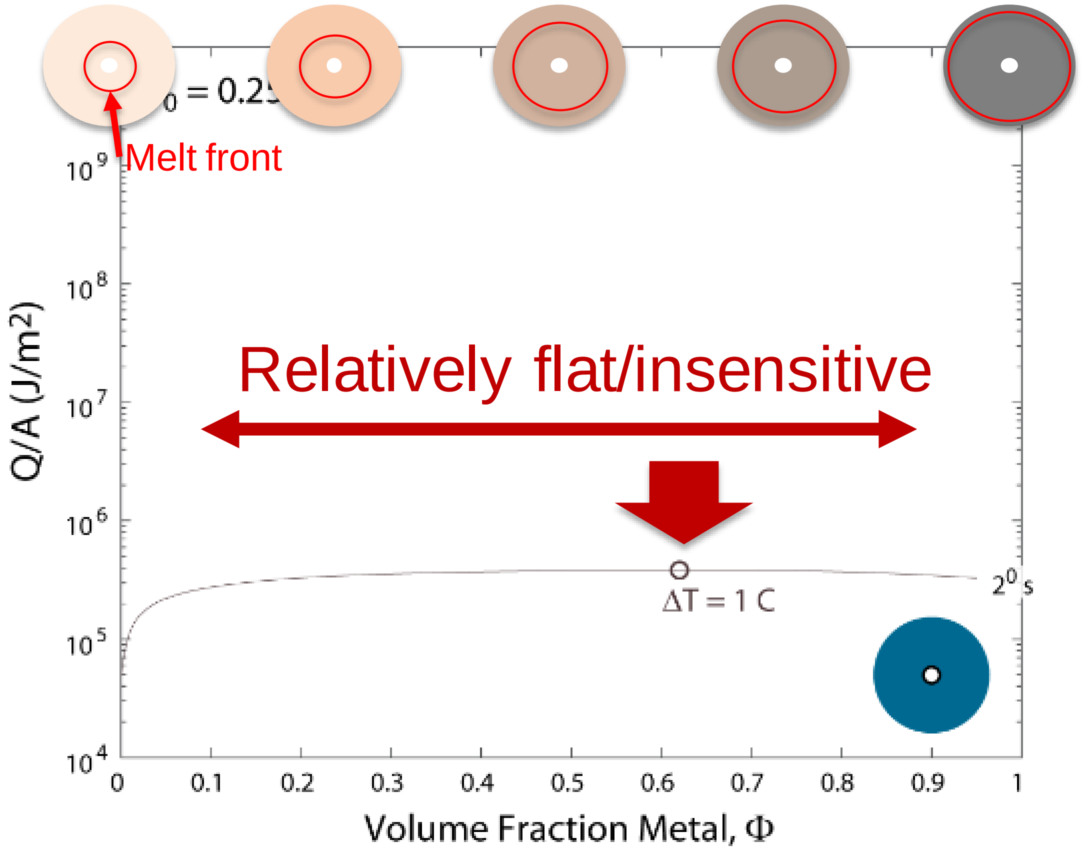
Effect of Volume Fraction on Q/A

- Larger ϕ, melt front penetrates farther.
- Relatively **flat/insensitive** at optimum



Pure PCM

Pure Meta

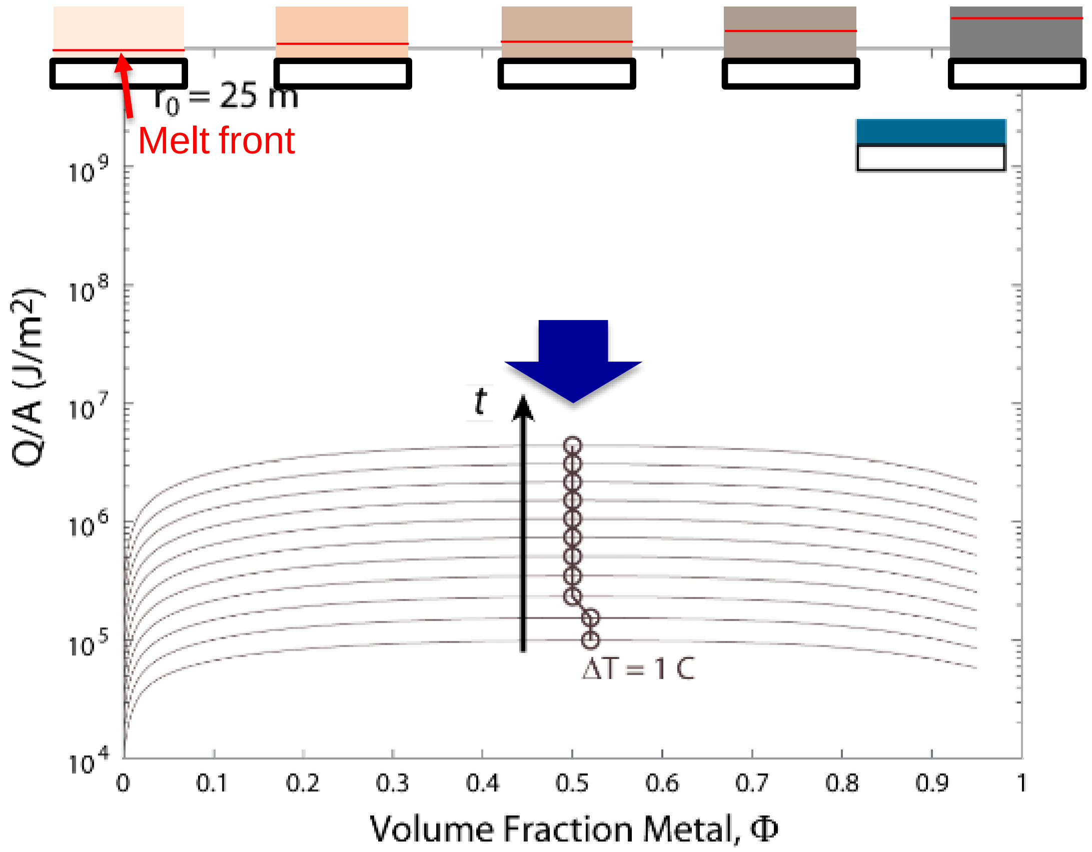


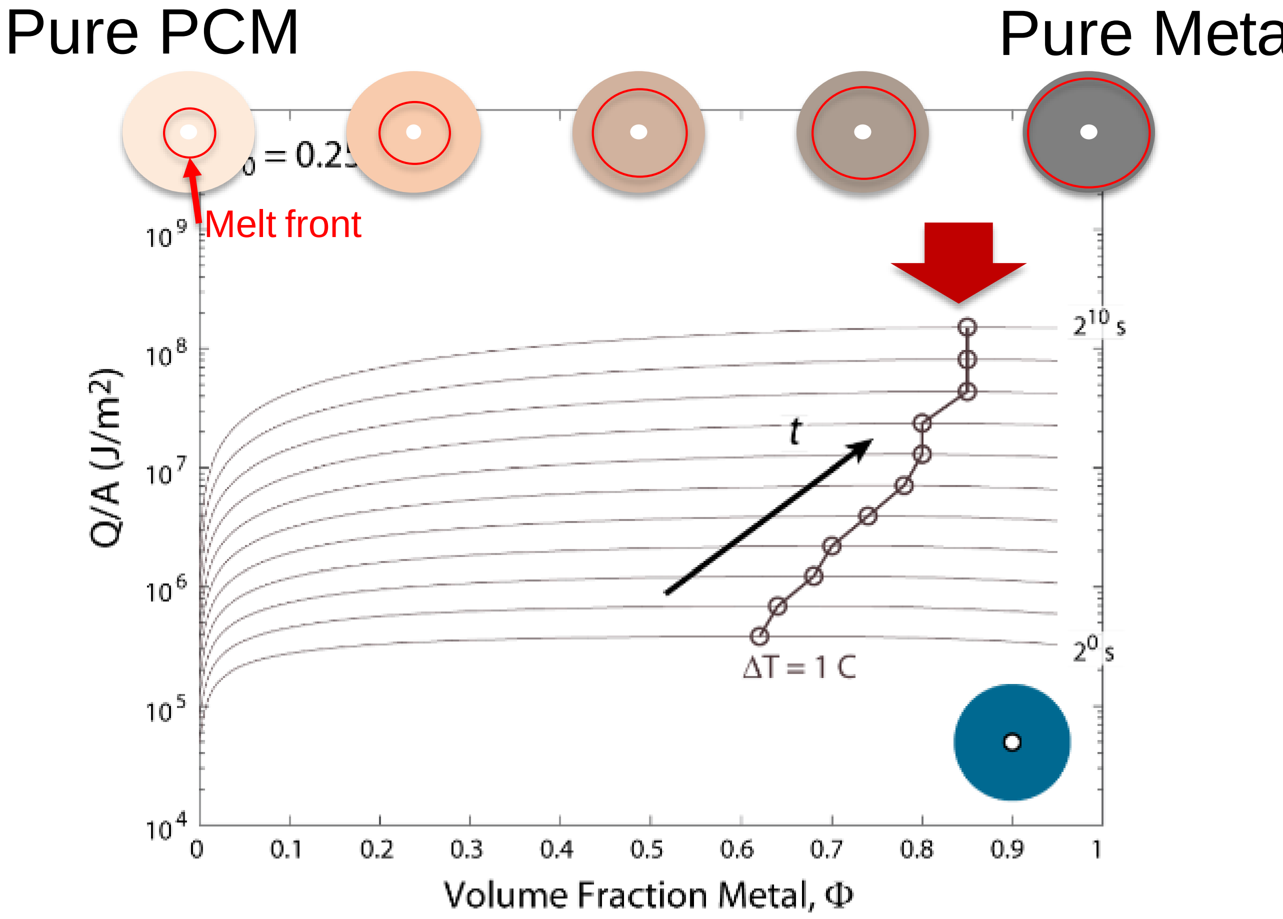
Relatively flat/insensitive

A. Hoe*, M. Deckard*, J. Felts, P.J. Shamberger, 19th IEEE Intersoc. Conf. on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm, 2020).

Effect of time on Q/A

- At longer *t*, geometric spreading in cylindrical geometry, as melt front penetrates farther.

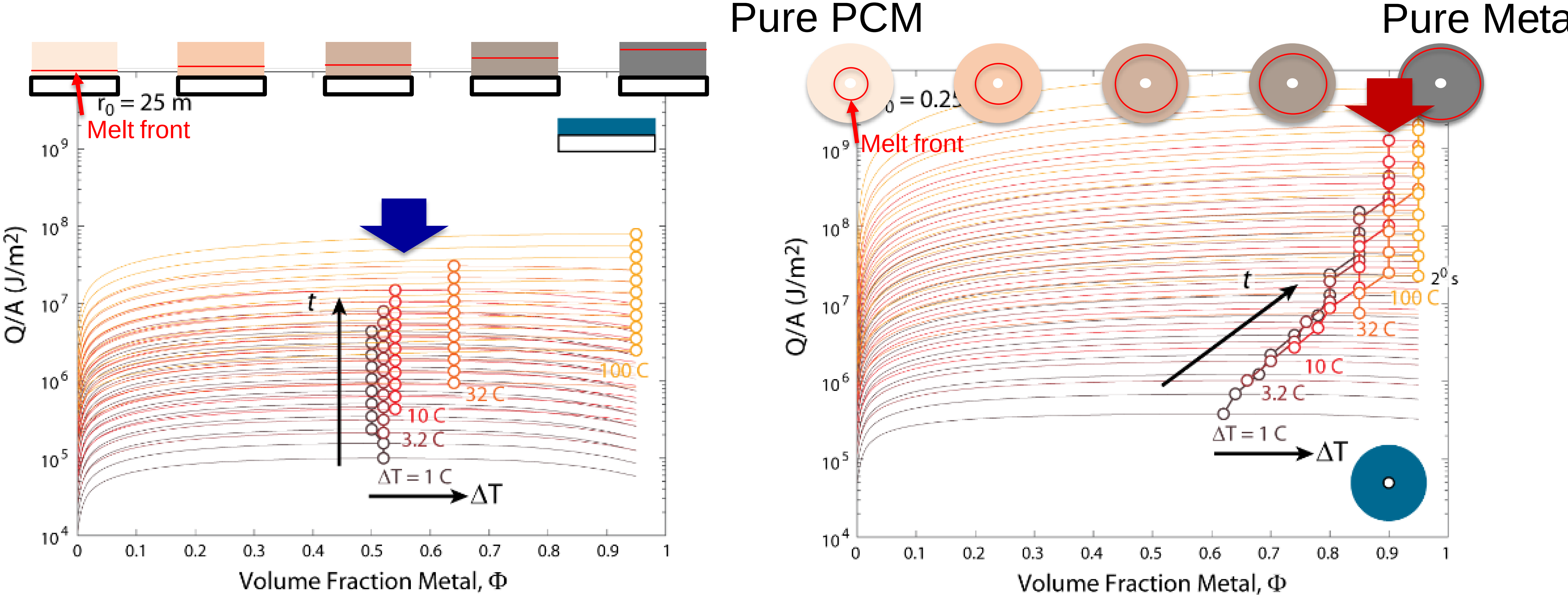




Hoe, Alison, et al. "A Numerical Analysis of Conductive Heat Transfer in Cylindrical Thermal Energy Storage Composites." *2019 18th IEEE Intersociety Conference on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm)*. IEEE, 2019.

Effect of Boundary Condition (ΔT) on Q/A

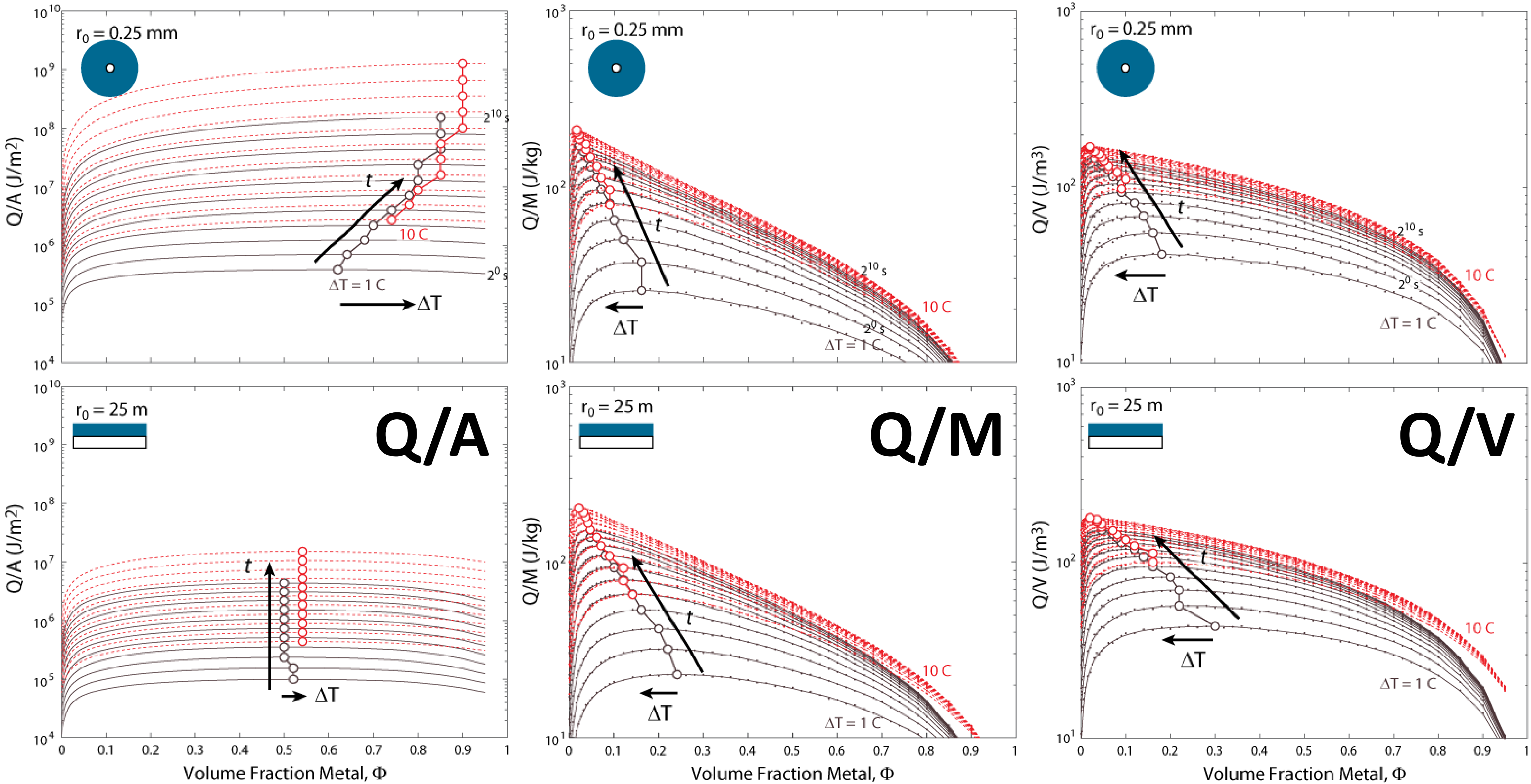
- At larger ΔT, sensible heating contribution shifts balance to more metal.
- Q/V weighted towards smaller ϕ.



Hoe, Alison, et al. "A Numerical Analysis of Conductive Heat Transfer in Cylindrical Thermal Energy Storage Composites." *2019 18th IEEE Intersociety Conference on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm)*. IEEE, 2019.

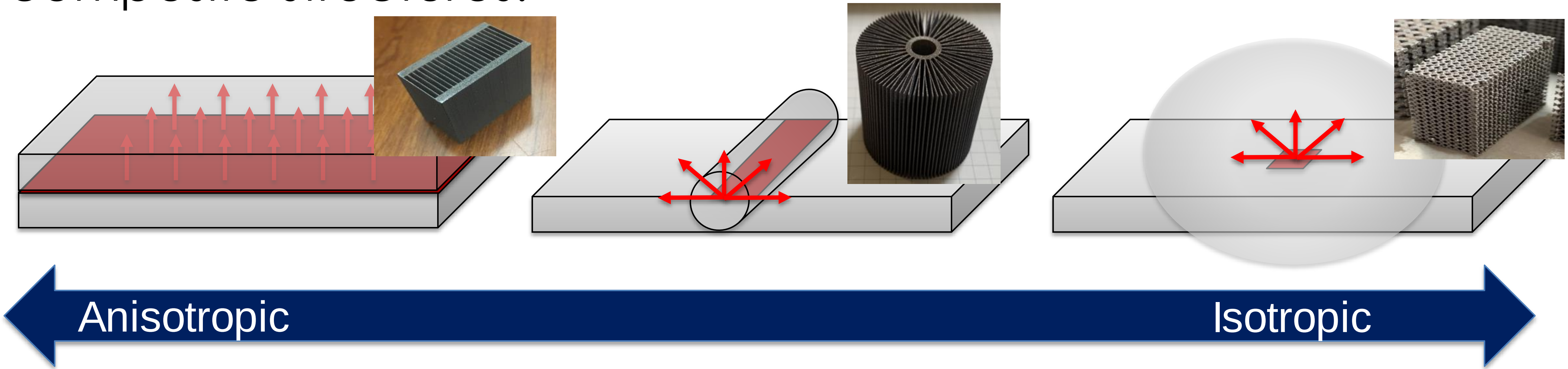
Effect of Constraint Function

- Q/M, Q/V weighted towards smaller ϕ. Shorter melt front distance.



Summary

Applying this strategy to different problems results in a diverse family of composite structures.



1. Increasing cooling power has an **opportunity cost** (energy density).
2. Highest cooling powers observed in **effective composites**.
3. Use analytical/computational design approaches for optimal performance.

Acknowledgements

TAMU:

Alison Hoe (PhD)
Michael Deckard (PhD)
Achutha Tamraparni (PhD)
Chen Zhang (PhD)
Abhishek Banerjee (MS)

Prof. J. Felts (TAMU, MEEN)

Prof. A. Elwany (TAMU, ISEN)

Support:

Office of Naval Research
ONR
Science & Technology

ONR: N00014-17-1-2802

CITMAV
Integrated Thermal Management Systems

Designing Thermal Energy Storage Devices using the Ragone Framework

Allison Mahvi and Jason Woods

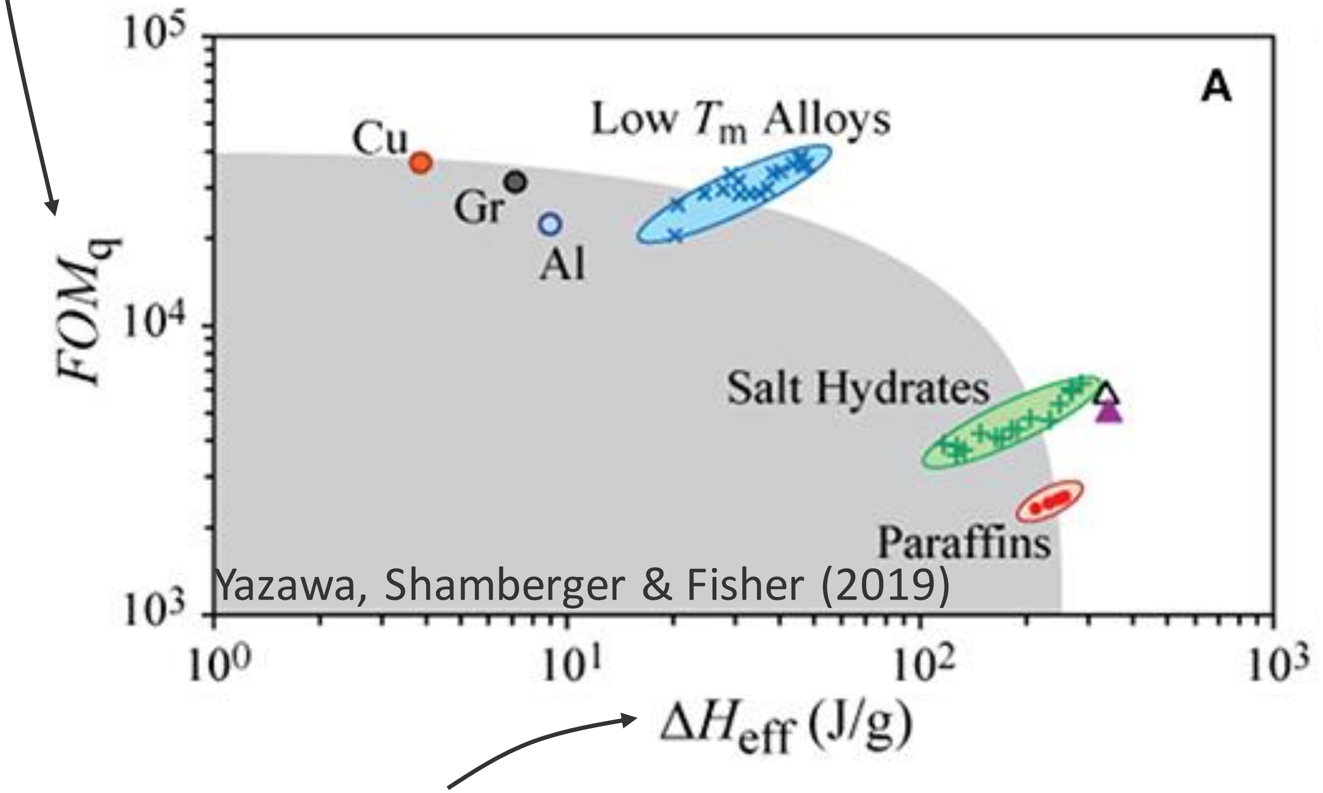
08-05-2020

This research has been submitted for publication
J. Woods *et al.* (2020), in review

Building Technologies Office Thermal Energy Storage Webinar Series:
Novel Materials in Thermal Energy Storage for Buildings

Past Work on Phase-Change Thermal Storage Materials

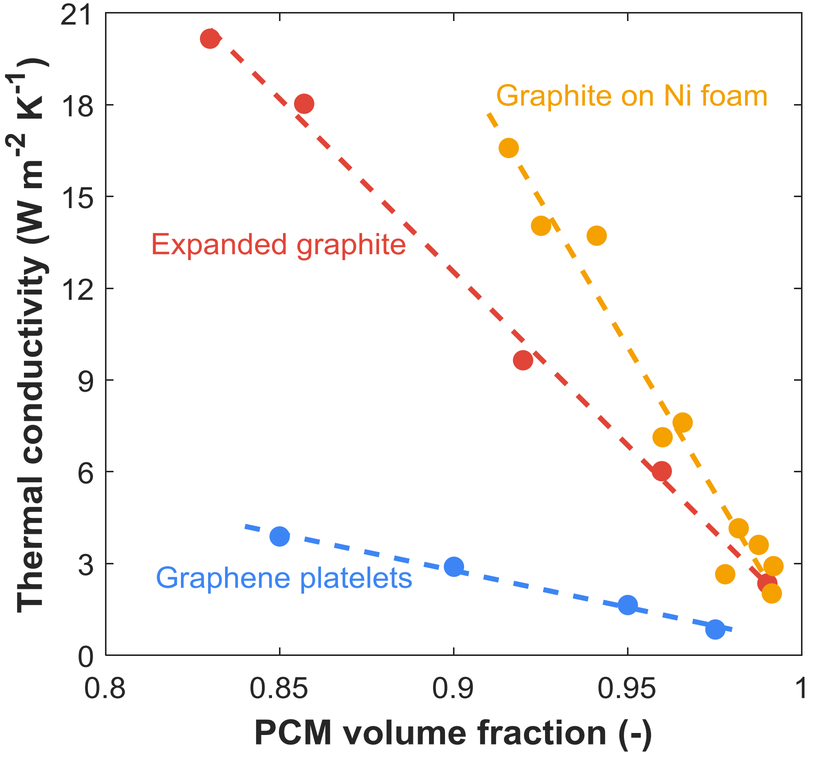
Proxy for power (function of **conductivity**, specific heat, **density**, **latent heat** and $\Delta T_{\text{c-disc}}$) $\sim\sqrt{k\rho L}$



Yazawa, Shamberger & Fisher (2019)

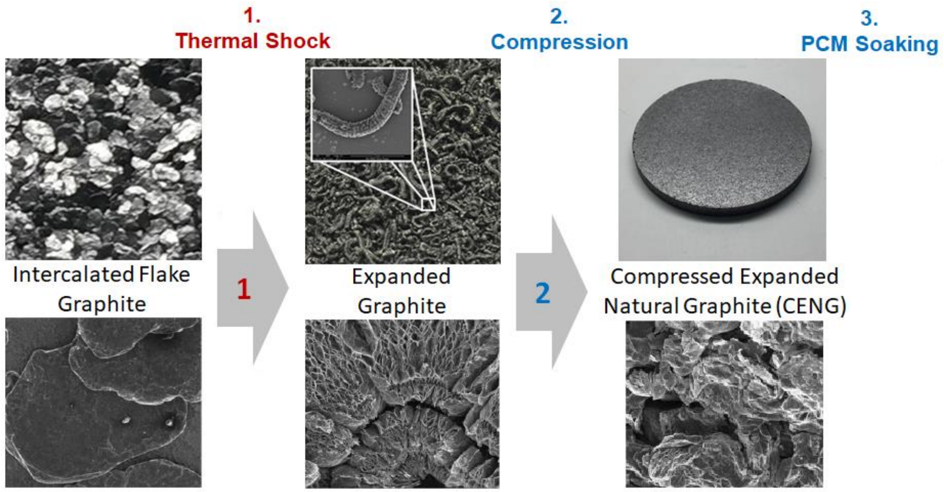
Capacity (function of **latent heat**, specific heat, and $\Delta T_{\text{c-disc}}$)

High *k* PCM composites



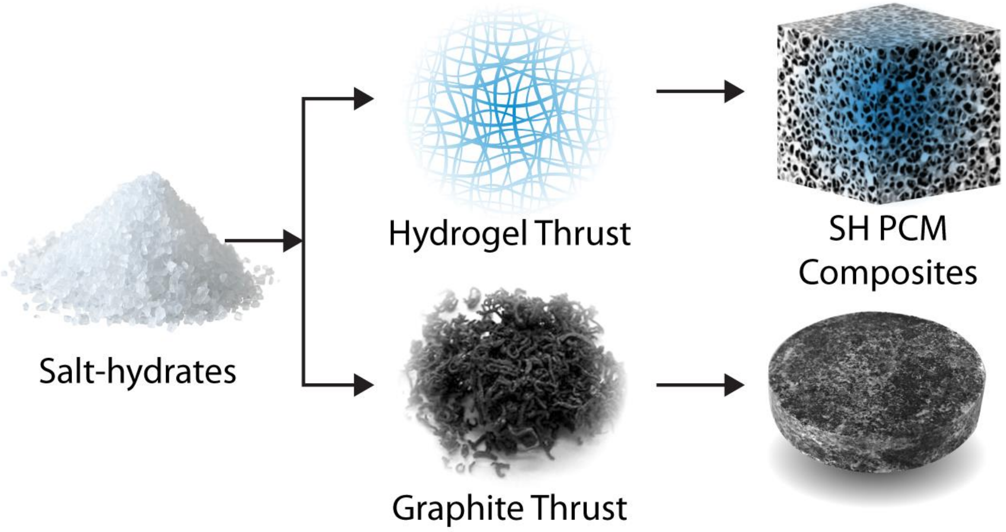
Phase Change Composites

Organic PCMs

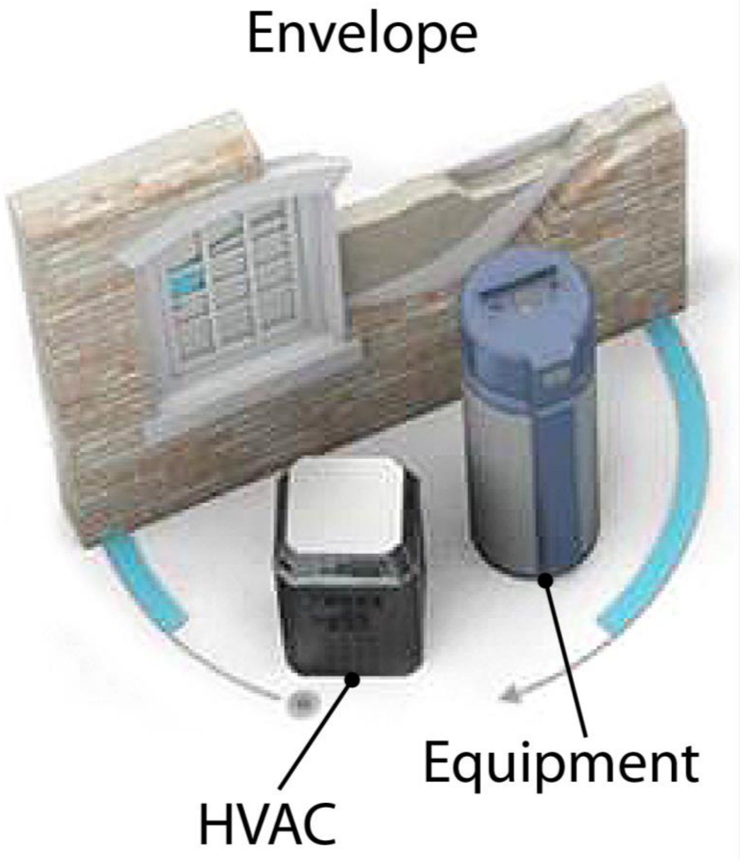


Alex Bulk *et al.* (NREL)

Salt Hydrates



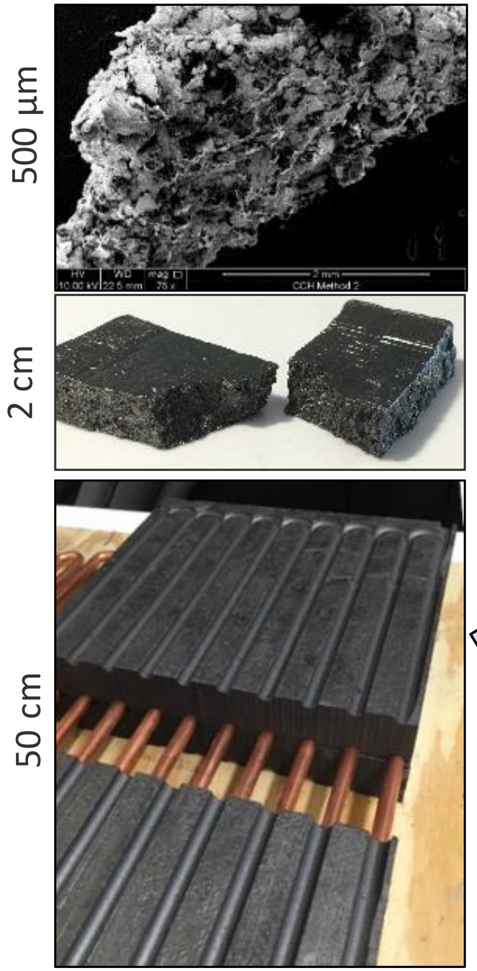
Adewale Odukomaiya *et al.* (NREL)



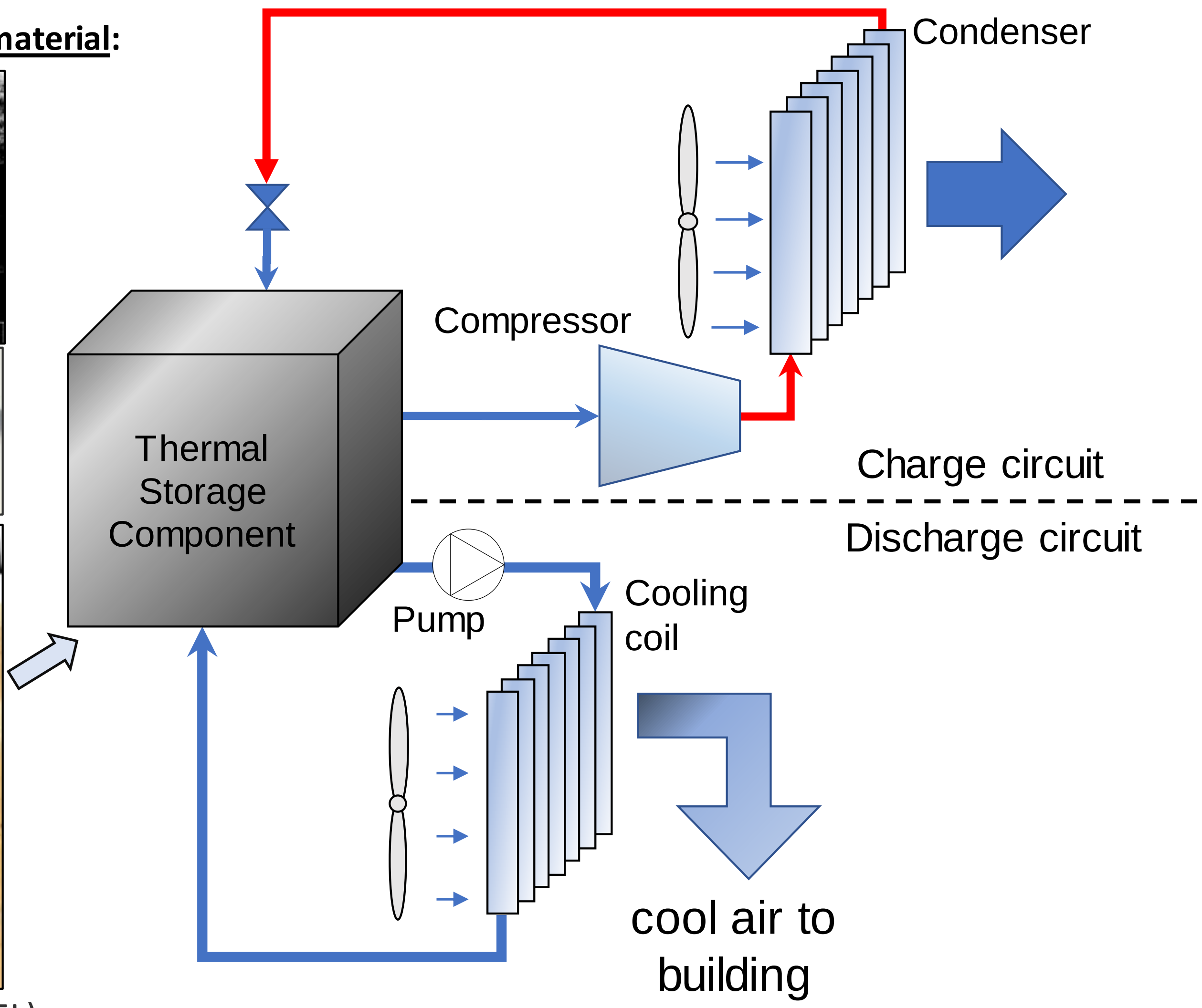
HVAC-Integrated Thermal Storage

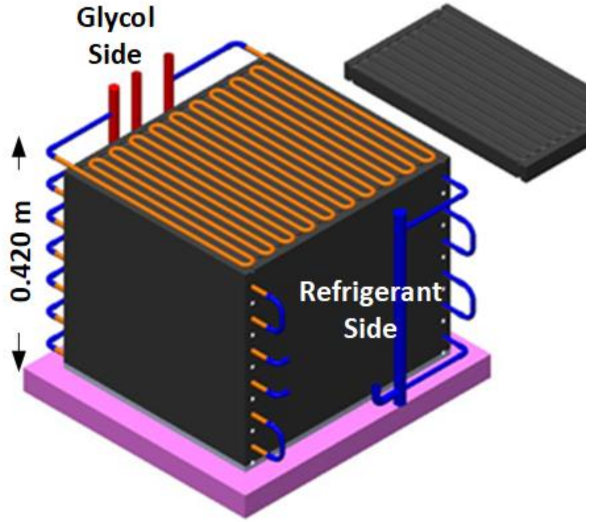
How should we design these components?

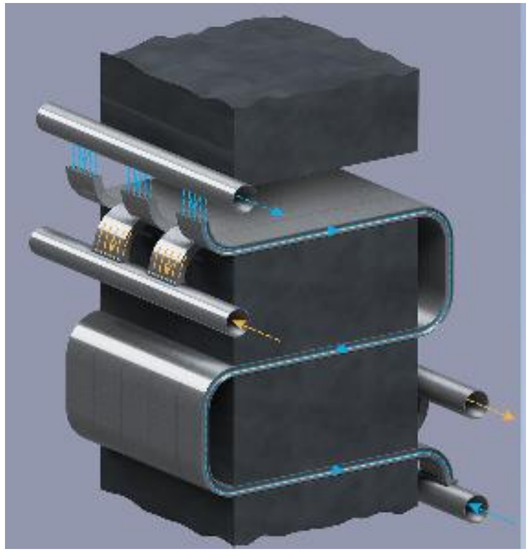
Phase-change composite material:



Anurag Goyal *et al.* (NREL)

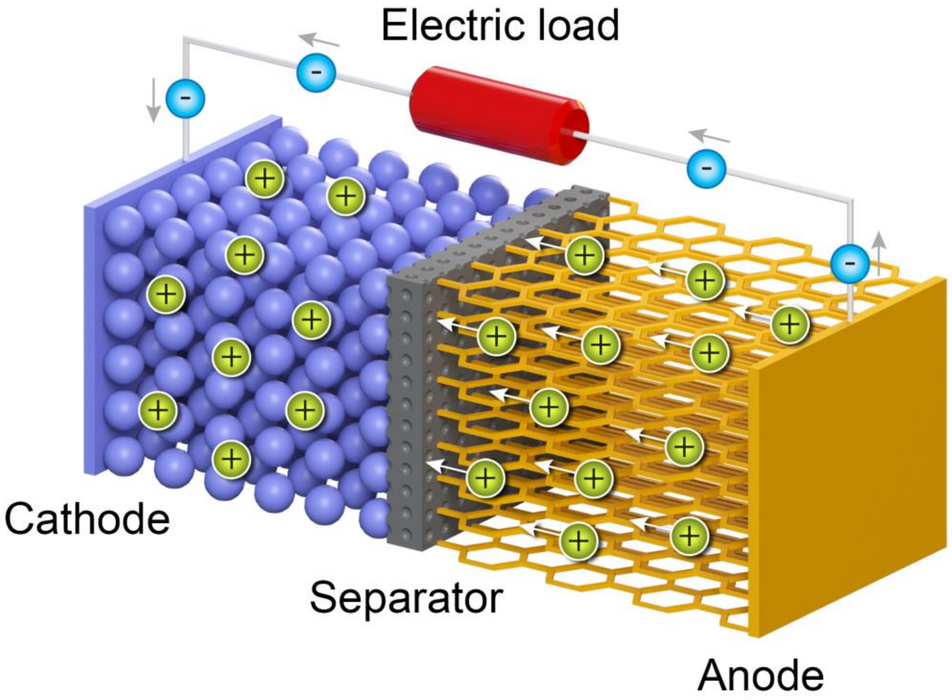




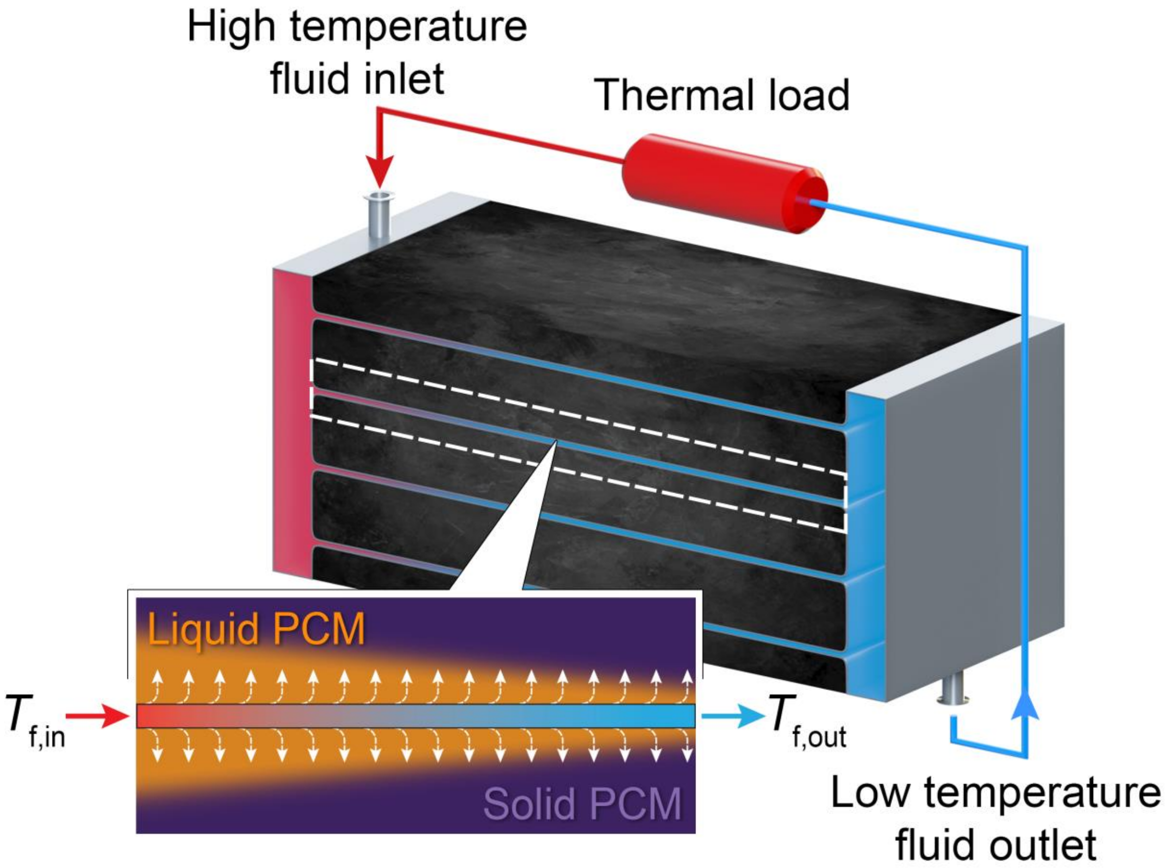


Electrochemical and Phase-Change Analogy

Electrochemical Storage

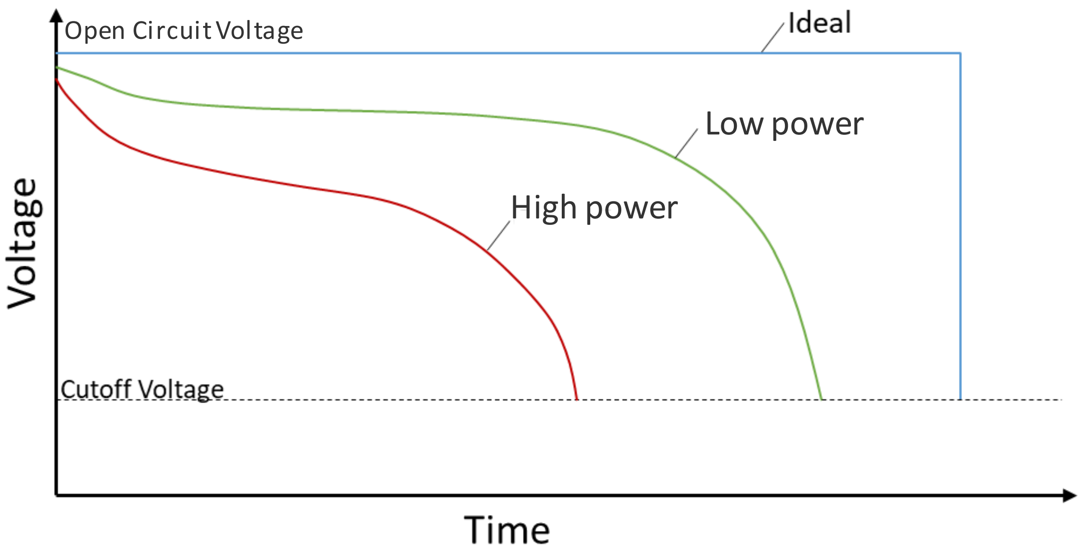


Phase-Change Storage

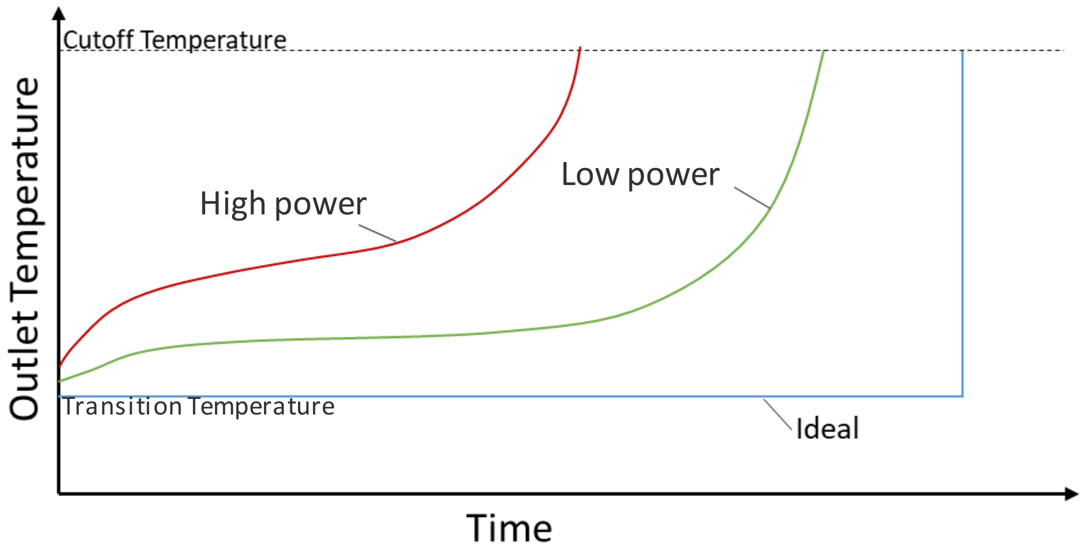


Electrochemical and Phase-Change Analogy

Electrochemical Storage



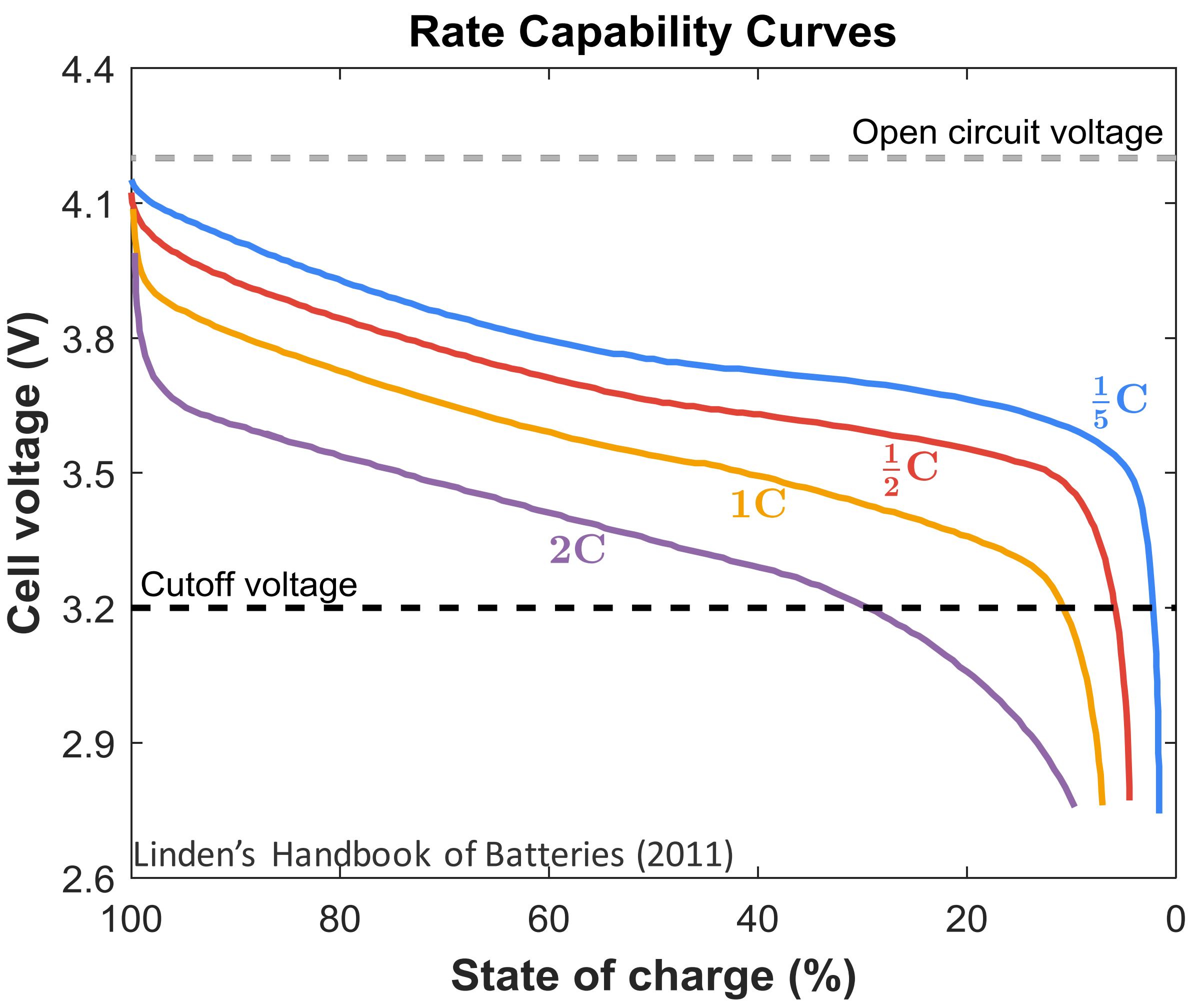
Phase-Change Storage



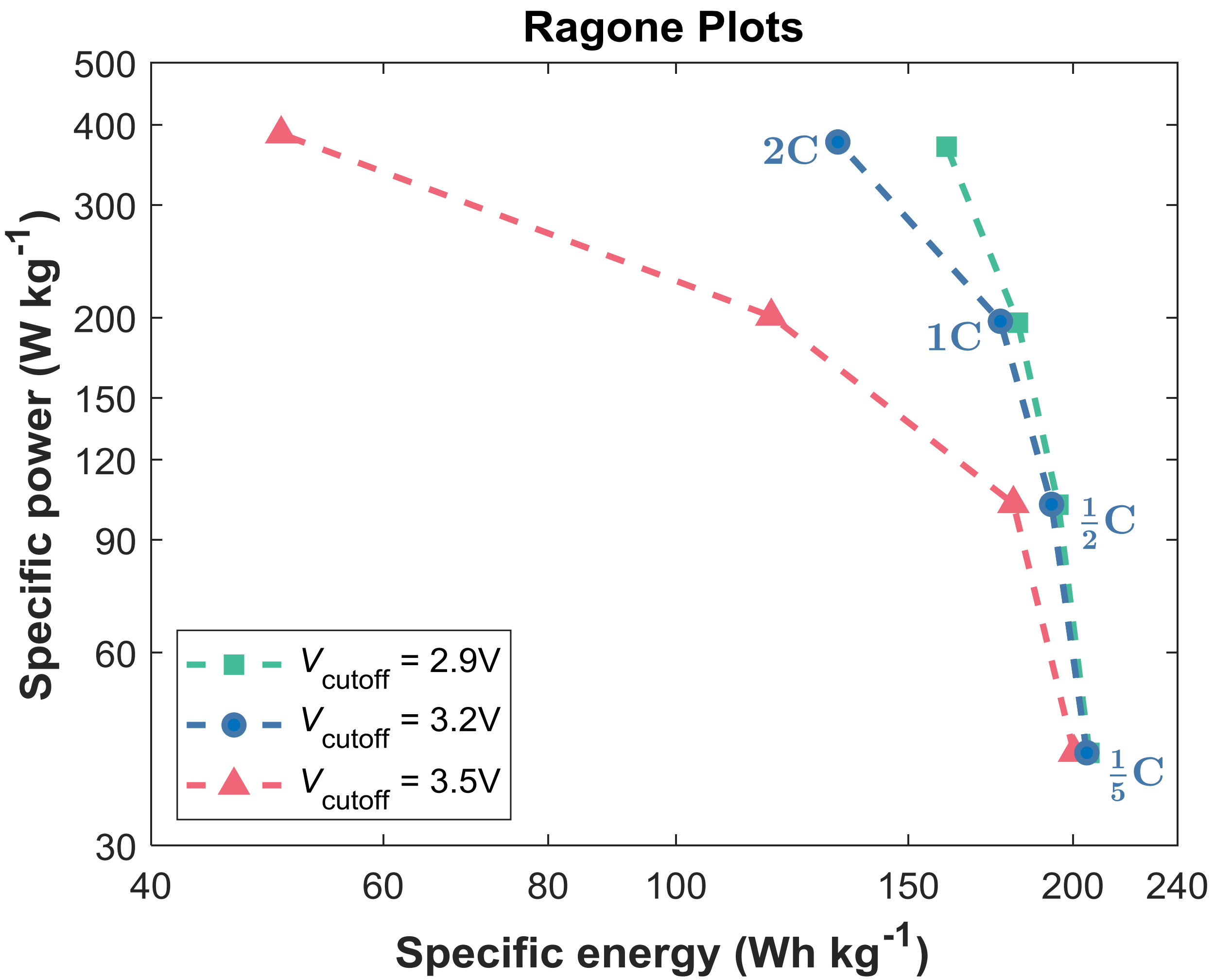
	Electrochemical storage	**Phase-change thermal storage**
Ideal output	Open Circuit Voltage (V)	Transition Temperature (K)
Actual output at constant current (or heat transfer rate)	$V = IR$ (V)	$T - T_t = \dot{q}R_{th}$ (K)

Rate Capability & Ragone Plots

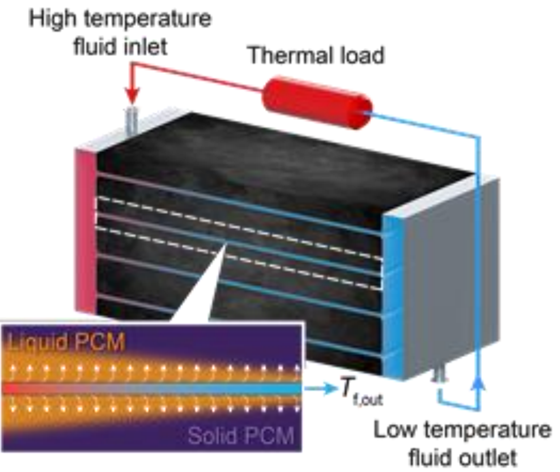
LiCoO$_2$/graphite lithium-ion battery

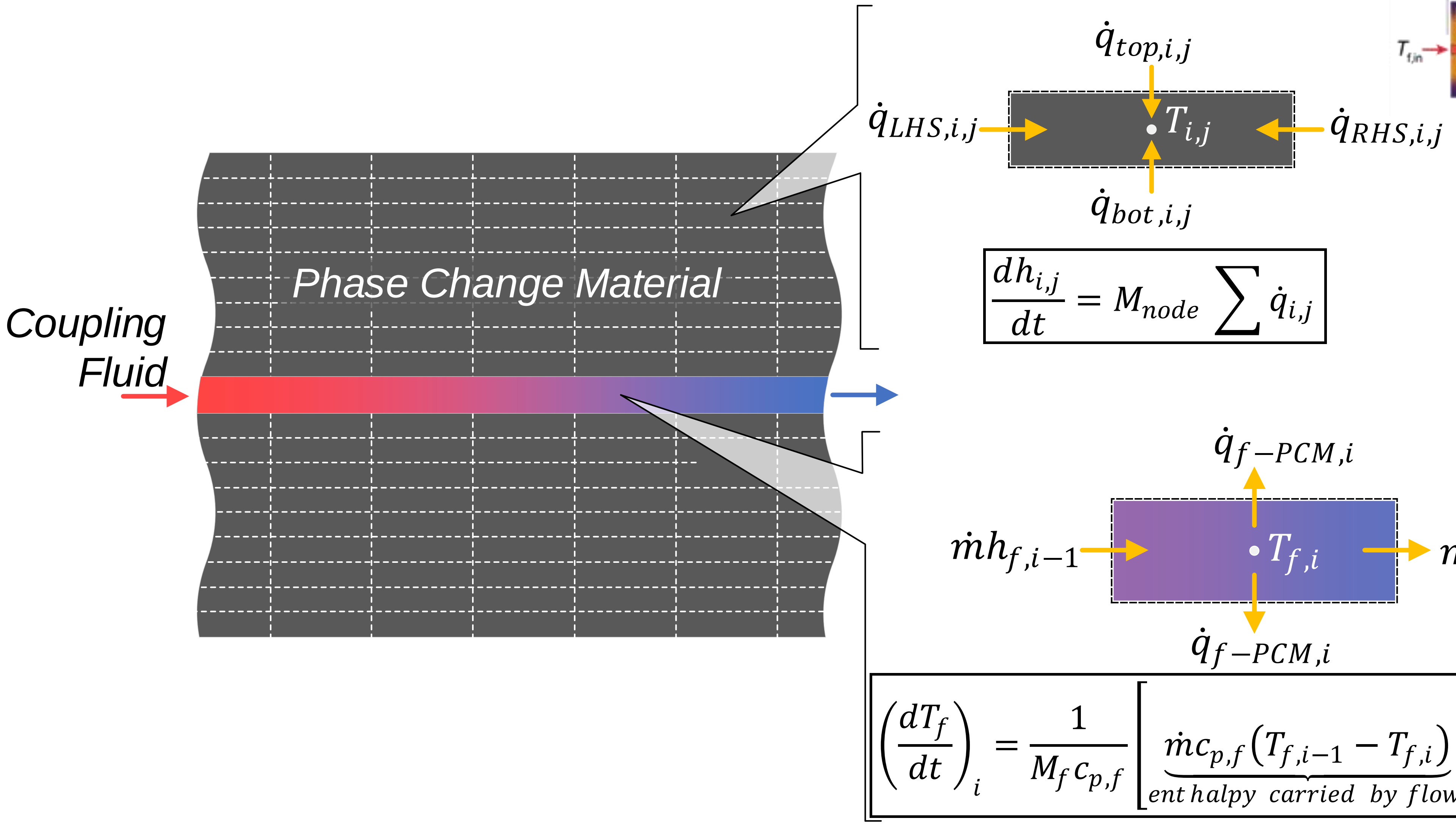


Linden's Handbook of Batteries (2011)



Heat Exchanger Model

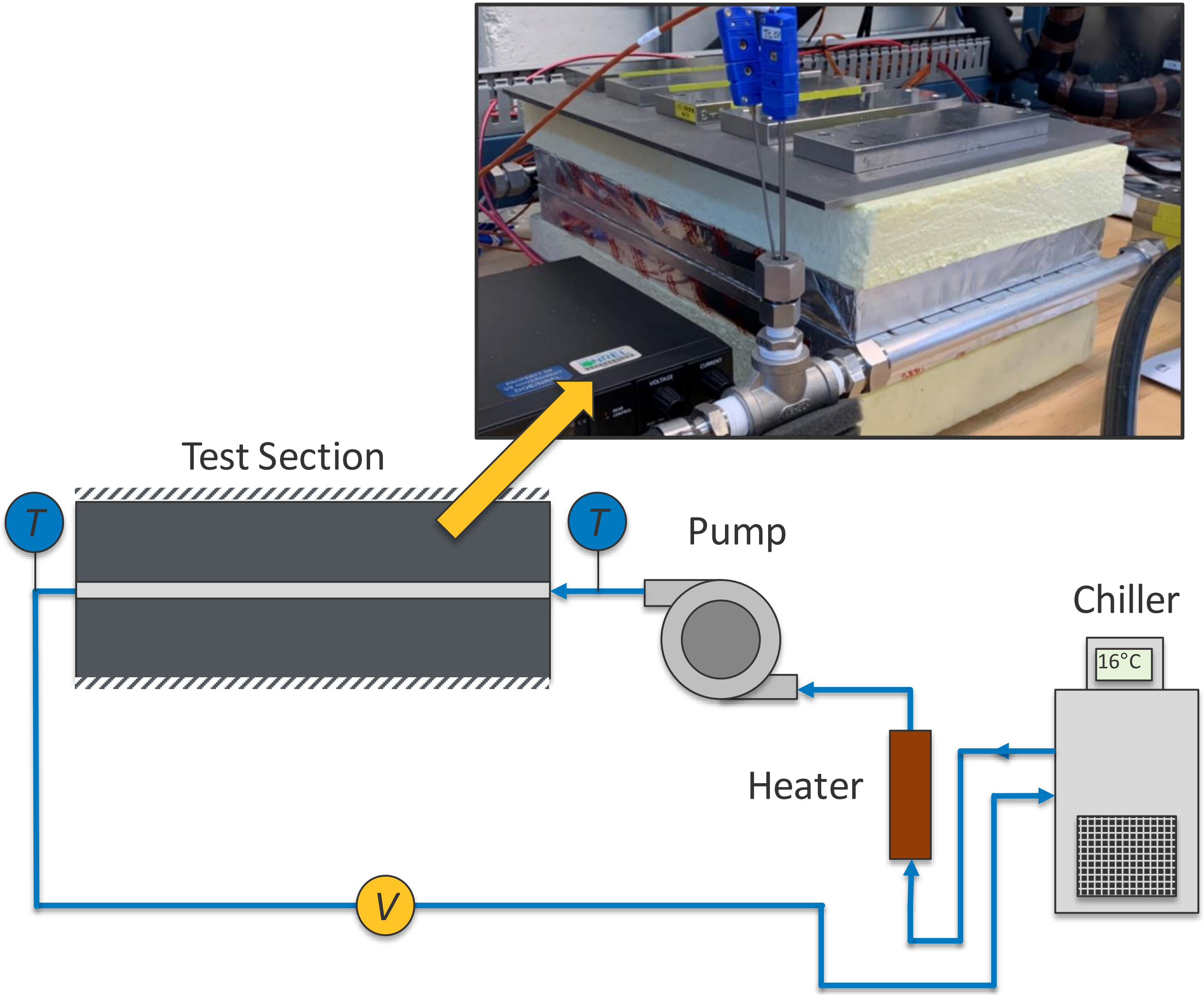


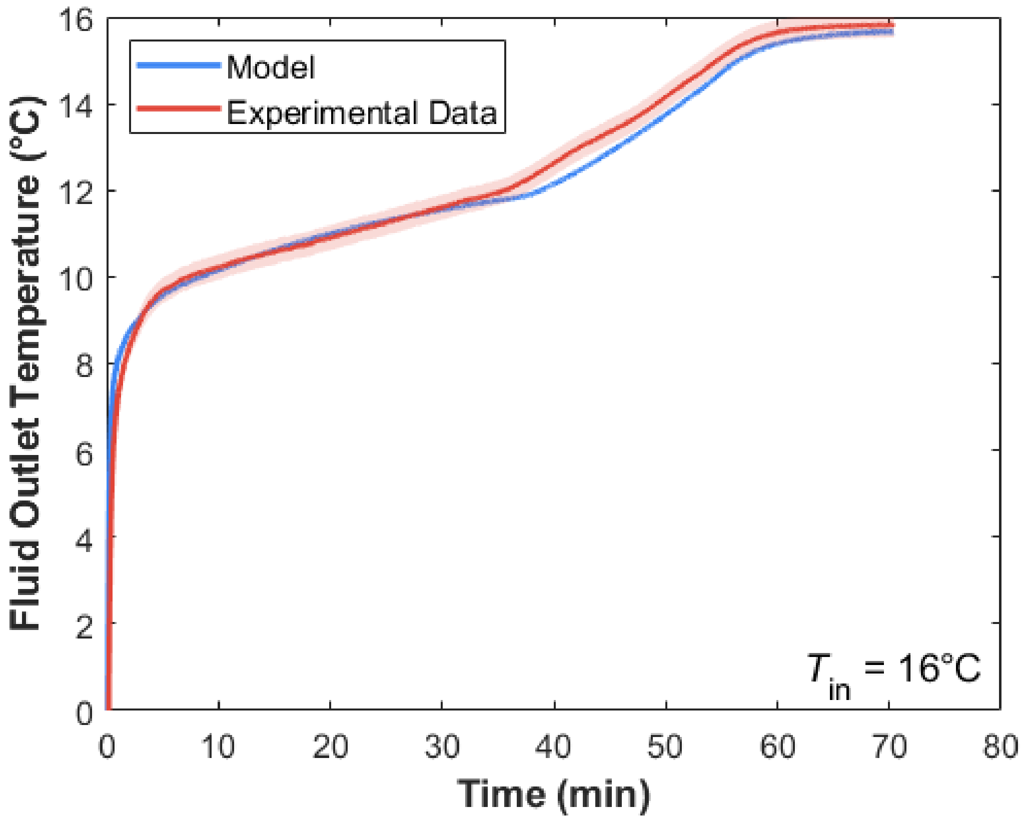


$$\boxed{\frac{dh_{i,j}}{dt} = M_{node} \sum \dot{q}_{i,j}}$$

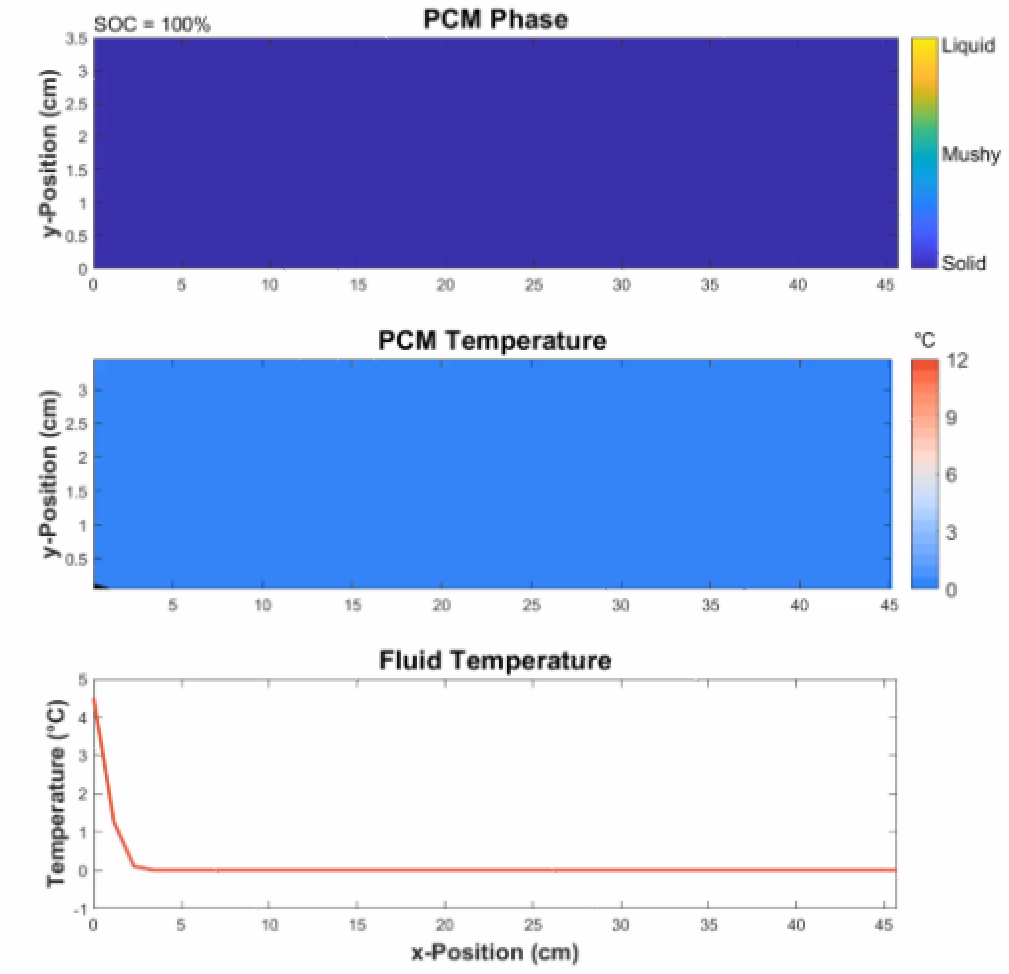
$$\boxed{\left(\frac{dT_f}{dt}\right)_i = \frac{1}{M_f c_{p,f}}\left[\underbrace{\dot{m}c_{p,f}\left(T_{f,i-1} - T_{f,i}\right)}_{enthalpy\ carried\ by\ flow} + \sum \dot{q}_{f,i}\right]}$$

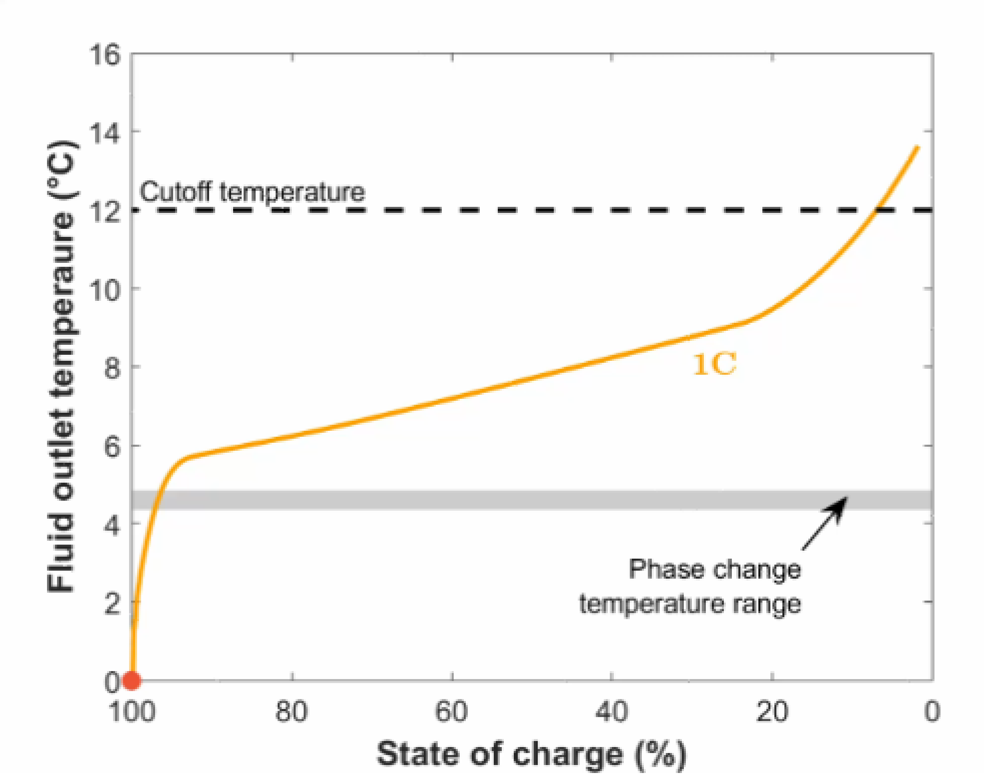
Model Validation



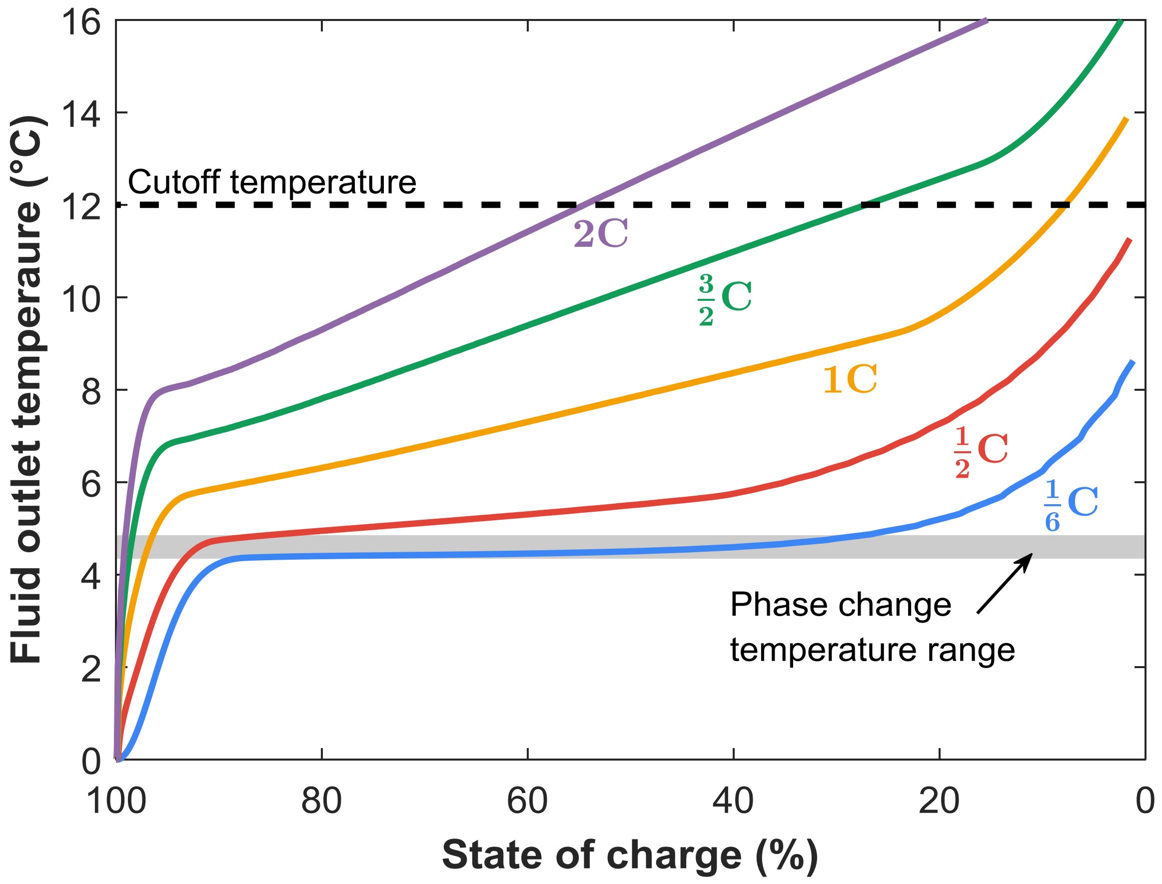


Thermal Battery Discharge (1C)





Constructing Ragone Plots



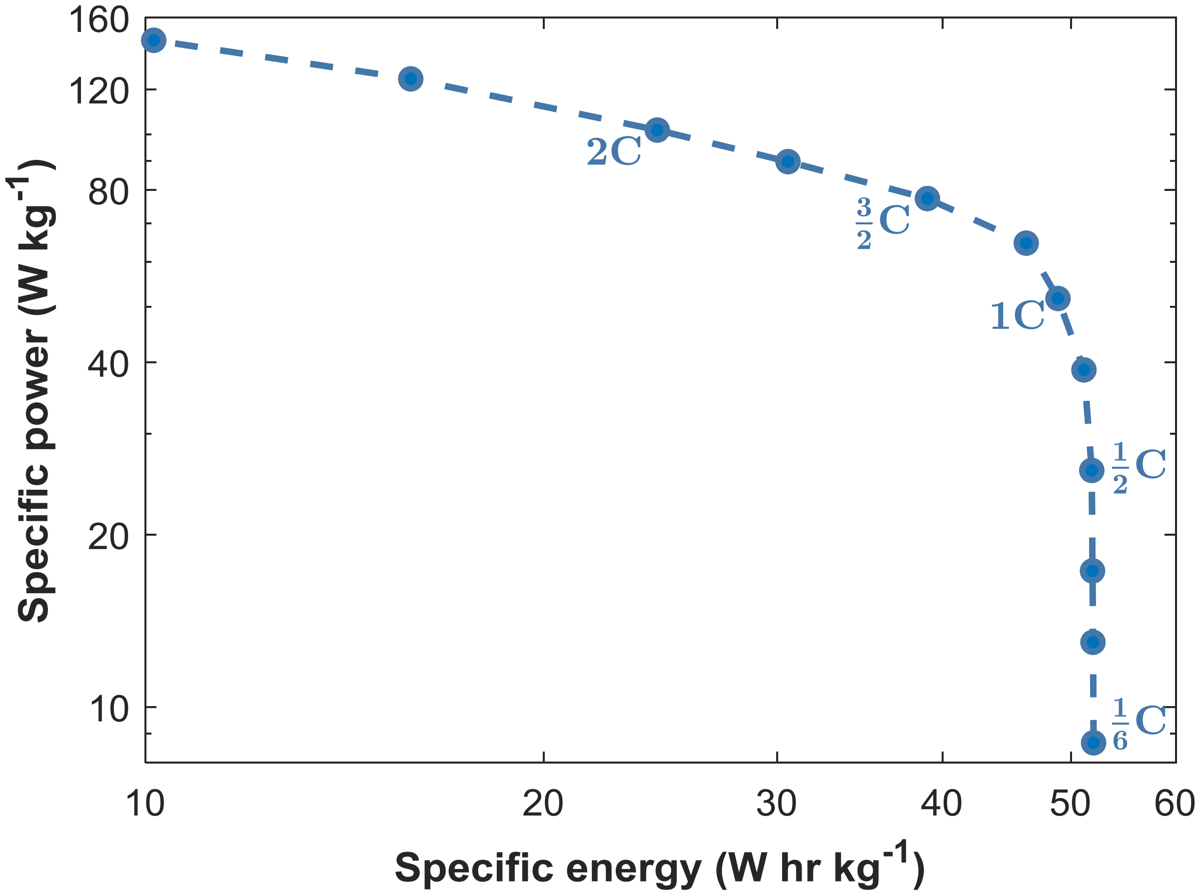
1) Generate the rate-capability curves at the desired power rate

2) Calculate how long the system can discharge before the outlet temperature is no longer useful (T_{cutoff})

3) Calculate the specific energy and power:

$$SP = \frac{\bar{q}_{f\rightarrow PCM}}{Mass} \qquad SE = \int_{t=0}^{t_{cutoff}} \frac{\dot{q}_{f\rightarrow PCM}}{Mass}\,dt$$

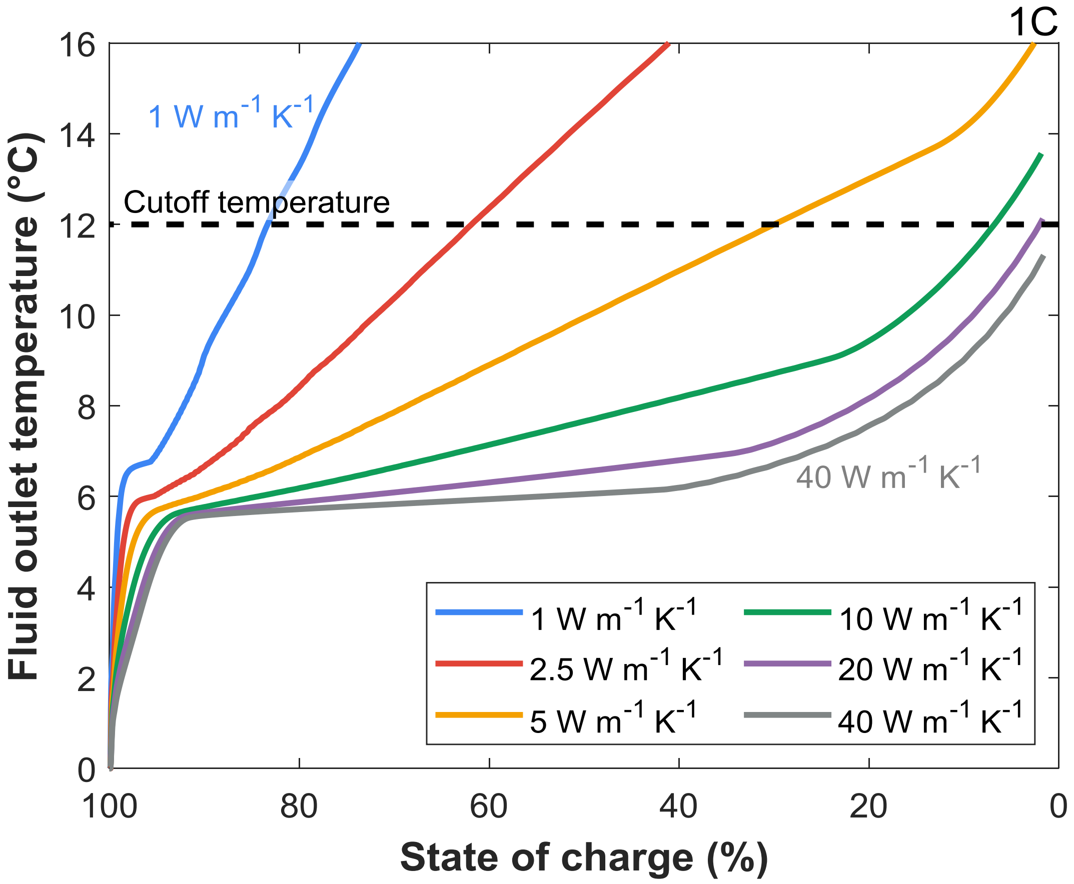
Constructing Ragone Plots

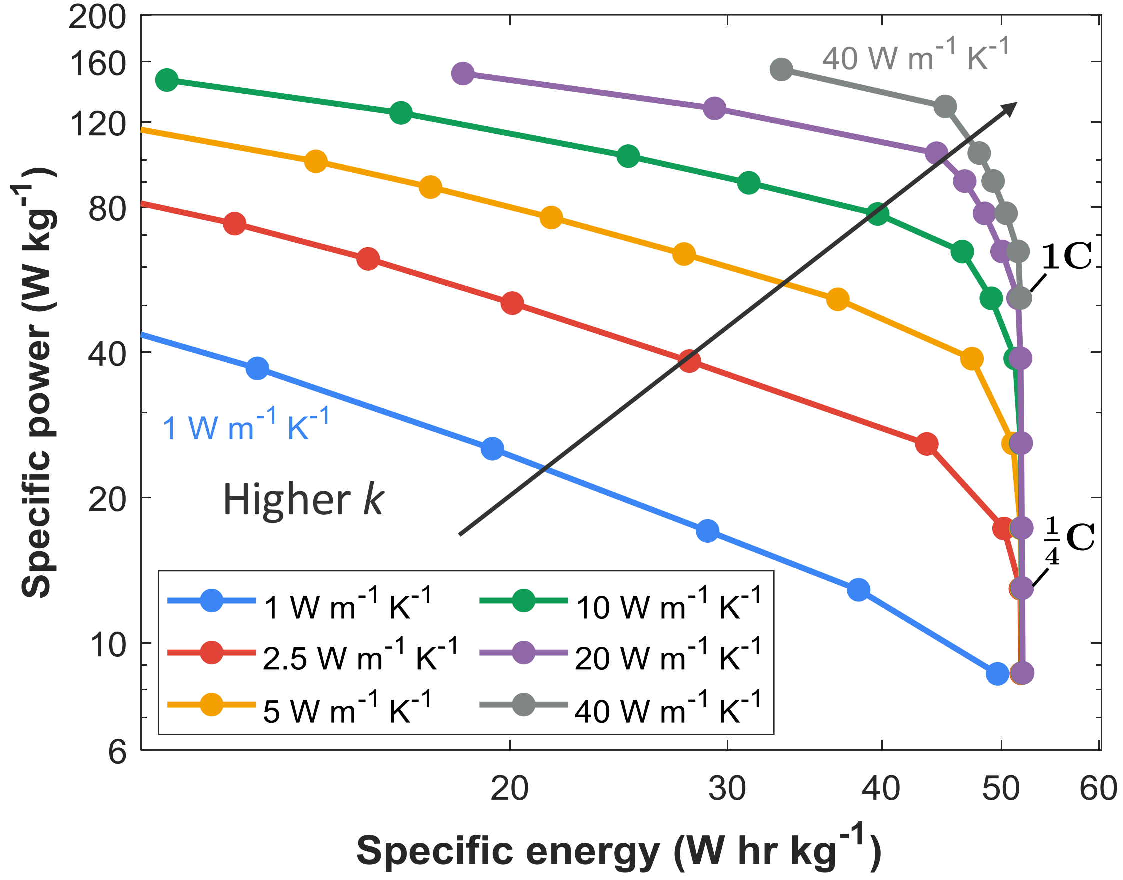


1) Generate the rate-capability curves at the desired power rate
2) Calculate how long the system can discharge before the outlet temperature is no longer useful (T_{cutoff})
3) Calculate the specific energy and power:
4) Plot the results on a log-log Ragone plot

$$SP = \frac{\bar{q}_{f\rightarrow PCM}}{Mass} \qquad SE = \int_{t=0}^{t_{cutoff}} \frac{\dot{q}_{f\rightarrow PCM}}{Mass}\, dt$$

Thermal Conductivity

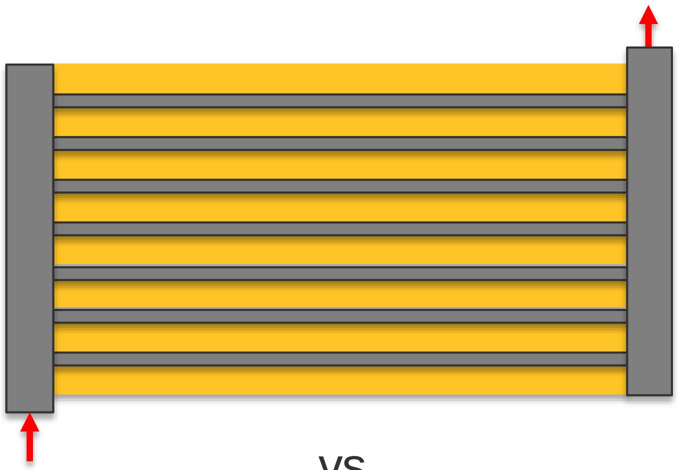




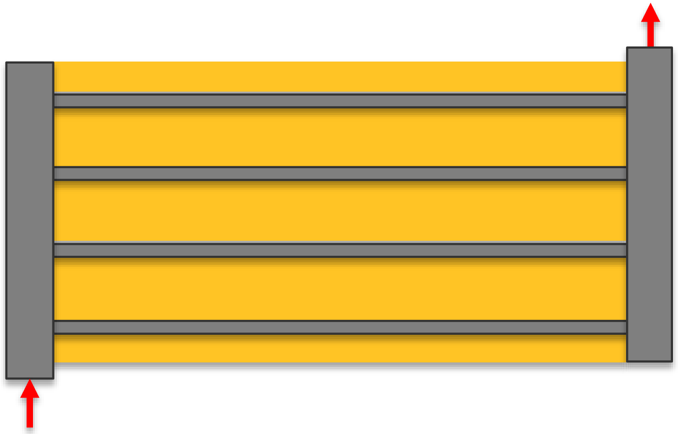
- Increasing thermal conductivity lowers fluid outlet temperatures (↑SE)
- Diminishing returns - low thermal conductivity can work fine at low discharge rates

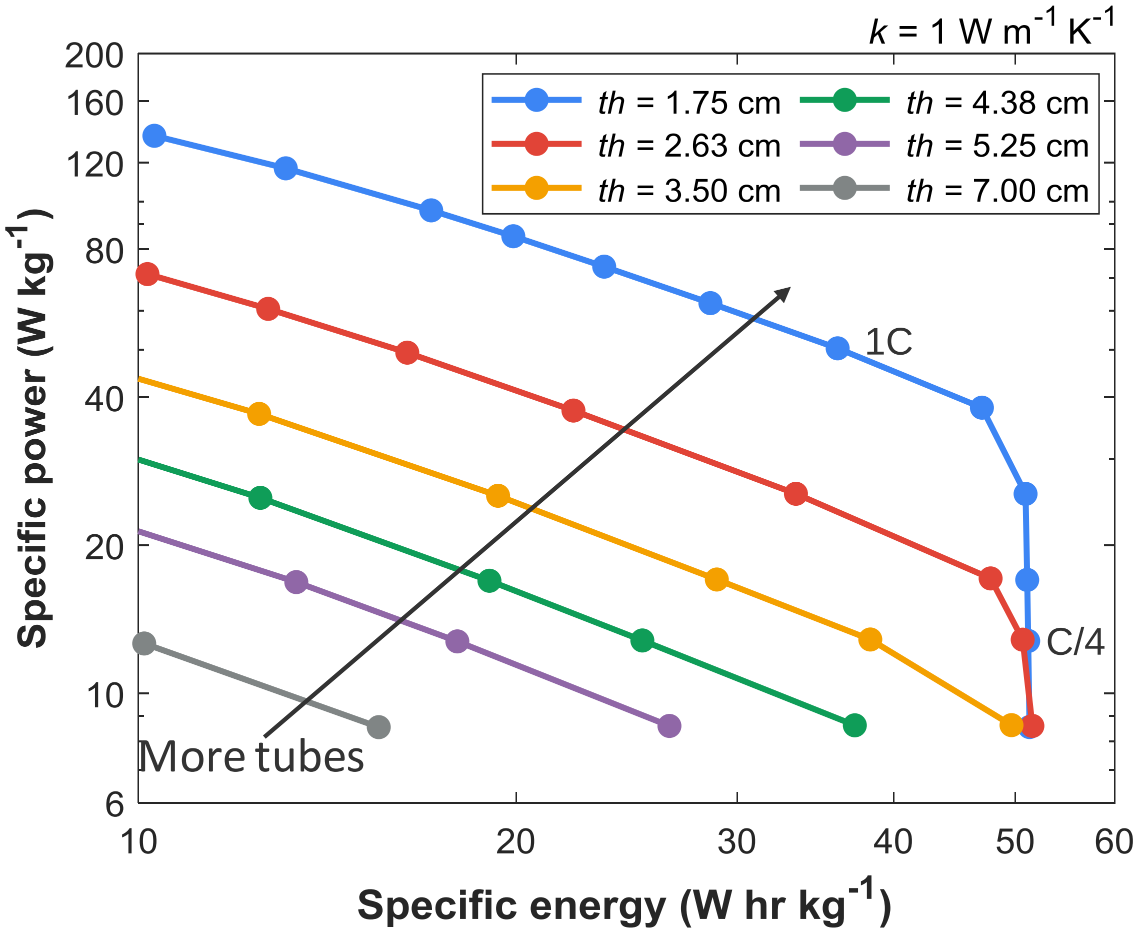
How much does geometry matter?

Decreasing the number of tubes will lower total weight, volume and cost



vs.





Thicker PCM will increase the maximum resistances → Reduces performance

Conclusions and Future Work

- Leveraged battery research to develop rate capability and Ragone plots for thermal energy storage

Can give insights into:

- Component design
- Material targets for given application
- Storage efficiency and system operation

Thank you

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Allison.Mahvi@nrel.gov
Jason.Woods@nrel.gov

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Building Technologies Office. The views expressed in the presentation do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

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