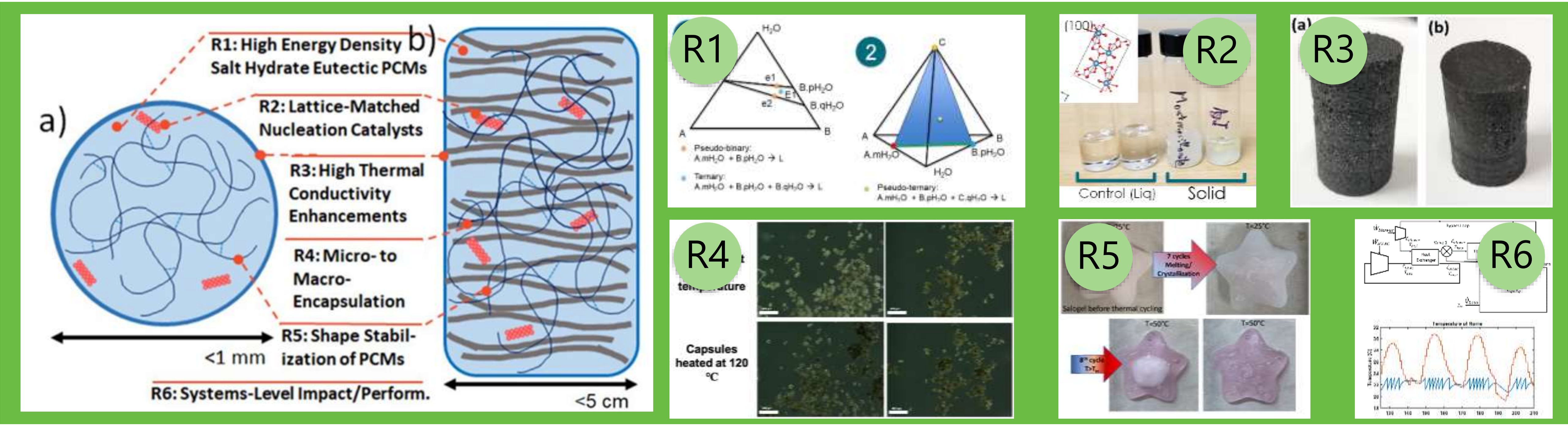
Salt Hydrate Eutectic Thermal Energy Storage for Building Thermal Regulation

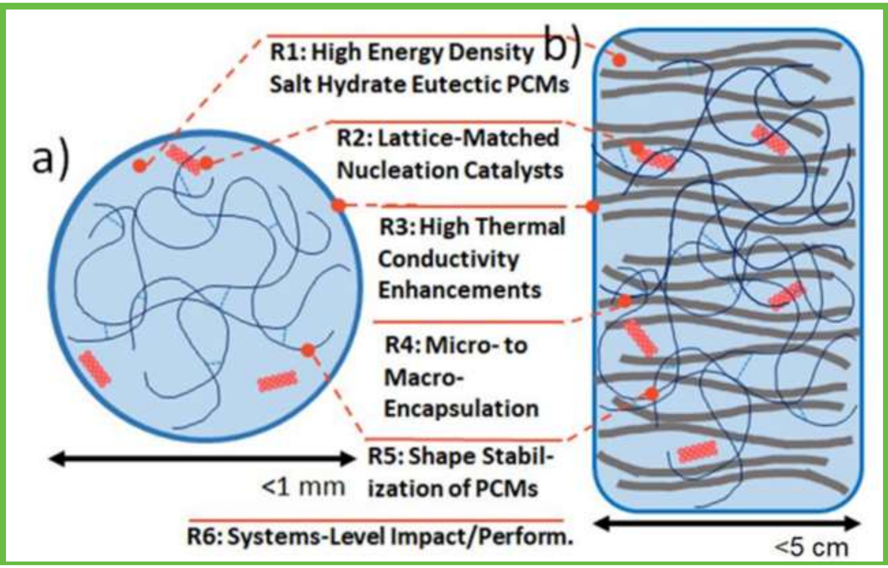


Performing Organization(s): **Texas A&M Engineering Experiment Station**
PI Name and Title: **Dr. Patrick Shamberger, Associate Prof.**
PI Tel and/or Email: **979.458.1086 / patrick.shamberger@tamu.edu**
Grant #: **DE-EE0009155**

Project Summary

Objective and outcome

- Low-cost, high energy-density, stable inorganic thermal energy storage material systems for integrating with HVAC: 5-25 ºC
- Develop new low-cost salt hydrate eutectics
- Design compatible additives to enhance robust performance



Team and Partners: 4 Dept's, 6 PI's/Co-PI's

- P. **SHAMBERGER** – Mat Sci Eng (**R1/R2**)
- C. **YU** – Mech Eng (**R3**)
- E. **PENTZER** - Mat Sci Eng (**R4**)
- S. **SUKHISHVILI** - Mat Sci Eng (**R5**)
- J. **FELTS** - Mech Eng (**R6**)
- C. **CULP** – Mech Eng / Arch (**R6**)

Stats: Performance Period: 04/01/2020 – 07/31/2023

DOE budget: $1,547k, Cost Share: $387k

Milestone 1: Identify 3-4 salt hydrate eutectics in each of target ranges; 08/2021

Milestone 2: Demonstrate decreased supercooling to <5 C in 2-5 eutectics; 08/2021

Milestone 3: Demonstrate graphitic composites with >1 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (up to 1000 cycles, >90 vol.% PCM; 02/2022

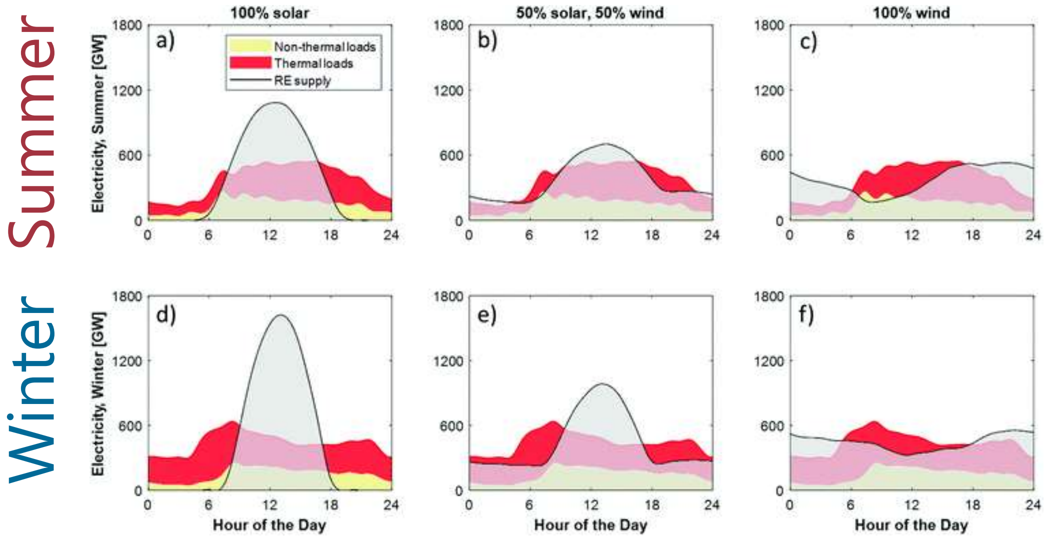
Milestone 4: Demonstrate the general ability to shape stabilize nitrate and chloride salt hydrates (up to 100 cycles, >90 vol.% PCM; 02/2022

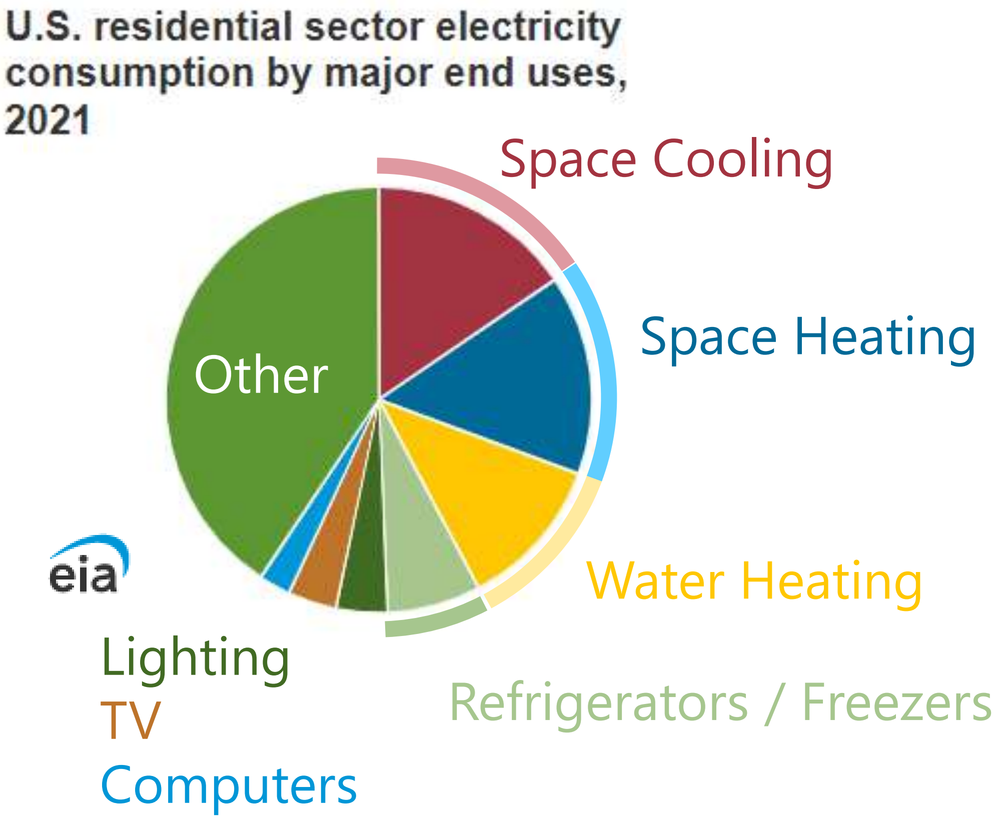
Milestone 5: Demonstrate robust micro-encapsulation with >95 vol.% and <5% degradation over 10^3 melt cycles; 08/2022

Problem

Problem Definition: Intermittent power generation and variable demand have resulted in variable electricity pricing schemes (peak prices are 5 to 40 ¢/kWh higher than off-peak prices). The largest segment of residential and commercial electricity consumption (~30 to 35%) corresponds to building HVAC.

To capture this differential pricing, consumers require a low cost, dependable approach to displace use of HVAC to off-peak hours. ***Current technologies are limited by the capability and cost of available thermal energy storage materials.***



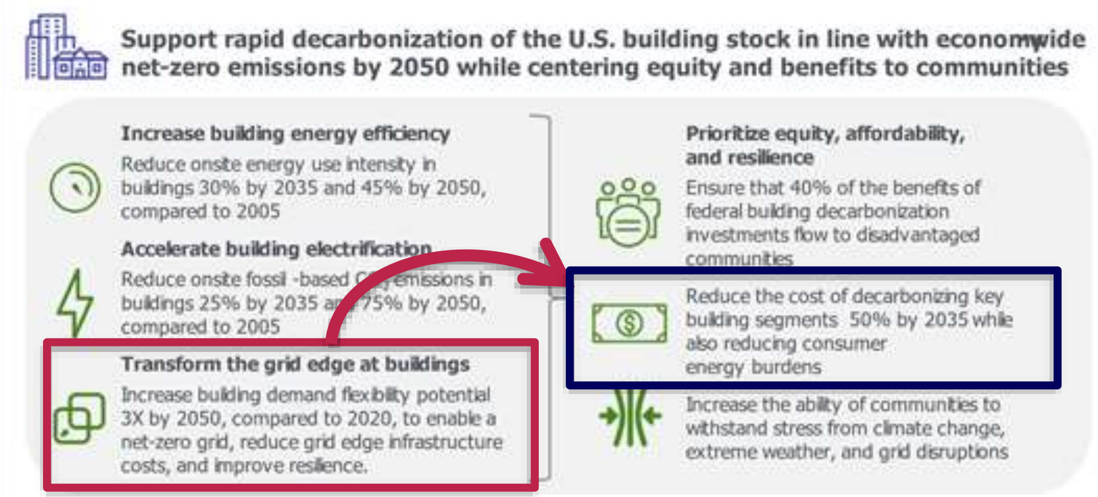


https://www.eia.gov/energyexplained/electricity/use-of-electricity.php

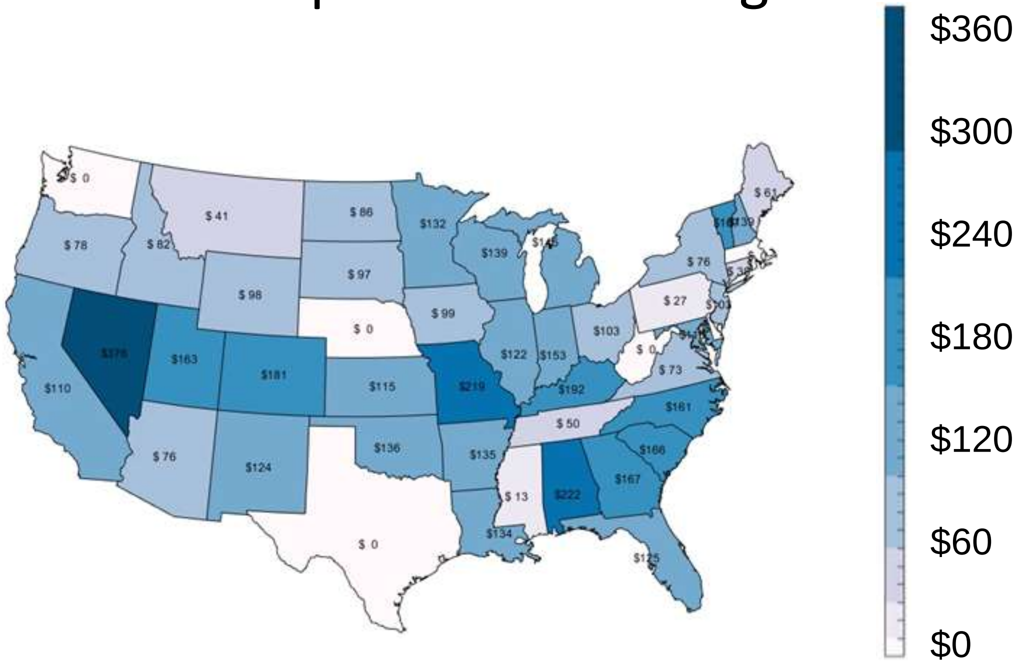
Odukomaiya, A., Woods, J., James, N., Kaur, S., Gluesenkamp, K. R., Kumar, N., ... & Prasher, R. (2021). *Energy & Environmental Science*, *14*(10), 5315-5329.

Alignment and Impact

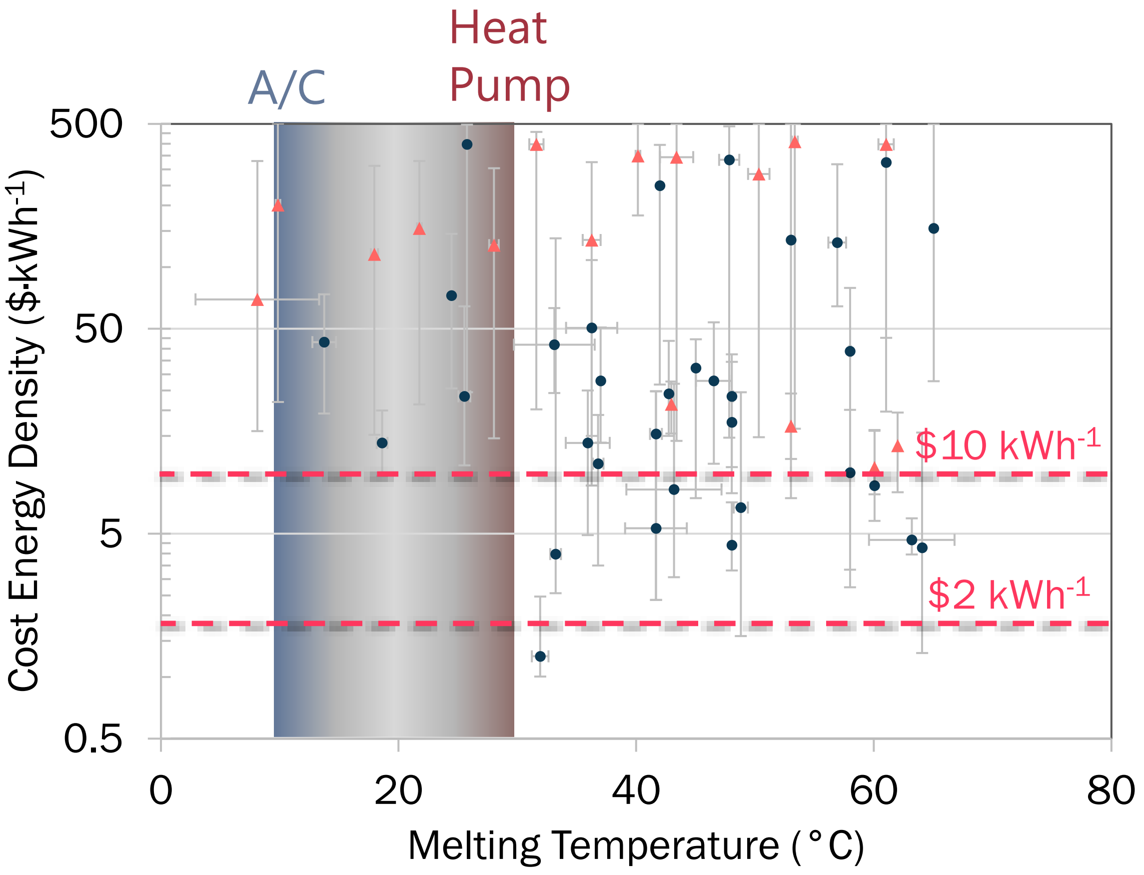
- Outcomes of this project enable flexible distributed thermal storage
- Resolve key limitation: **low cost TES materials**
- *DOE Alignment:* **Increase demand flexibility** through **low-cost energy storage**



Avg. per capita potential savings for residential peak load shifting.



Alignment and Impact: How to Define Success



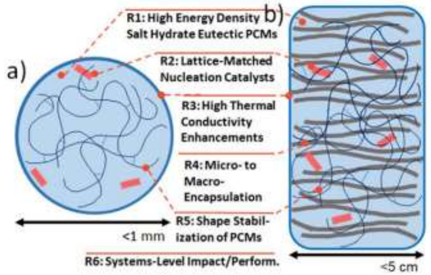
J.R. Hirschey, N. Kumar, T. Turnaoglu, K.R. Gluesenkamp, S. Graham (2021). "Review of Low-Cost Organic and Inorganic Phase Change Materials with Phase Change Temperature between 0° C and 65° C," 6th International High Performance Buildings Conference, virtual online, May 24-28, 2021.

SUCCESS IS…

- A palette of bespoke PCMs
- Relevant Temp.: 10 to 30 °C
- Low cost: <$2 kWh^{-1}
- Tech transition through IAB, licensing, integration in demo systems

… including COOPERATIVE TECHNOLOGIES

- Low ΔT: < 5 °C
- High *k*: >1 W·m^{-1}·K^{-1}
- Robust w/ cycling, time
- Shape stable



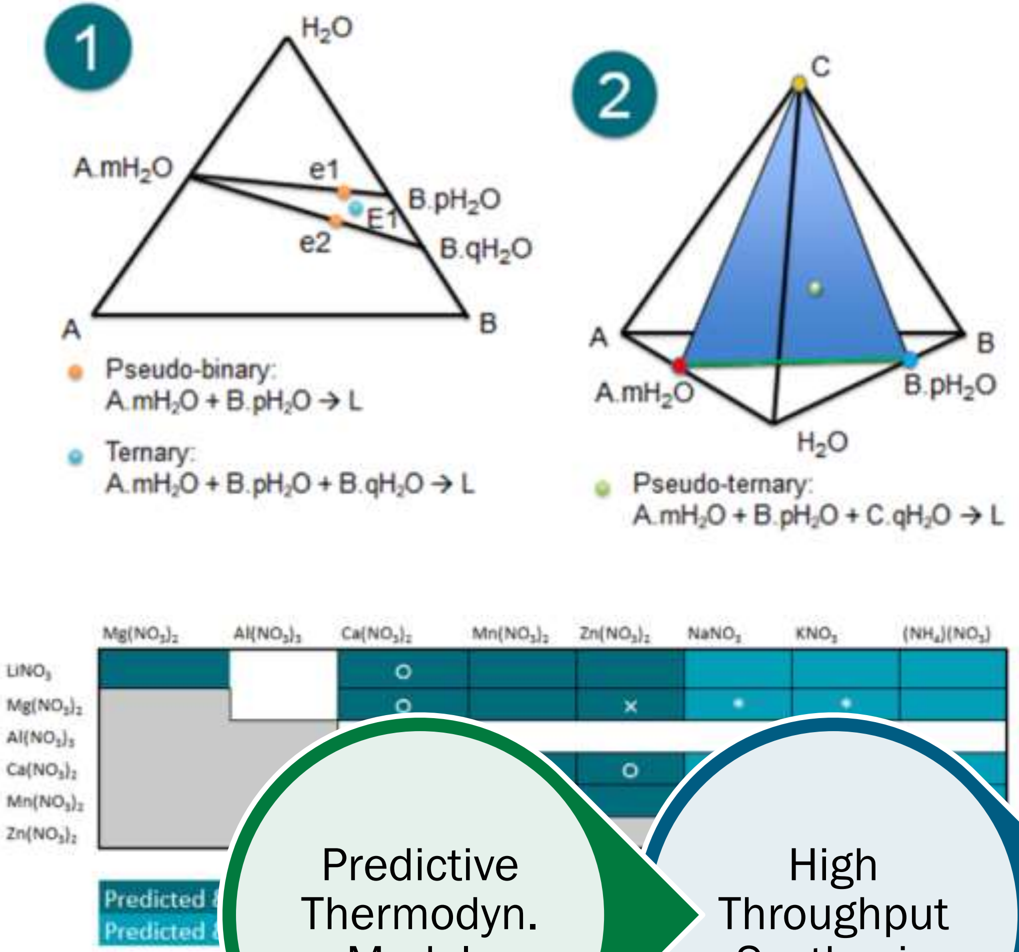
Approach: R1 Identify and validate stable salt hydrate eutectics

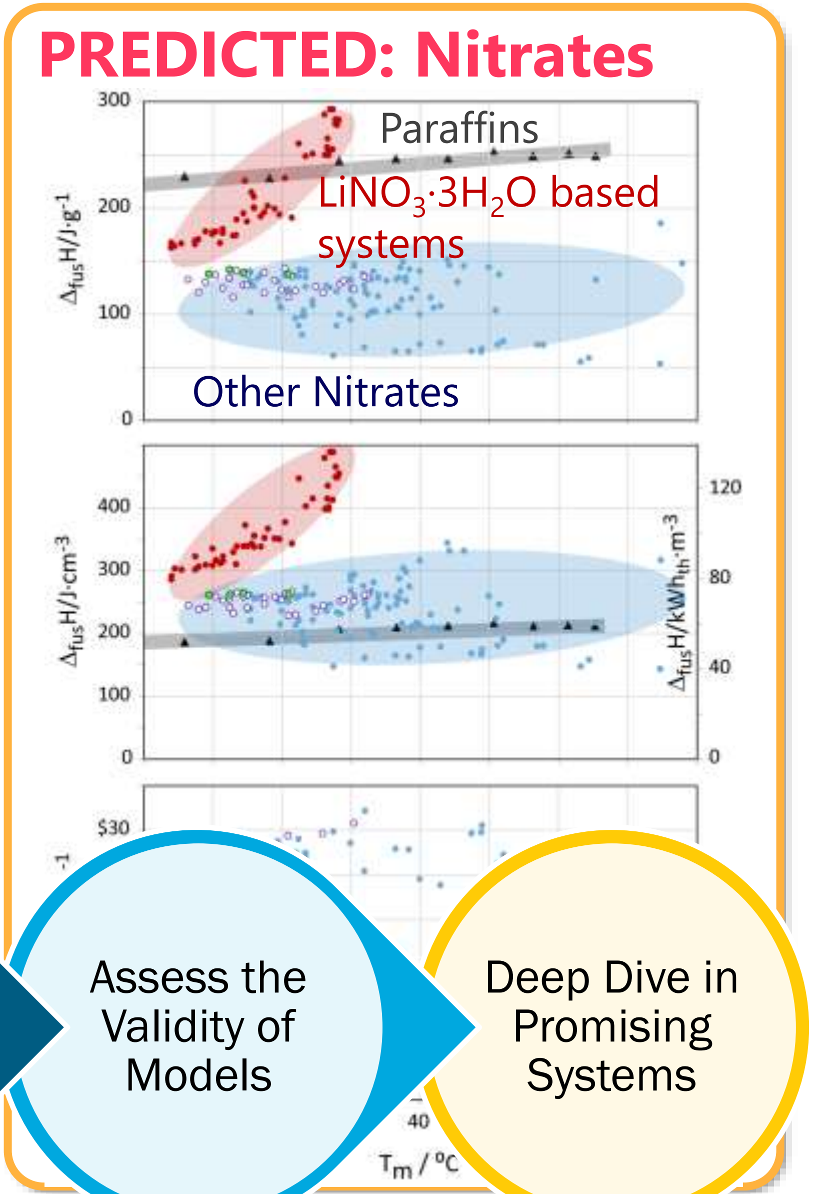
CHALLENGE:

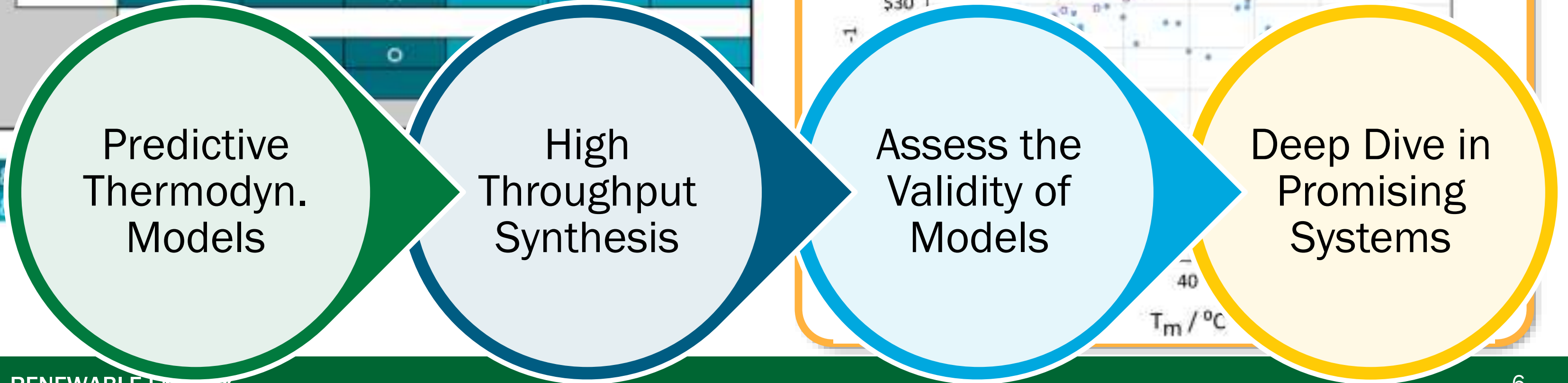
- Vast compositional space
- Currently assessed in ad hoc manner

APPROACH:

- Binary / Pseudo-binary / Ternary Eutectics
- Comprehensive evaluation of nitrate/ chloride systems







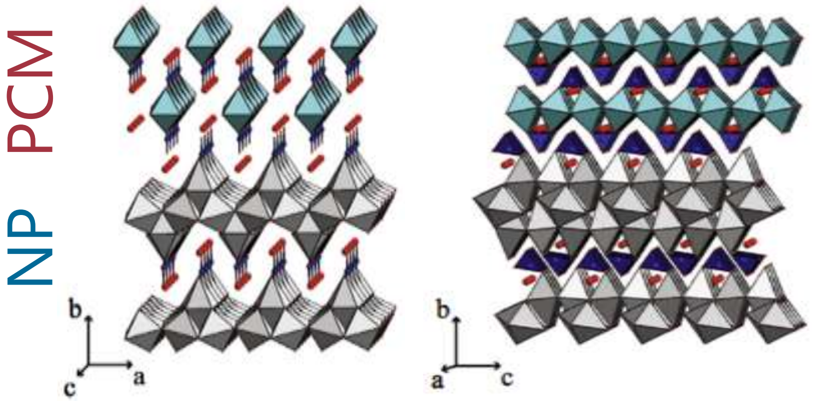
Approach: R2 Nucleation particles to decrease ΔT to <5 °C

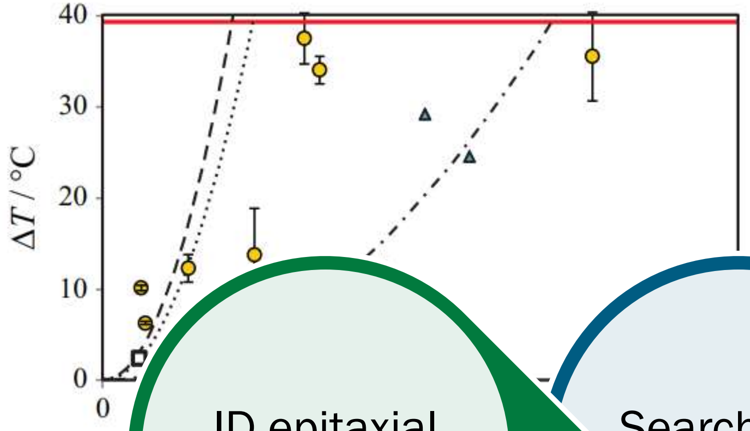
CHALLENGE:

- Reversible solidification in PCMs
- Decrease undercooling (higher efficiency)

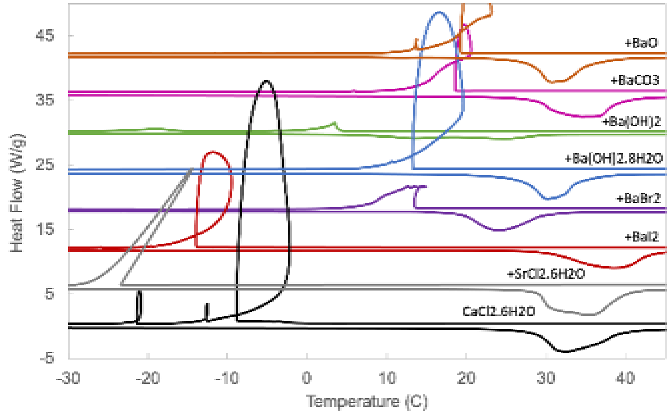
APPROACH:

- Promote hetero-geneous nucleation
- ID stable active nucleation particles (NPs)
- Use lattice-matching epitaxial approach





High throughput evaluation



Scaled Volume/ Cycling: Isothermal

ID epitaxial surfaces → Search XRD databases → ID / test candidate phases → Deep Dive into Promising Phases

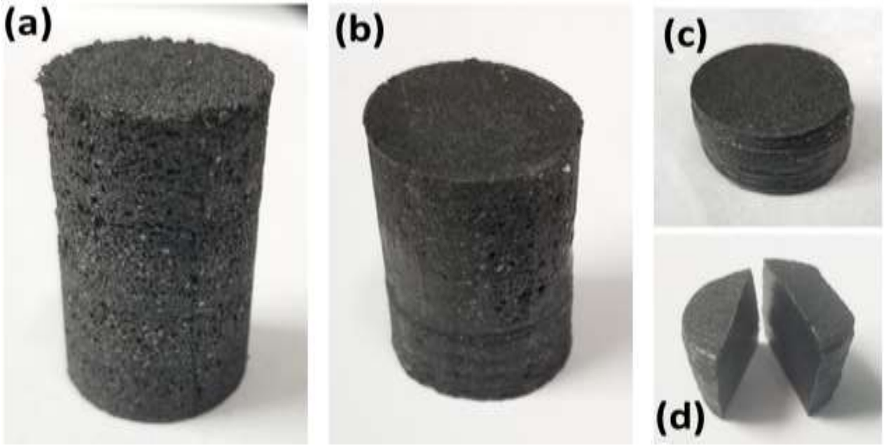
Approach: R3 Stable thermal conductivity enhancement

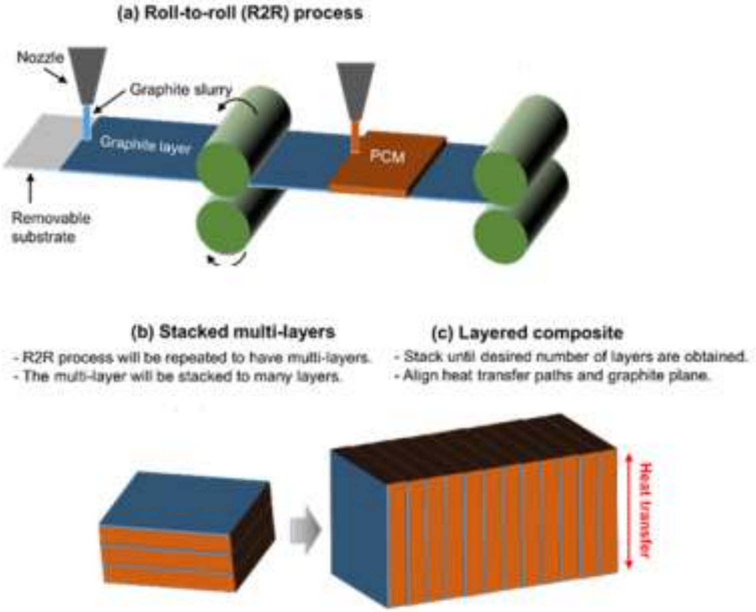
CHALLENGE:

- Increase the charge / discharge time scale

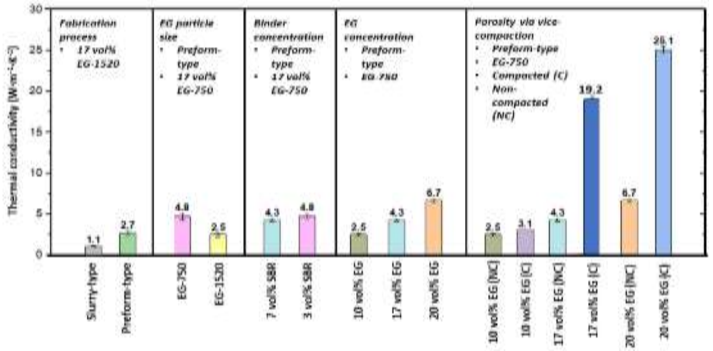
APPROACH:

- Expanded graphitic matrices
- Polymeric binders / surfactants to improve wetting / stability
- Scalable processing strategies

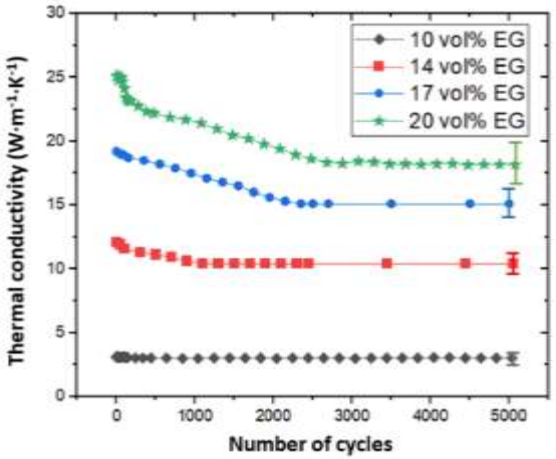




Evaluate processing techniques (binders):



Long-term cycling behavior:



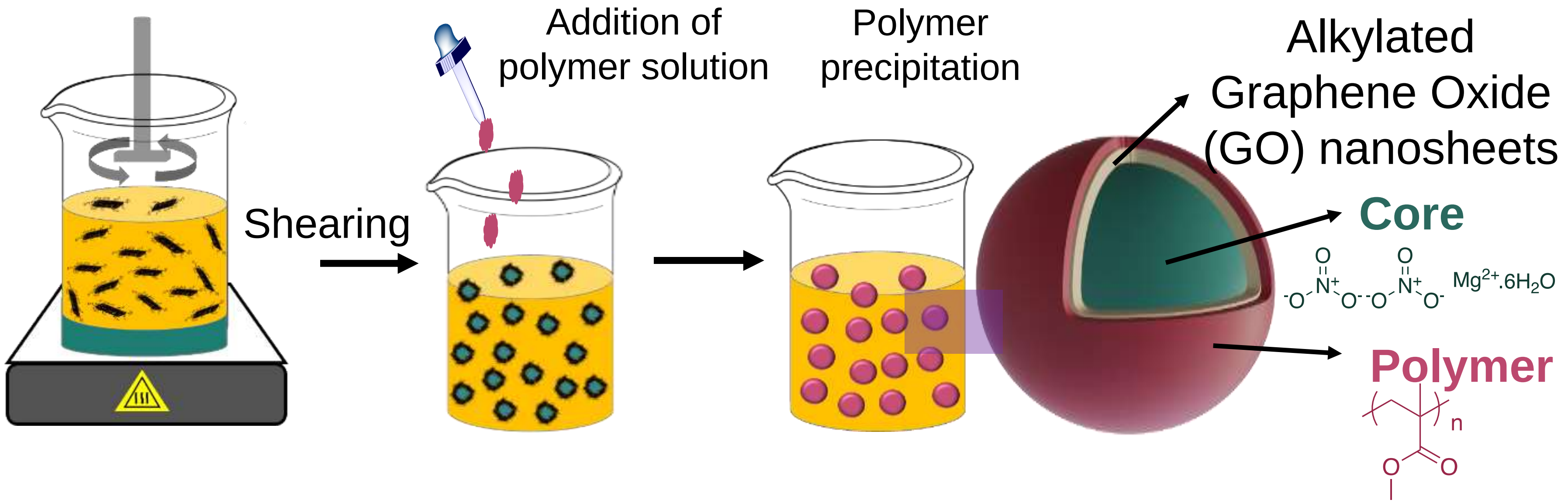
Approach: R4 Microencapsulation of Salt Hydrates

CHALLENGE:

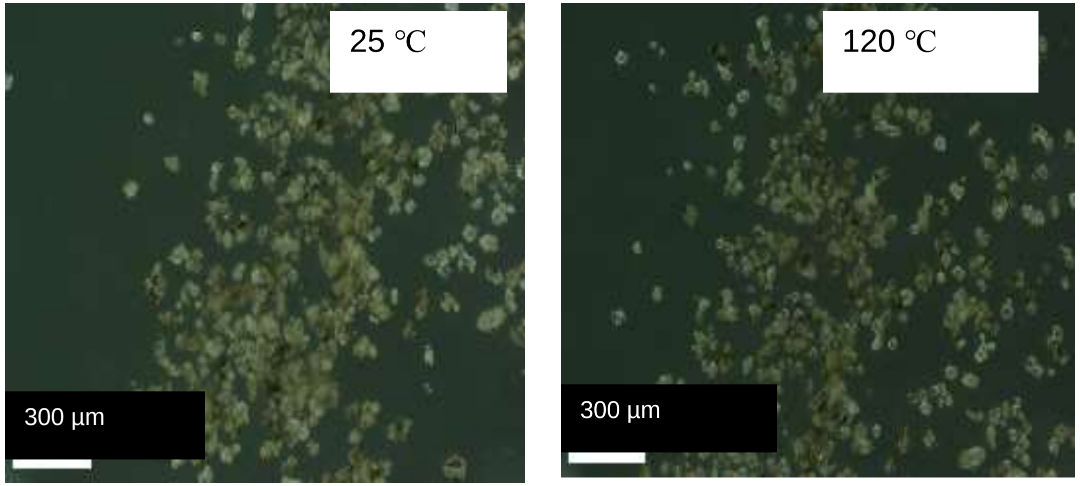
- **Avoid degradation due to water gain /loss from the atmosphere**

APPROACH:

- **PCM-agnostic microencapsulation based on Pickering emulsions**



$Mg(NO_3)_2.6(H_2O)$ Capsules



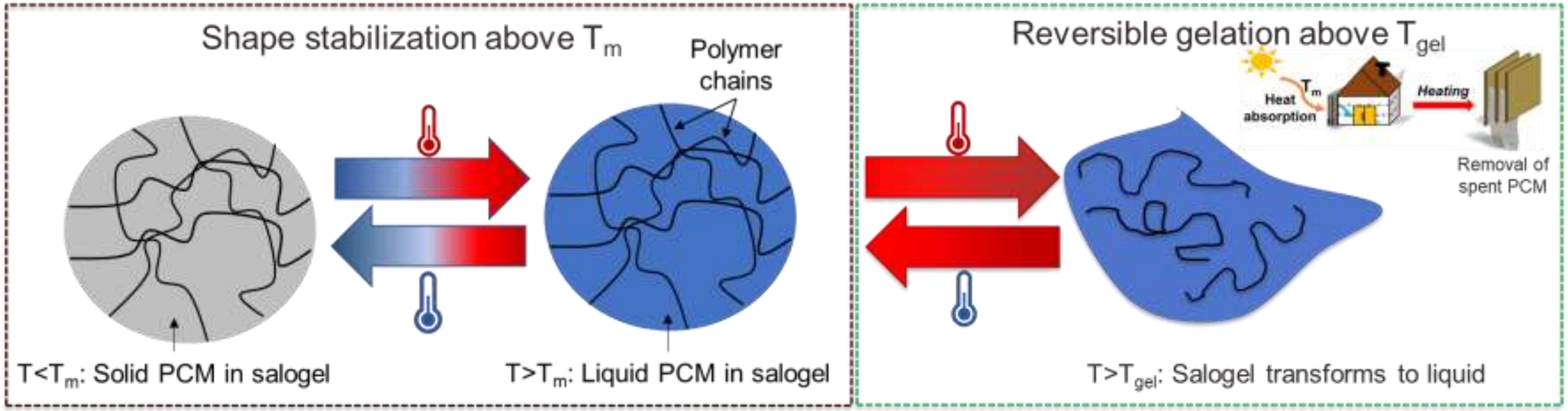
Approach: R5 Thermoreversible Shape Stabilization

CHALLENGE:

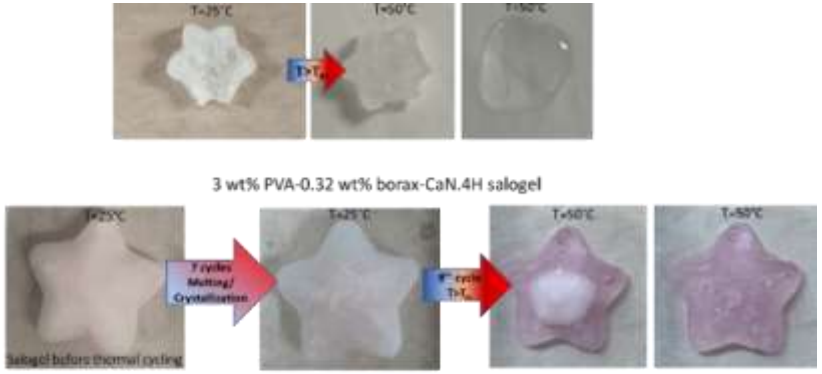
- Avoid phase segregation
- Retain shape to integrate for use in heat exchangers

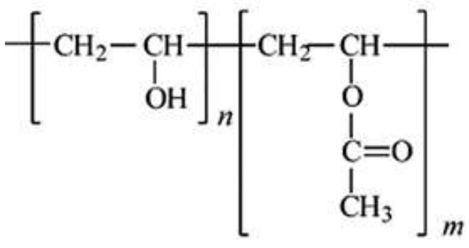
APPROACH:

- Thermoreversible physical gels (Allows for higher-T filling)
- Use hydrogen-bonded-network forming polymers (PVA, PAAM)
- Low polymer concentrations to retain heat of fusion, T_{fus}

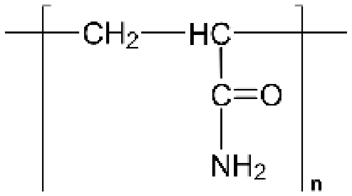


T_m – melting point of salt hydrate PCM
T_{gel} – gel to sol transition temperature





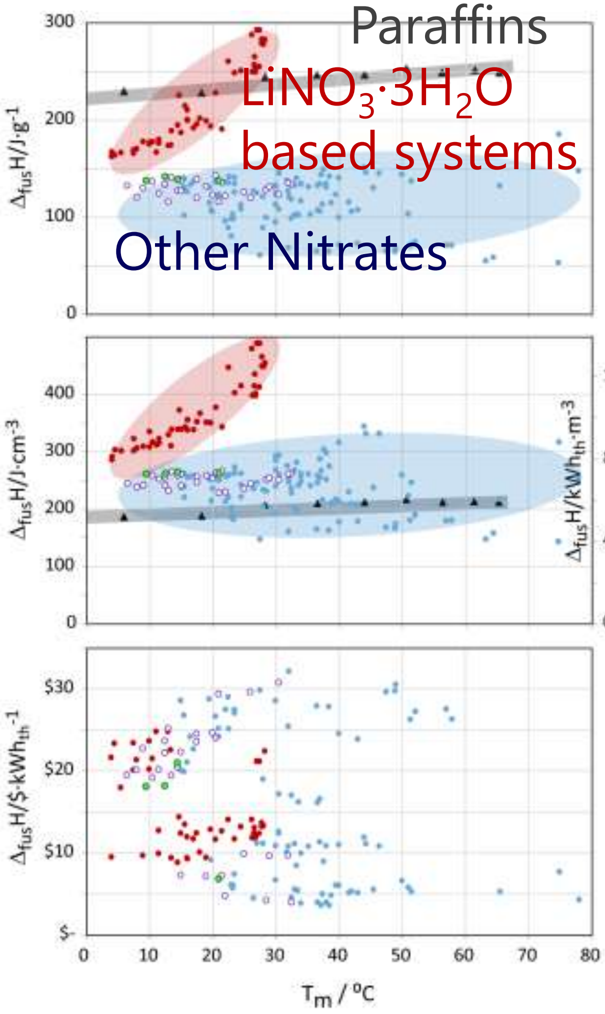
PVA



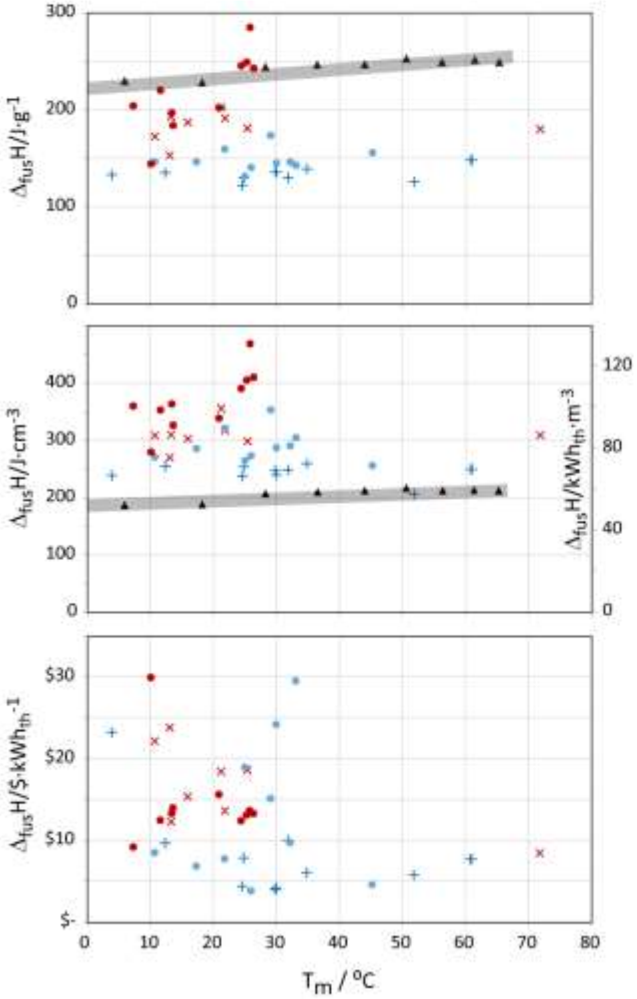
PAAM

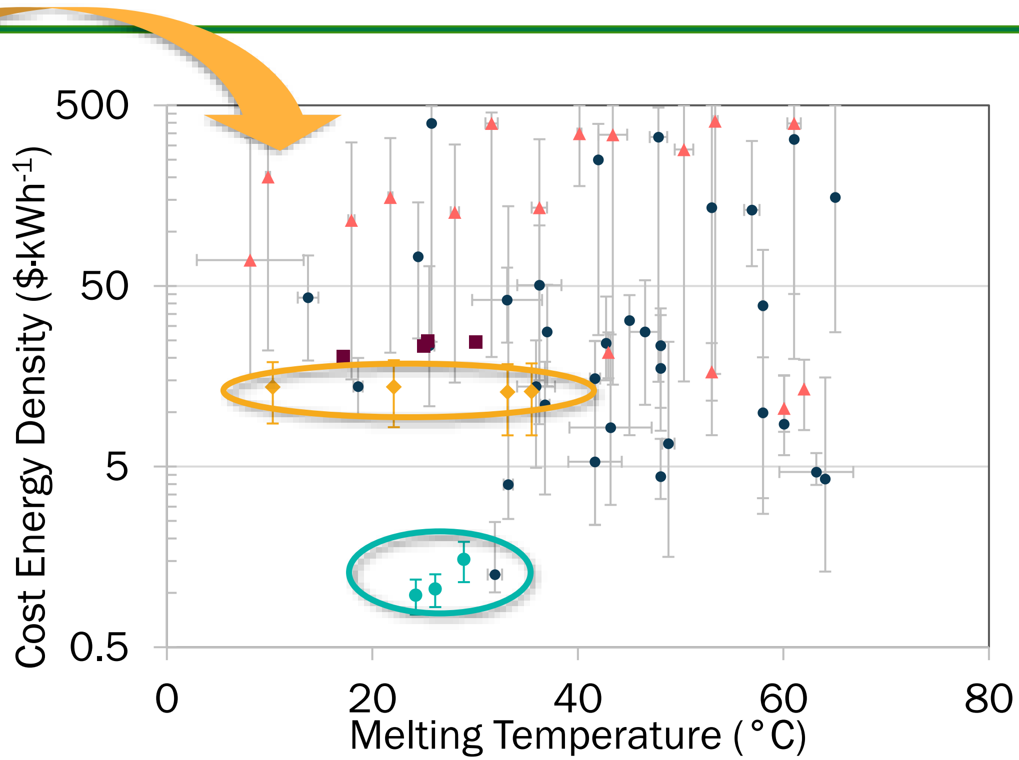
Progress: 1) Newly Developed Eutectic Families

PREDICTED



EXPERIMENTAL

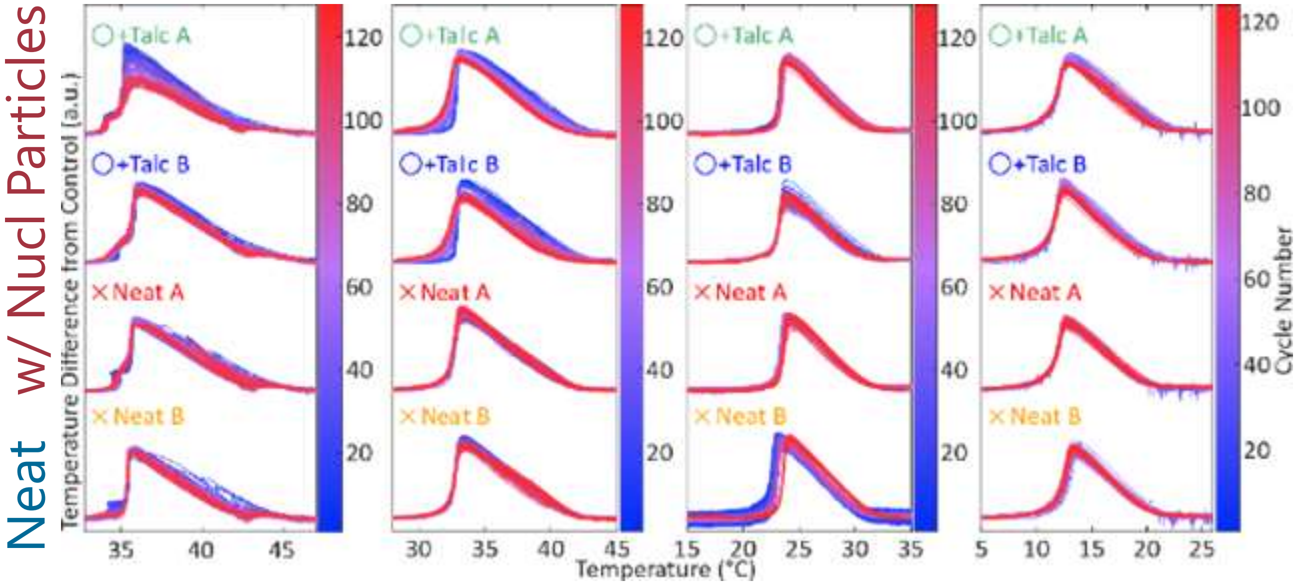




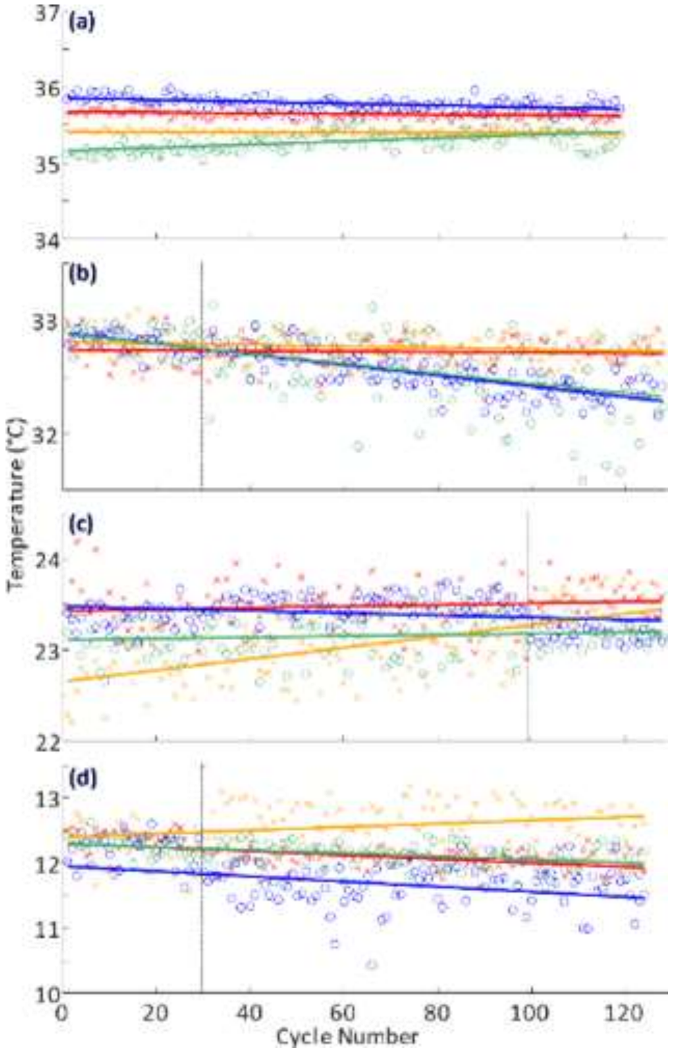
- Family of binary eutectics
  - $Zn(NO_3)_2 \cdot 6H_2O$ – X
  - $CaCl_2 \cdot 6H_2O$ – X
- *Ongoing: Expand to ternary systems*

Progress: 2) Eutectics are Generally Stable to Cycling

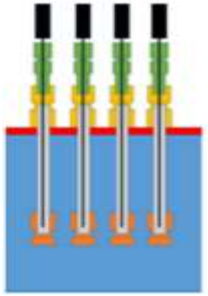
$Zn(NO_3)_2 \cdot 6H_2O$ + X + Y + Z



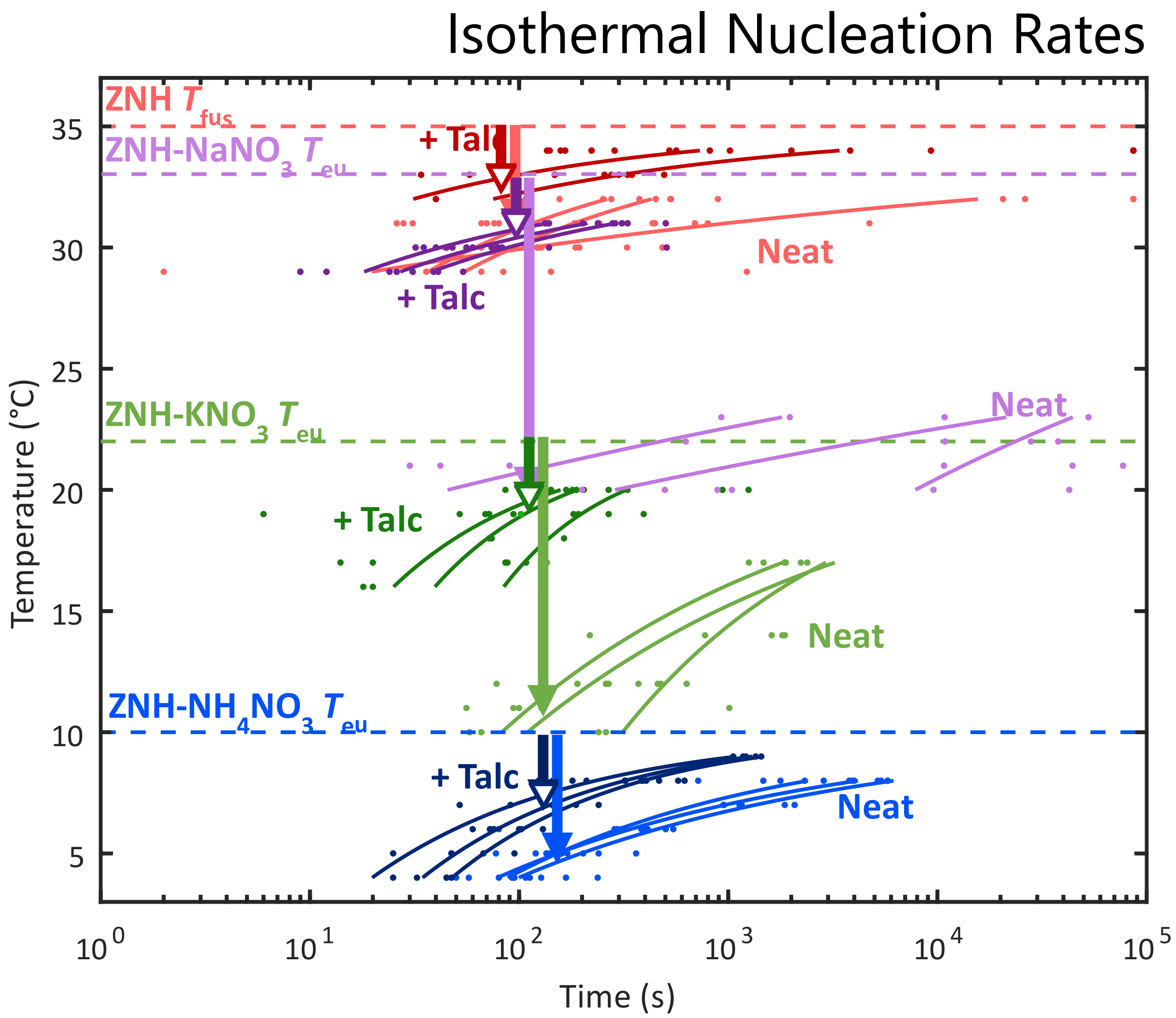
Melting Temperatures:

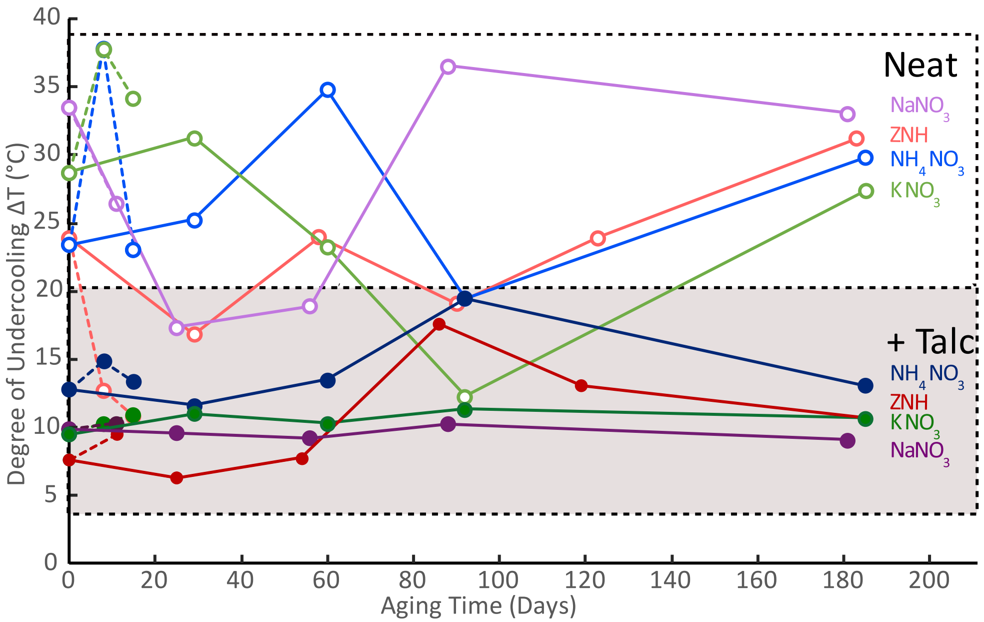


- Stable over 100-200 cycles
- *Ongoing: Evaluate stability of salogels*



Progress: 3) Nucleation Particles Developed for Eutectic Systems

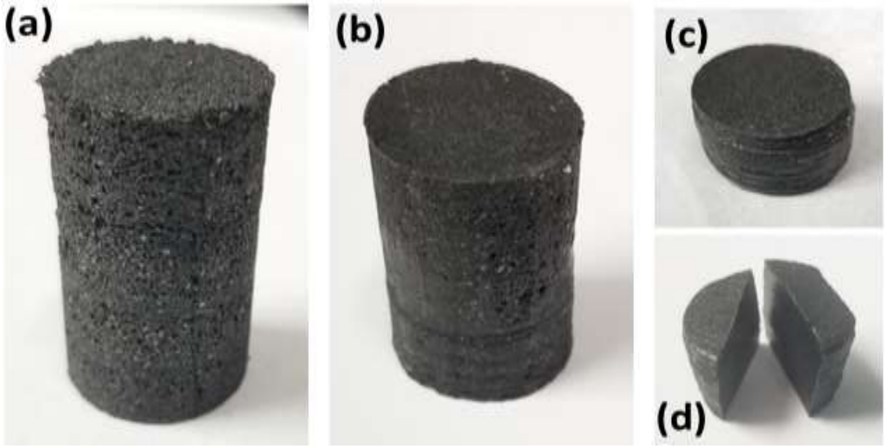




- NPs effective for eutectics
  - Generally can focus on primary phase
- Stable against thermal aging
- Demonstrated for:
  - $Zn(NO_3)_2 \cdot 6H_2O$
  - $CaCl_2 \cdot 6H_2O$

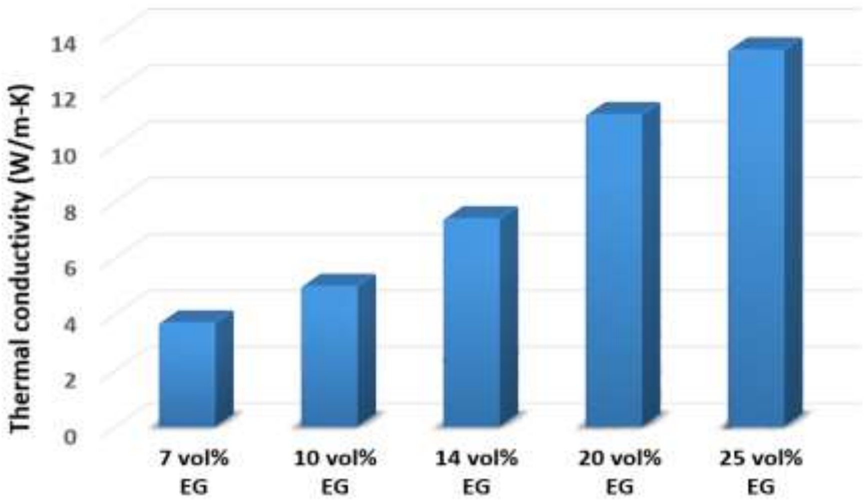
Progress: 4) Stable thermal conductivity enhancement

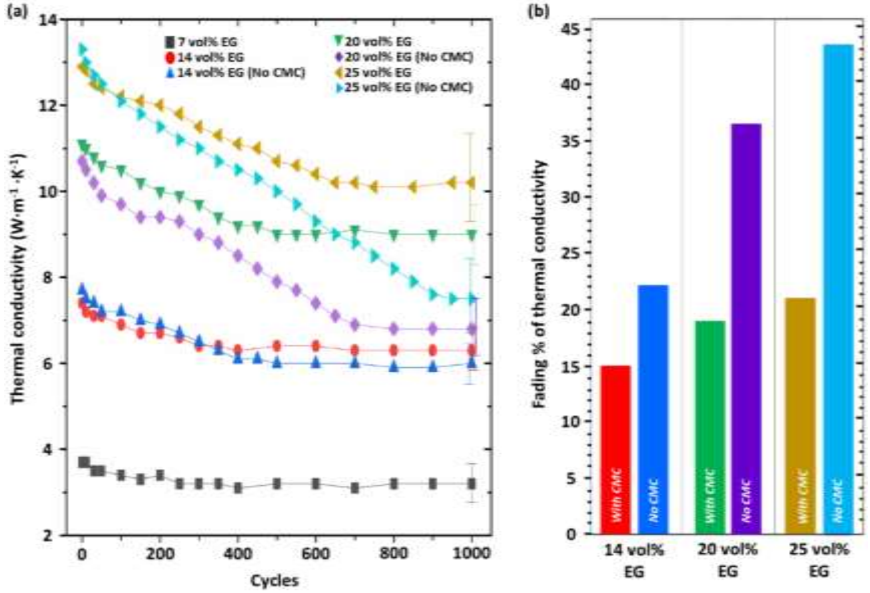
H-bonded network forming polymers



- Infiltrated Salt Hydrates into expanded graphite lattices
- High *k* at low vol. fraction
- Degradation of thermal transport with cycling
    - Less dramatic in presence of thickeners

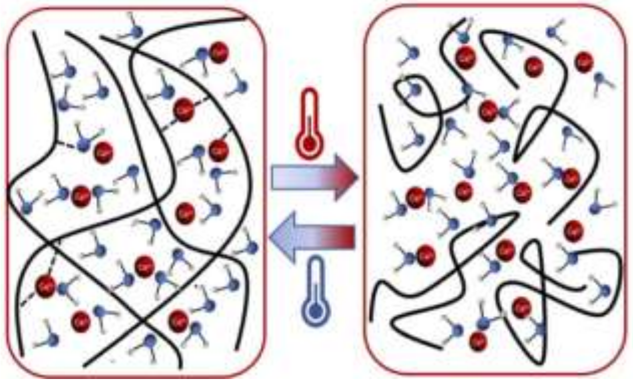
- *Ongoing: Evaluate Roll-to-roll Processing*





Progress: 5) Thermoreversible Shape Stabilization

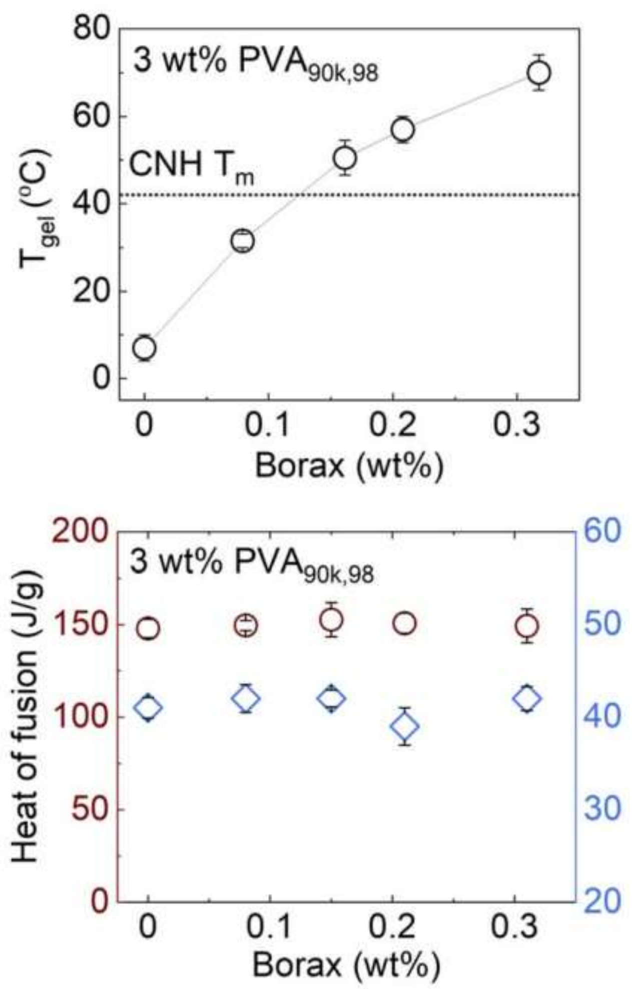
H-bonded network forming polymers



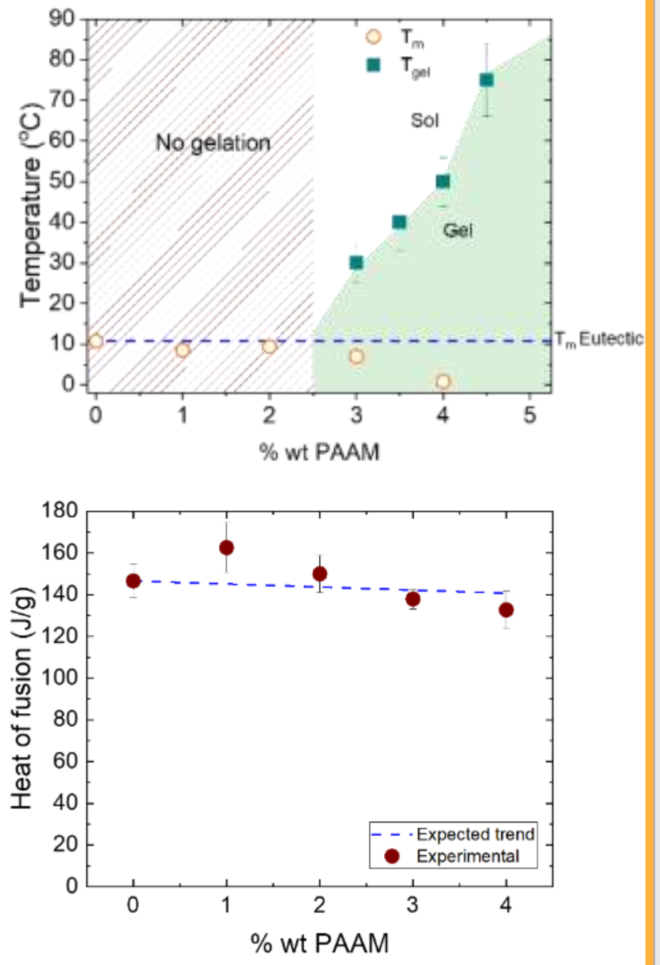
- Effective for multiple nitrate hydrate systems (Zn, Ca, …)
- Equivalent chemistries work for family of eutectics
- Initial success with $CaCl_2 \cdot 6H_2O$

- *Ongoing:*
  - *Polymer blends for stronger gels*
  - *Evaluate the effect of gel in stabilizing robust systems*

$Ca(NO_3)_2 \cdot 4H_2O$



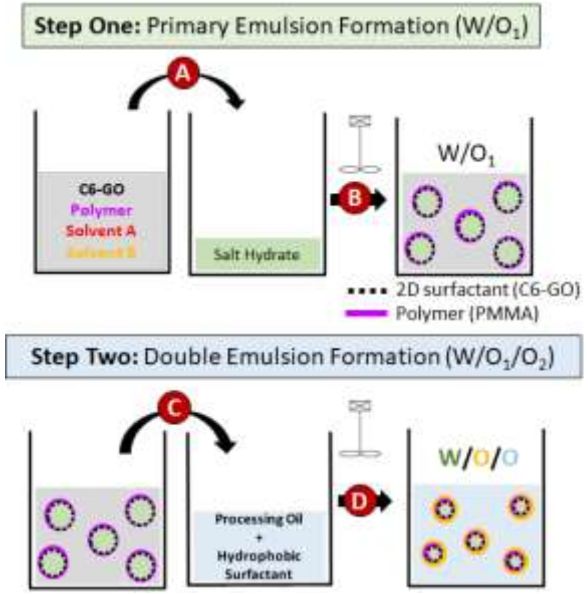
$Zn(NO_3)_2 \cdot 6H_2O + NH_4NO_3$



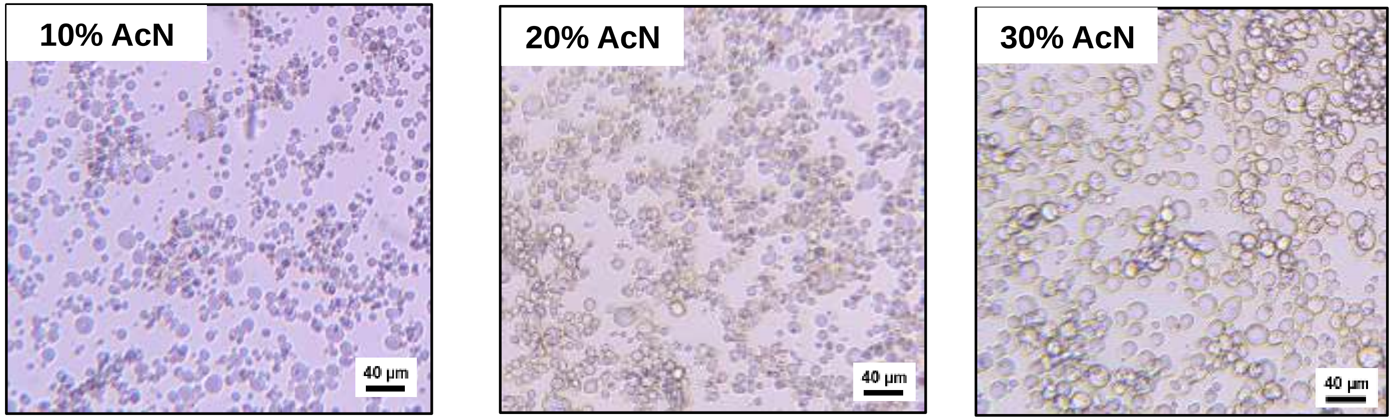
Progress: 6) Microencapsulation of Salt Hydrates

- Switch to double emulsion process: modified 2-step emulsification method **to decrease capsule porosity**

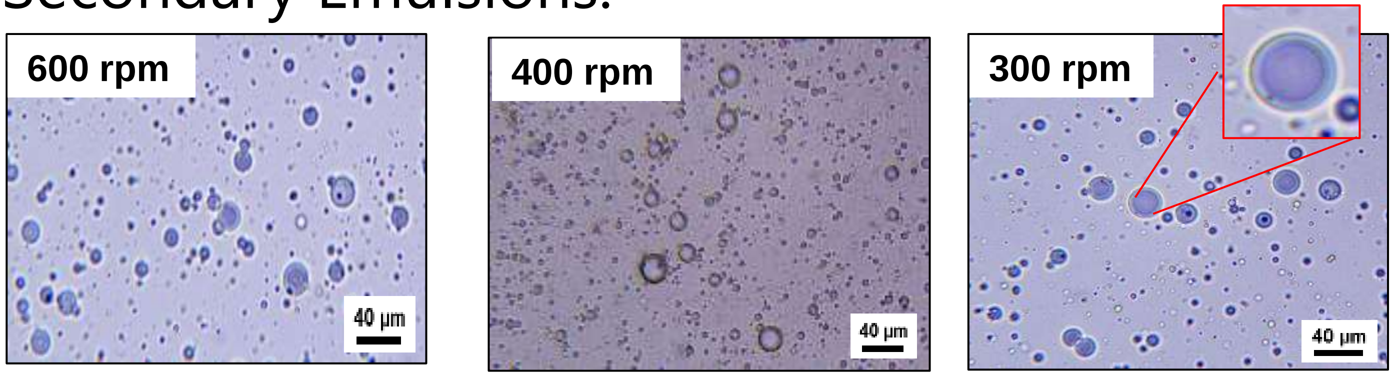
- *Ongoing:*
  - *Evaluate processing conditions to increase yield, dense capsules*



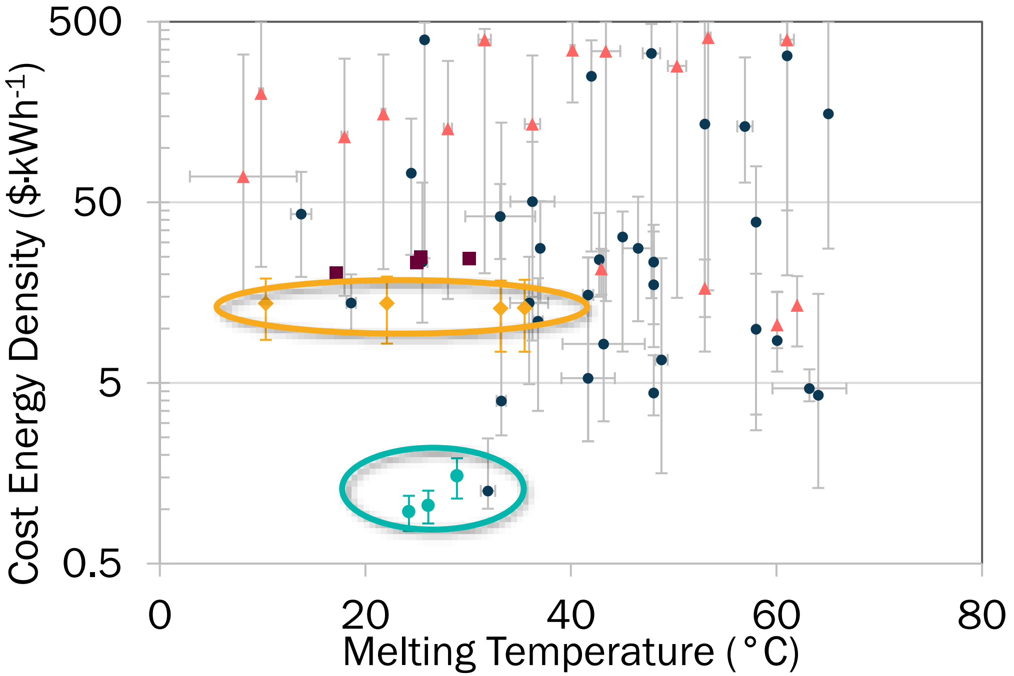
Primary Emulsions:



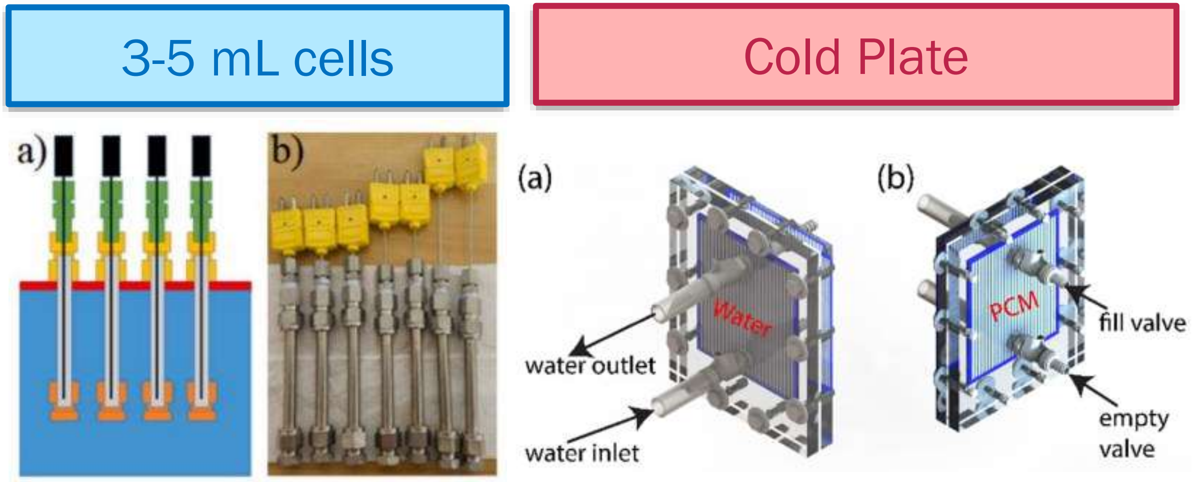
Secondary Emulsions:



Progress and Future Work: Summary



- **Developed 2 families of binary eutectics**
  - $Zn(NO_3)_2 \cdot 6H_2O$ – X
  - $CaCl_2 \cdot 6H_2O$ – X
- **Demonstrated general strategy for cooperative technologies**



ONGOING:

- Evaluate sub-scale robust cycling behavior
- Clarify interactions (+/-) between different constituents
- Pair w/ IAB members or university/ lab partners to demo PCMs in sub- or full-scale battery

Salt Hydrate Eutectic Thermal Energy Storage for Building Thermal Regulation

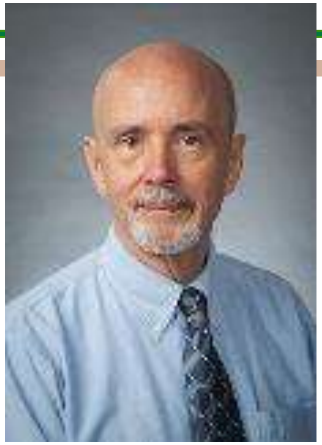

P. Shamberger **R1 / R2**


C. Yu **R3**


E. Pentzer **R4**


S. Sukhishvili **R5**


J. Felts **R6**


C. Culp **R6**

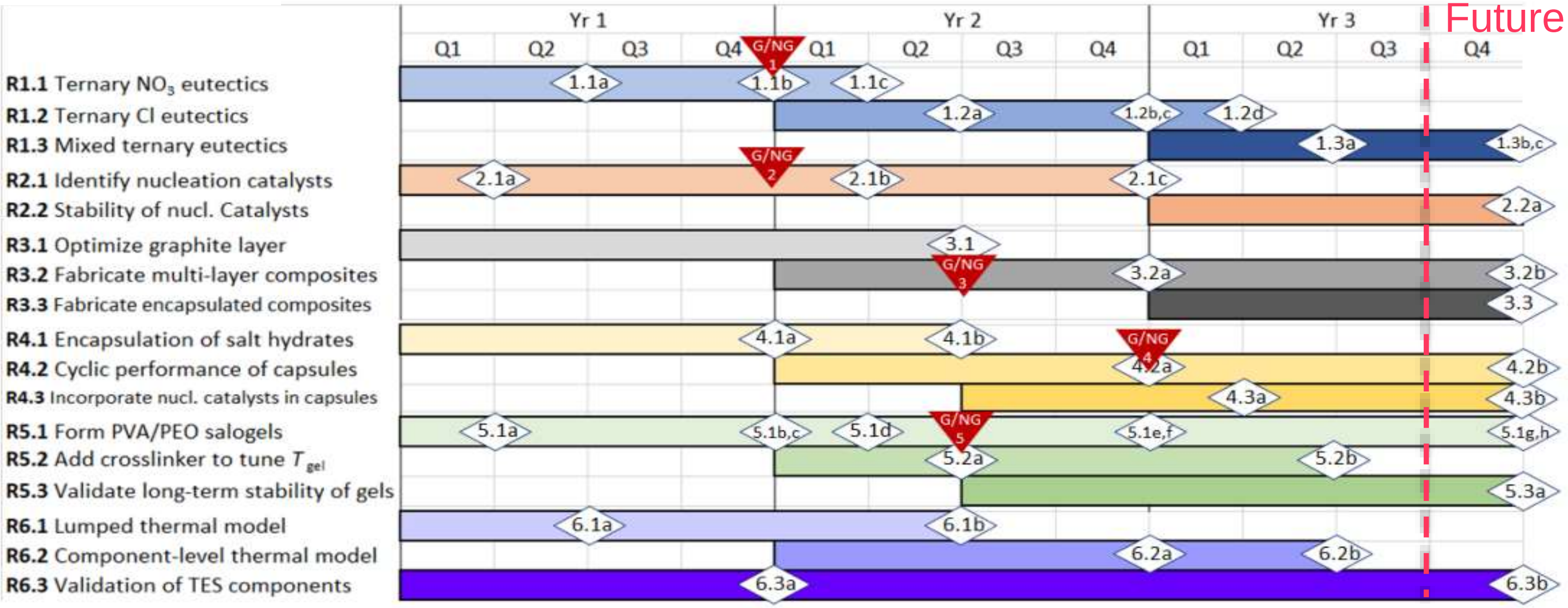
Thank You

Performing Organization(s): **Texas A&M Engineering Experiment Station**
PI Name and Title: **Dr. Patrick Shamberger, Associate Prof.**
PI Tel and/or Email: **979.458.1086 / patrick.shamberger@tamu.edu**
Grant #: **DE-EE0009155**

REFERENCE SLIDES

Project Execution

	Budget History					
	BP 1: 04/2020 – 07/2021		BP 2: 08/2021 – 07/2022		BP 3: 08/2022 – 07/2023	
	DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
Planned:	$466,749.	$163,058.	$533,090.	$110,212.	$546,717.	$113,369.
Spent:	$466,749.	$163,058.	$533,090.	$110,212.	$317,776.	$113,369.



Start date: 04/01/2020

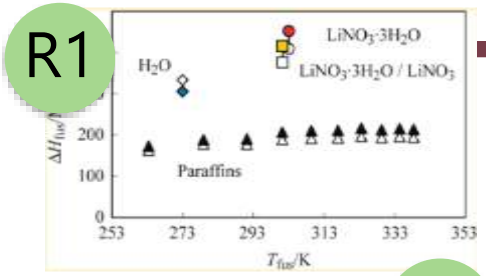
Planned end date: 07/31/2023

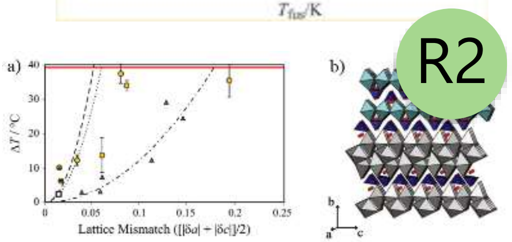
4 mo. no-cost extension at end of BP1 related to slow-start due to limitations in lab associated with COVID protocols. After this, tasks, Go/No-Go's remained on schedule.

G/NG 1	Yr1, Q4	Are the posed PCM discovery approaches converging on acceptable PCMs? Identify eutectic nitrate PCMs which maintain high volumetric density (>80 kWh/m^3), while reducing cost to <$10/kWh.
G/NG 2	Yr1, Q4	Is undercooling generally surmountable in salt hydrate PCMs through ID of appropriate nucleation catalysts? Demonstrate DT < 5 C in (a) ~2 to 5 nitrate hydrate eutectic phases, and (b) ~2 to 5 nitrate chloride eutectic phases of interest.
G/NG 3	Yr2, Q2	Can lamellar graphitic PCM composites increase directional thermal transport, while sustaining repeated melt cycles? Demonstrate effective thermal conductivity of >1 $W{\cdot}m^{-1}{\cdot}K^{-1}$ for >90 vol.% PCM, and survivability for >1000 melt/freeze cycles with minimal degradation of thermal properties.
G/NG 4	Yr2, Q4	Are capsules of salt hydrates with less than 10 vol% shell stable to extended aging? Microencapsulation of target salt hydrate phase with >95% yield, and <5% degradation of DH_{fus} over extended aging (up to ~3 to 6 mo.).
G/NG 5	Yr2, Q2	Are polymer-based salogels capable of shape stabilization for both nitrate and chloride hydrate eutectics? Demonstrate thermo-reversible gelation in salogel consisting of >90 vol.% PCM for proto-typical nitrate hydrate eutectic and chloride hydrate eutectics.

Team

Salt Hydrate Eutectic Thermal Energy Storage for Building Thermal Regulation





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C. Yu **R3**

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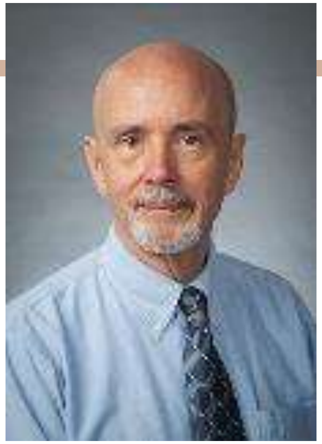
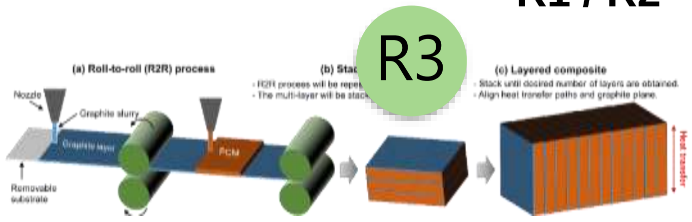
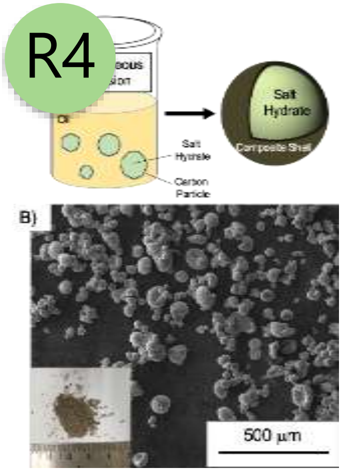
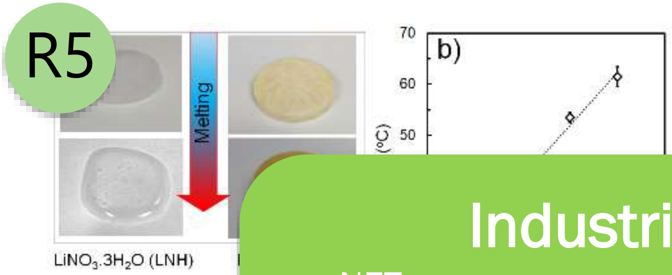
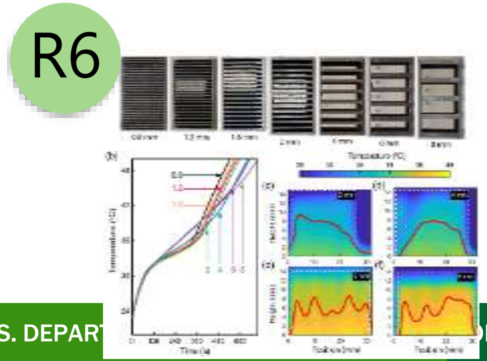


C. Culp **R6**









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