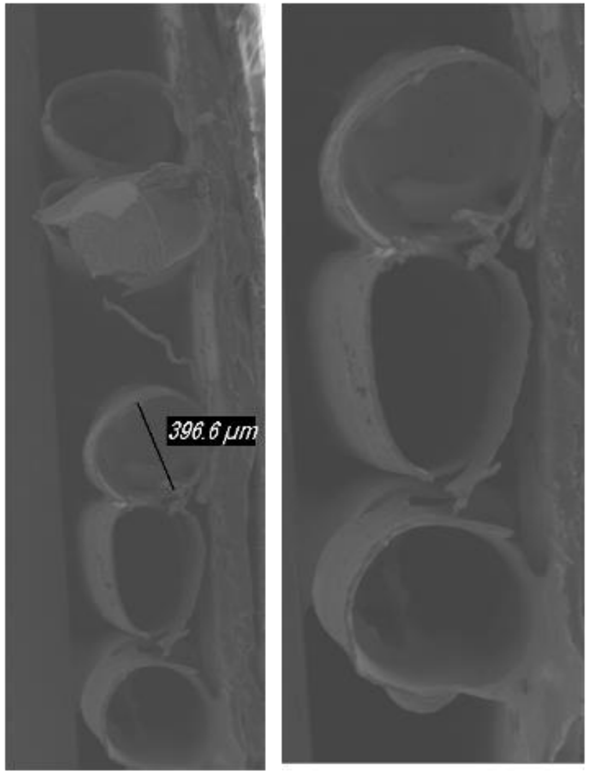
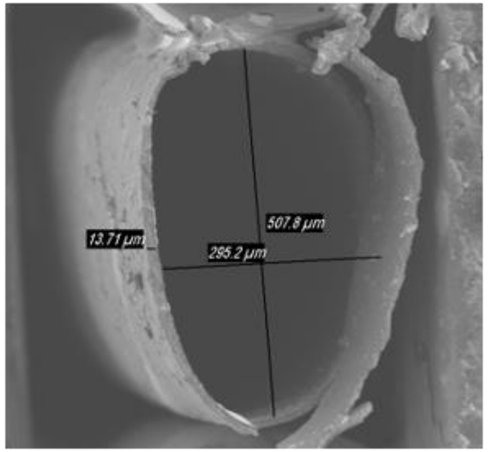
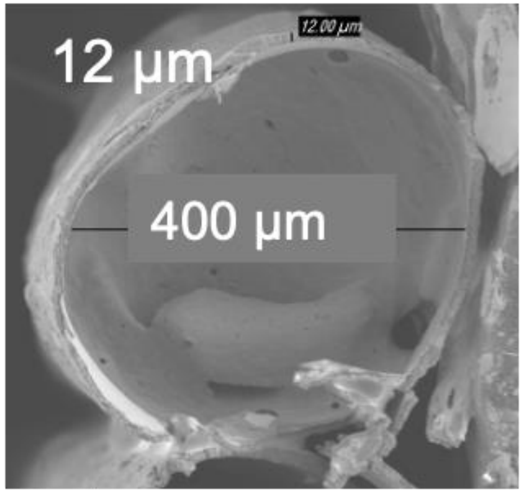
A New Approach to Encapsulate Salt Hydrate PCM





Core diameter: 400 µm
Core-shell diameter: 412 µm



Coating: 3-5%
Salt hydrate: 95-97%

ORNL and Phase Change Energy Solutions
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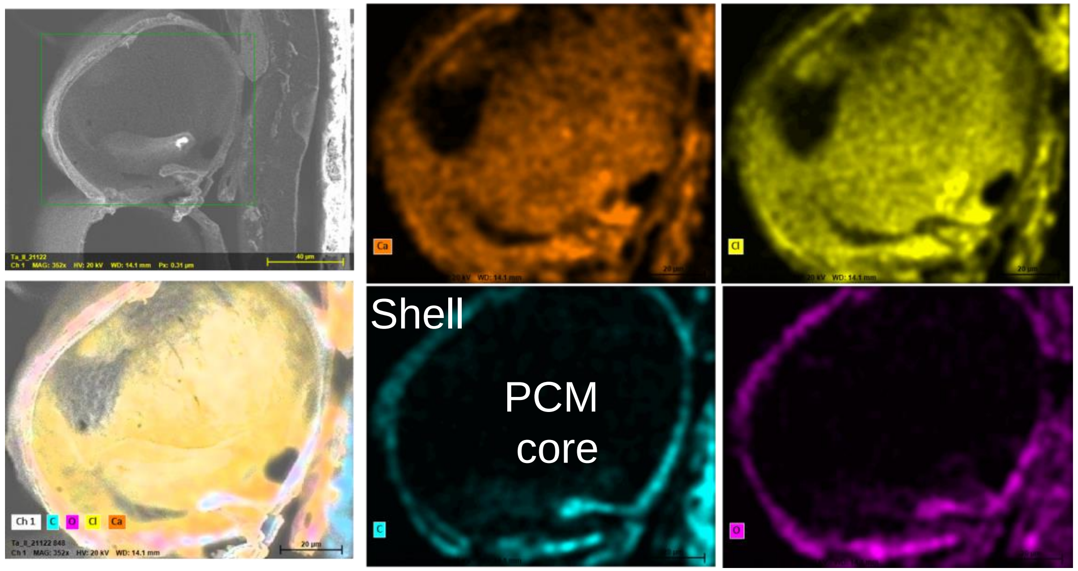
WBS # 3.2.6.108, FOA Project # 2090-1591

Project Summary

Objective and outcome

The project aims to address the long-standing problem of encapsulation of salt hydrate PCMs. The project outcome will have a low cost and scalable encapsulation process that can provide encapsulated salt hydrates with high energy densities, and minimal issues of supercooling and phase segregation.



Team and Partners

OAK RIDGE
National Laboratory

PHASE CHANGE
SOLUTIONS™

Stats

Performance Period: 10/01/2020 – 09/30/2023

DOE budget: $1,200,000, Cost Share: $300,000

Milestone 1: Demonstrate successful PCM encapsulation (Achieved)

Milestone 2: Achieve salt hydrate loading capacity ≥ 90% (Achieved)

Milestone 3: Achieve supercooling temperature ≤ 2 ºC (in progress, 3.6 ºC now)

Problem

- ☐ 42 million (12.8% of population) US households are below the poverty line, and lowering their utility bill will be a big help
- ☐ Utility bills can be reduced by upgrading appliances, less use of appliances, better thermal insulation, or thermal energy storage (e.g., by using phase change materials; PCMs)
- ☐ The use of salt hydrate PCMs is hindered by several technical challenges, e.g., leakage, low charge/discharge rate, supercooling, and phase segregation
- ☐ Microencapsulation can address most of these challenges, But currently it is hard to microencapsulate salt hydrate PCMs
- ☐ Project focused on addressing this issue of encapsulation of salt hydrate PCMs (inorganic PCMs)

Organic PCMs (e.g., Paraffin)

- ➢ Expensive
- ➢ low energy density

X

Inorganic PCMs (e.g., salt hydrates)

- ➢ low cost
- ➢ higher energy density

✔

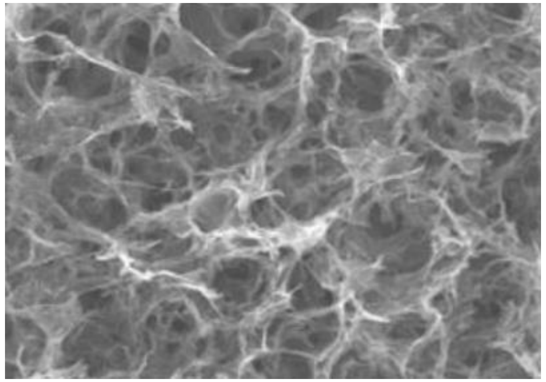
Alignment and Impact

- ☐ Support rapid decarbonization of U.S. Buildings in line with economywide net-zero emissions by 2050
- ☐ Reduce onsite energy use intensity in buildings 30% by 2035 and 45% by 2050, compared to 2005
- ☐ Will contribute to EERE/BTO's mission of lowering the CO_2 emissions by lowering the electricity consumption in households
- ☐ The project outcome is aiming to address the challenge of salt hydrate PCM encapsulation, which will allow the widespread use of salt hydrate PCMs in the building envelope and other building related applications
- ☐ The project outcome will provide better volumetric and gravimetric energy density in comparison to the conventional PCM encapsulation approaches but at lower costs
- ☐ The project's market impact will be estimated by calculating the possible energy savings that can be achieved by incorporating these encapsulated salt hydrate (PCM) fibers in the building envelope

Approach: Current solutions and their challenges

- ☐ Form stable approaches
  - ➢ Composites with conductive porous materials (e.g., expanded graphite, graphene flakes)

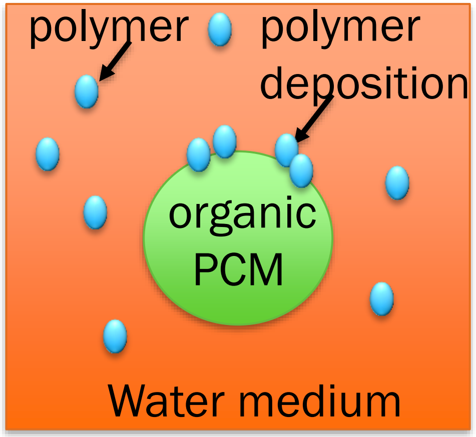
  Challenges
  - ➢ Not suitable for envelope applications
  - ➢ Low volumetric energy density



Graphene flakes/ porous network

- ☐ Encapsulation approaches
  - ➢ Emulsification
  - ➢ In-situ polymerization

  Challenges
  - ➢ Scalability
  - ➢ Reproducibility
  - ➢ Low (≈ 50%) volumetric energy storage capacity



Emulsification/in-situ polymerization of organic PCM

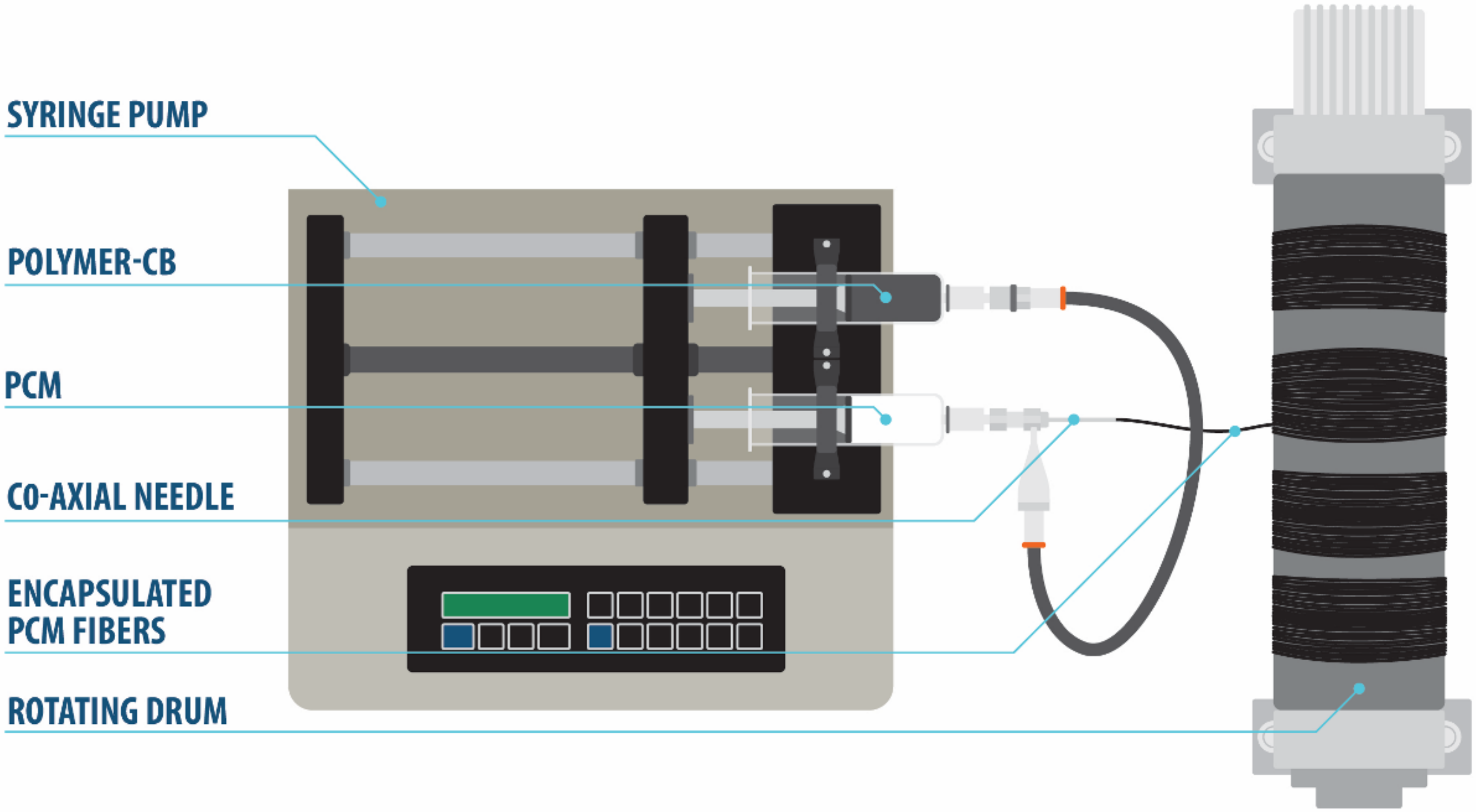
Works for organic PCMs but not for salt hydrate PCMs, as salt hydrates are soluble in water

No reliable encapsulation strategy for salt hydrates

Our approach: Modified co-axial electrospinning

Benefits

- ☐ Lower cost
- ☐ Better control of coating composition
- ☐ Better thermal conductivity
- ☐ Better energy density
- ☐ Reproducible/quality control
- ☐ Scalable and easily adaptable for industry scale production
- ☐ Easy to incorporate in current building materials/products



Schematic of fiber encapsulation setup

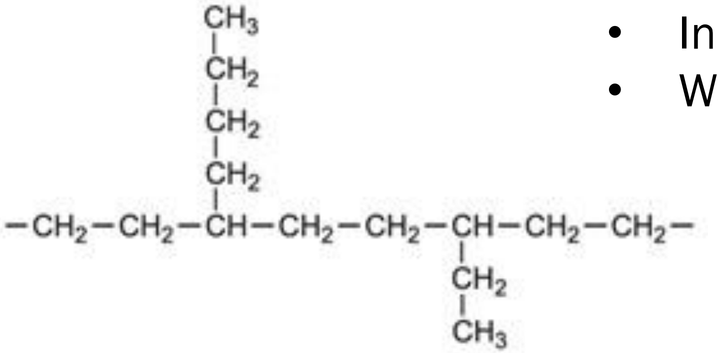
Approach: Achieving project targets

1. **Cost**
   - Minimize use of electricity
   - Use of inexpensive materials

2. **Thermal conductivity**
   - Add high thermal conductivity additives

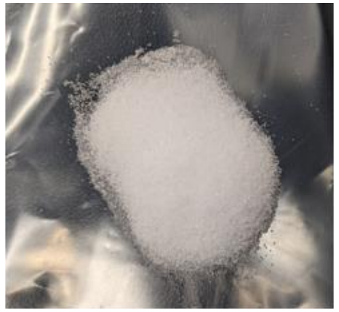
3. **Supercooling**
   - Add nucleation agents

4. **Energy density**
   - Increase the salt hydrate core/polymer shell ratio



Low/high-density polyethylene

- Inexpensive
- Water repelling



Nucleating agent (SrCl2 • 6H2O)

Carbon black/graphite powder

Thin coating

Thick salt hydrate core

Approach: Key risks and their mitigation

Risk 1. Leakage

- Use of water insoluble coatings--achieved
- Optimization of coating composition

Risk 1. Water vapor escape

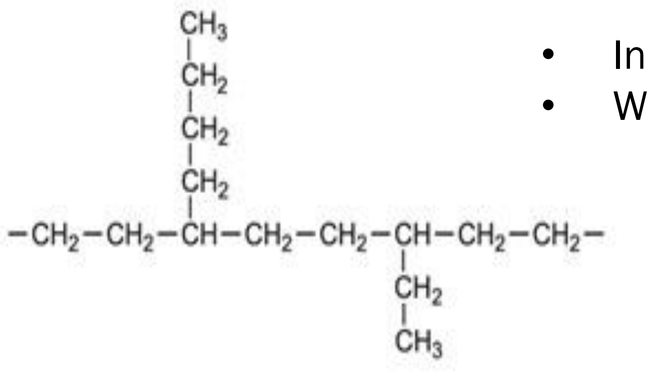
- Use of water insoluble coatings--achieved
- Coating thickness optimization
- Gradient coatings

Risk 3. Phase segregation

- Thickening agents--achieved
- Fumed silica
- cellulose
- expanded graphite

Risk 3. Flexibility of fibers

- Use of flexible polymer coatings--achieved



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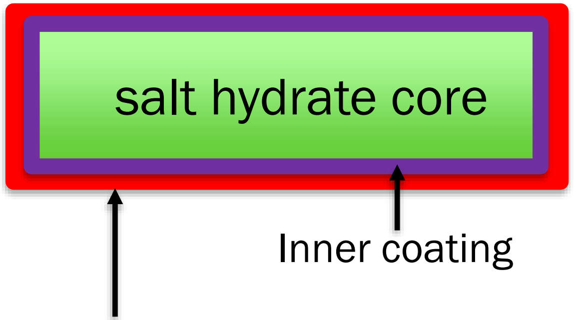
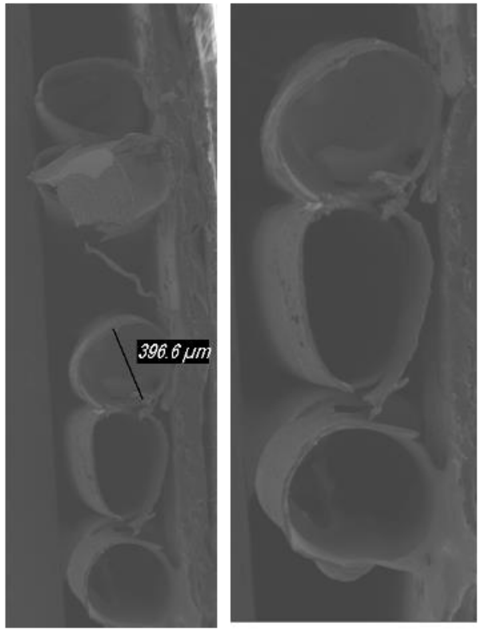


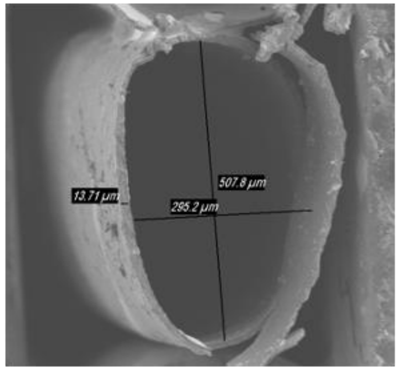
Fumed silica

Approach: Commercialization and stakeholder engagement

- ☐ Phase Change Energy Solutions (PCES) has performed initial cost analysis and is working to incorporate these encapsulated PCM fibers into their own products, and commercialize those
- ☐ Non-provisional patent *(Application# 18/119,890)* has been filed
- ☐ Team has involved ORNL technology to market manager for presenting the work at various platforms, e.g., TechConnect Conference
- ☐ Some startup companies showed interest in these encapsulated fibers for different applications
- ☐ Submitted R&D 100 award application
- ☐ Several manuscripts are in the process of publication

Progress: Encapsulation with 95% volumetric energy density





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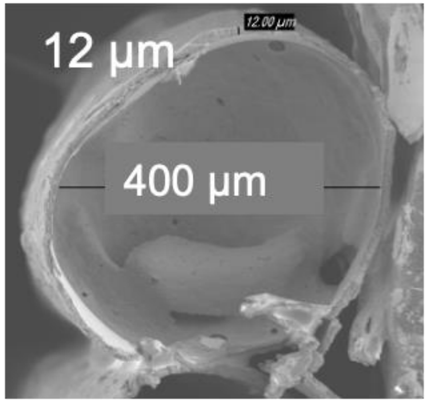
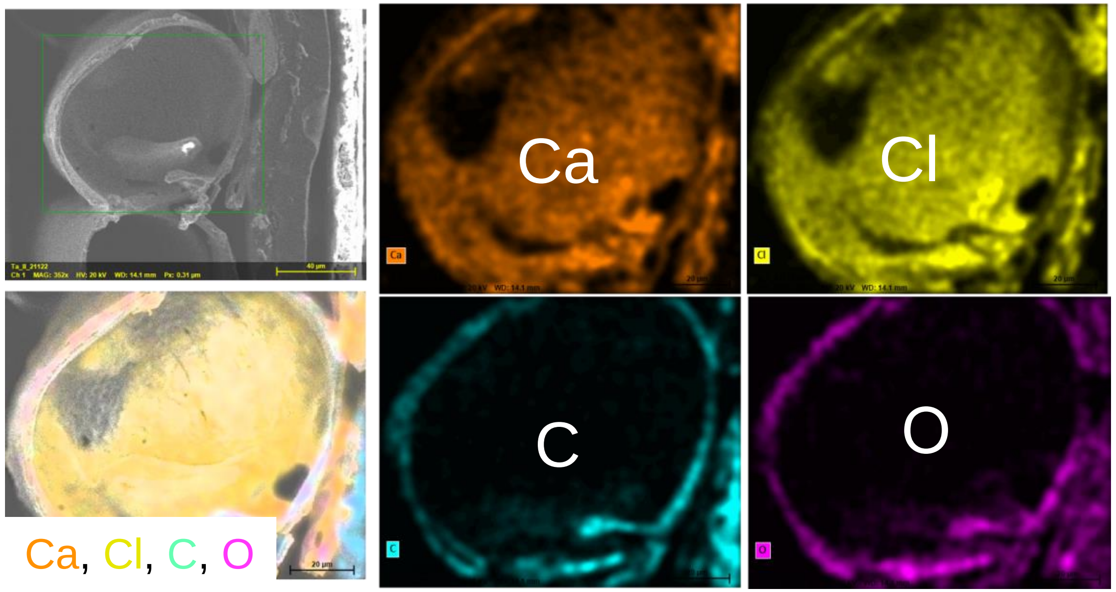


Theoretical loading: 95%
Experimental loading: >90%

Coating: 3-5%
Salt hydrate: 95-97%

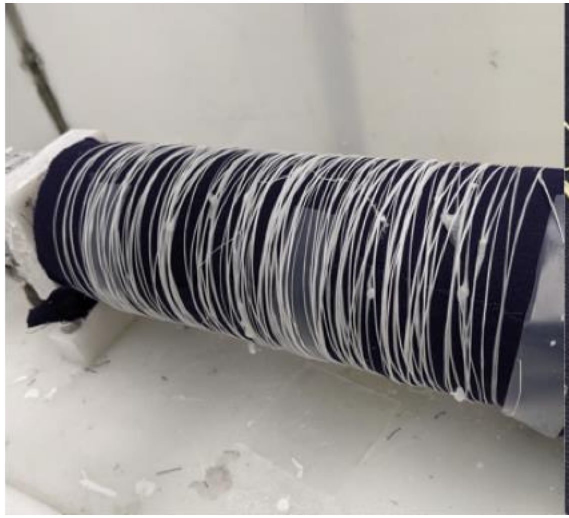
EDX maps showing salt hydrate in core and polymer in shell



30-50 g

Fibers without and with carbon black in the shell

Progress: Flexible fibers with hydrophobic coating



Fibers on drum

Fragile fibers

>90% $CaCl_2 \bullet 6H_2O$
≤10% Polymethyl methacrylate (PMMA) shell

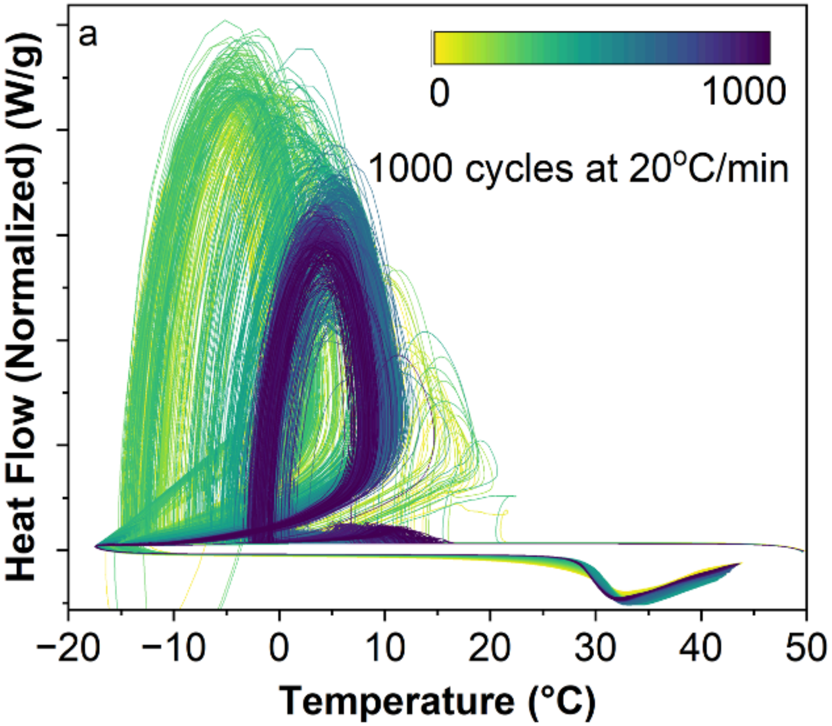
Outcome: Nice encapsulation but somewhat fragile fibers

- ☐ Flexible fibers are easy to handle
- ☐ Easy to incorporate in other products

>90% $CaCl_2 \bullet 6H_2O$
≤10% polyacrylonitrile (PAN) shell

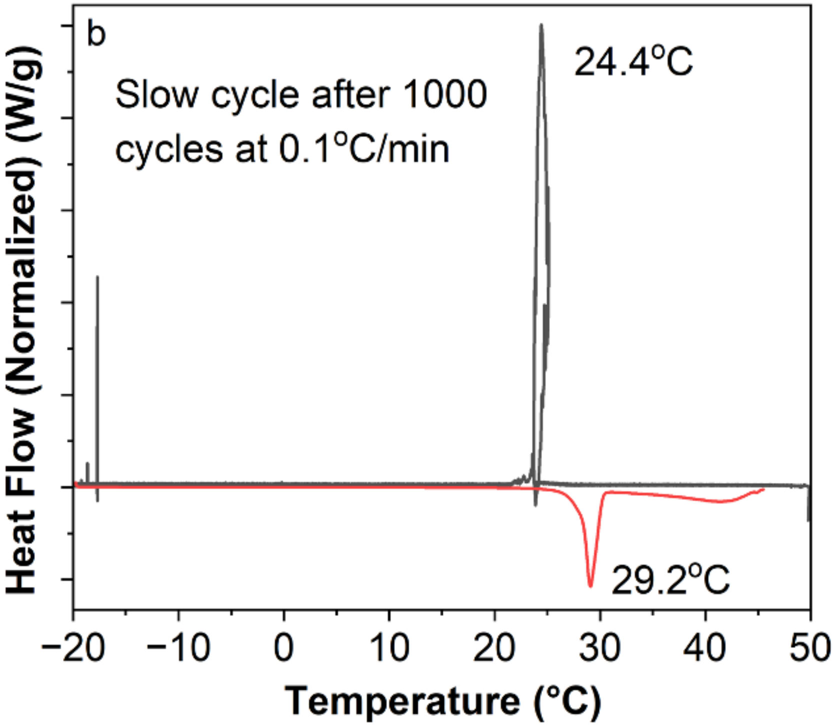
Flexible fibers

Progress: 96.5% energy density retained after 1000 thermal cycles



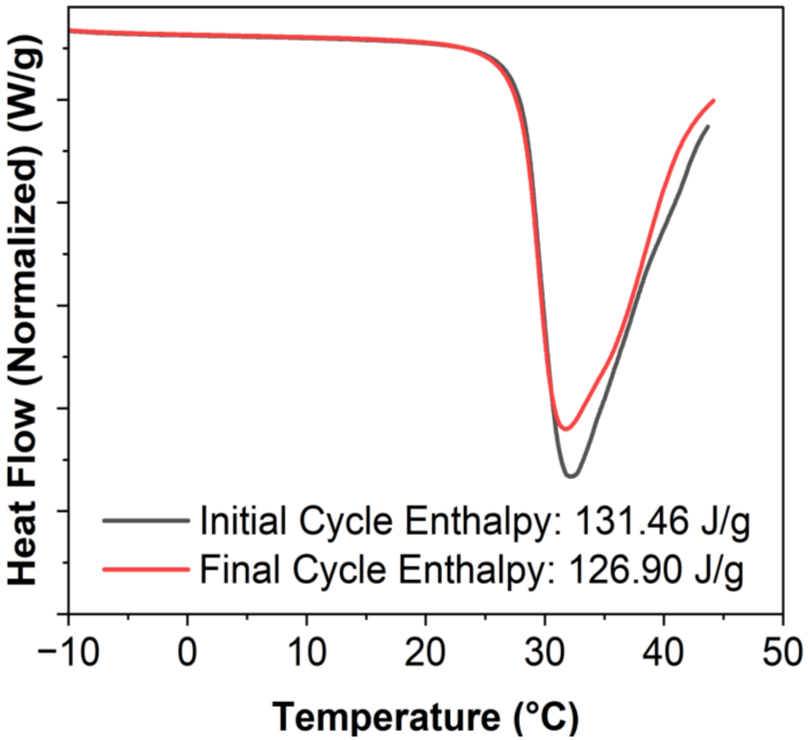
☐ Crystallization exotherm drops in the initial cycles, but reaches a stable temperature >0°C.

☐ Stability is maintained over 1000 cycles indicating the higher crystallization temperature afforded by $SrCl_2$ does not compromise the long-term stability of the PCM composition



☐ A slower heat/cool cycle on the same sample subjected to 1000 cycles indicated a crystallization temperature of 24.4°C.

☐ Supercooling temperature ≈ 3.6 °C



☐ The melt transition enthalpies on the initial and final cycles were compared.

☐ The calculated energy density retained after the end of cycling steps is about **96.5%** of the initial cycle.

Progress: Minimal leakage (<1%) of salt hydrate PCM through the fiber shell after 1000 cycles

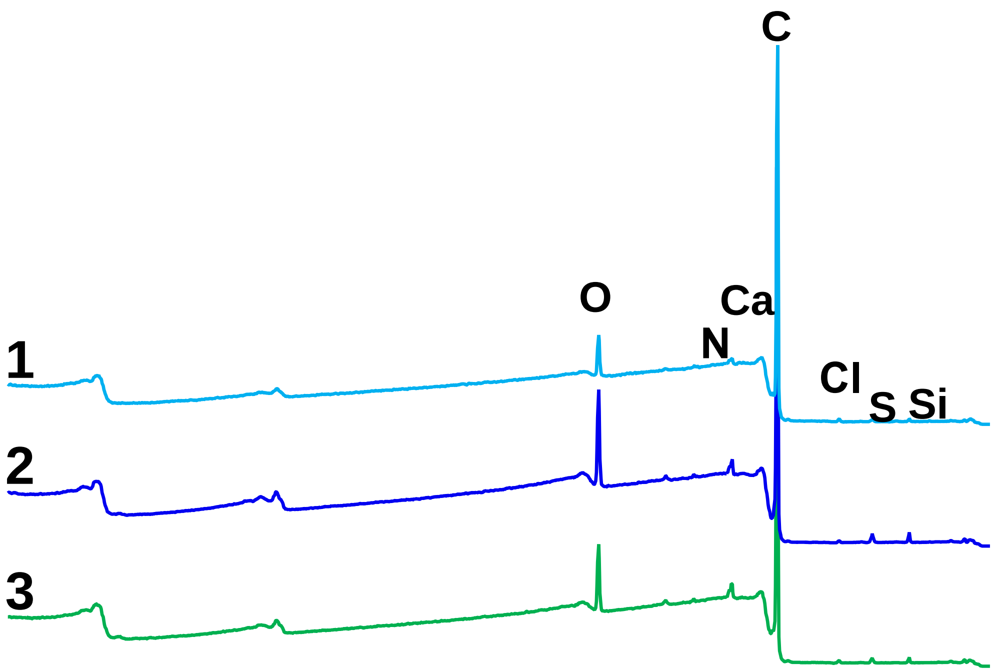
PCM 1000 cycle test

Procedure

- Fibers were coated with a thin layer of polystyrene
- Coated fibers underwent 1000 cycles of -20 - 40 ° C at 20 ° C/min
- After cycling, chemical characterization of sample surfaces were characterized using XPS

Results

- Low N at.% confirms consistent polystyrene coating
- Low Ca, Cl surface concentrations confirm limited salt diffusion through outer shell
- Combined XPS and DSC confirms salt hydrate stability through 1000 cycles



Surface Composition (at.%)

Sample#	C	O	Ca	Cl	Si	N	S	Al
1	89.7	6.9	1.0	0.4	1.3	0.6	0.1	0.0
2	86.5	9.7	0.9	0.2	2.1	0.4	0.1	0.1
3	93.1	4.7	0.5	0.3	0.7	0.4	0.1	0.3

Polymer (PS)

(SiO_2), surface hydroxide

Surface salt

(SiO_2), surface hydroxide

Limited PAN signal

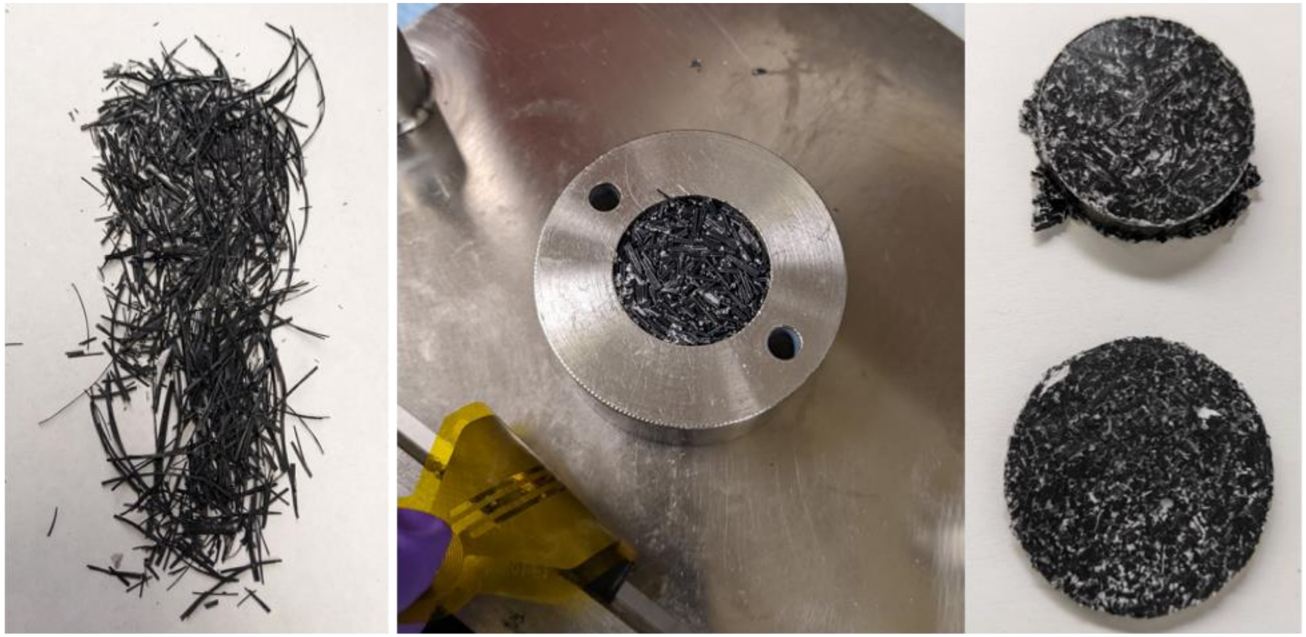
Progress: Good thermal conductivity and lower water vapor loss

☐ Less than 1 wt% (water vapor) loss after 1000 thermal cycles

☐ Thermal conductivity can be further increased or decreased

☐ Shell is stable up to 60 ºC

☐ Some cracks were observed at 80 ºC when kept for a month



Thermal conductivity ≈ 0.5-0.55 W/m•K

Progress: Estimate of manufacturing costs excluding labor

Entity	Vendor price/unit	Estimated Required amount for 1 kWh	Estimated cost ($)
$CaCl_2 \bullet 6H_2O$	$250/ton	21-25kg	$5.25
Polymer (low density/high density polyethylene):	800-1000/ton	5-10% polymer coating	$1.00
Organic solvent	$1/L	10 L (assuming 80% recovered)	$2.00
Solvent Retrieval	$0.01/L	8 L recovered at 80% efficiency and $0.01/L retrieval cost	$0.80
Electricity	0.10/kwh	1kWh	$0.10
		Total	$9.10

Future work

What has been achieved

- PCM encapsulation with a low cost and scalable strategy
- PCM encapsulation with ≥ 95% PCM loading capacity
- Targeted thermal conductivity (≈0.55 W/m•K)
- Minimal or no leakage of PCM material through fiber shell
- Minimal evaporation of water vapors
- Supercooling 3.6 ºC
- 95% energy density retention after 1000 cycles
- >90% experimental energy density

Remaining work

- Lower the supercooling temperature from 3.6 ºC to 2 ºC

Potential work beyond this project

- CRADA project for scale up for commercialization

Thank you

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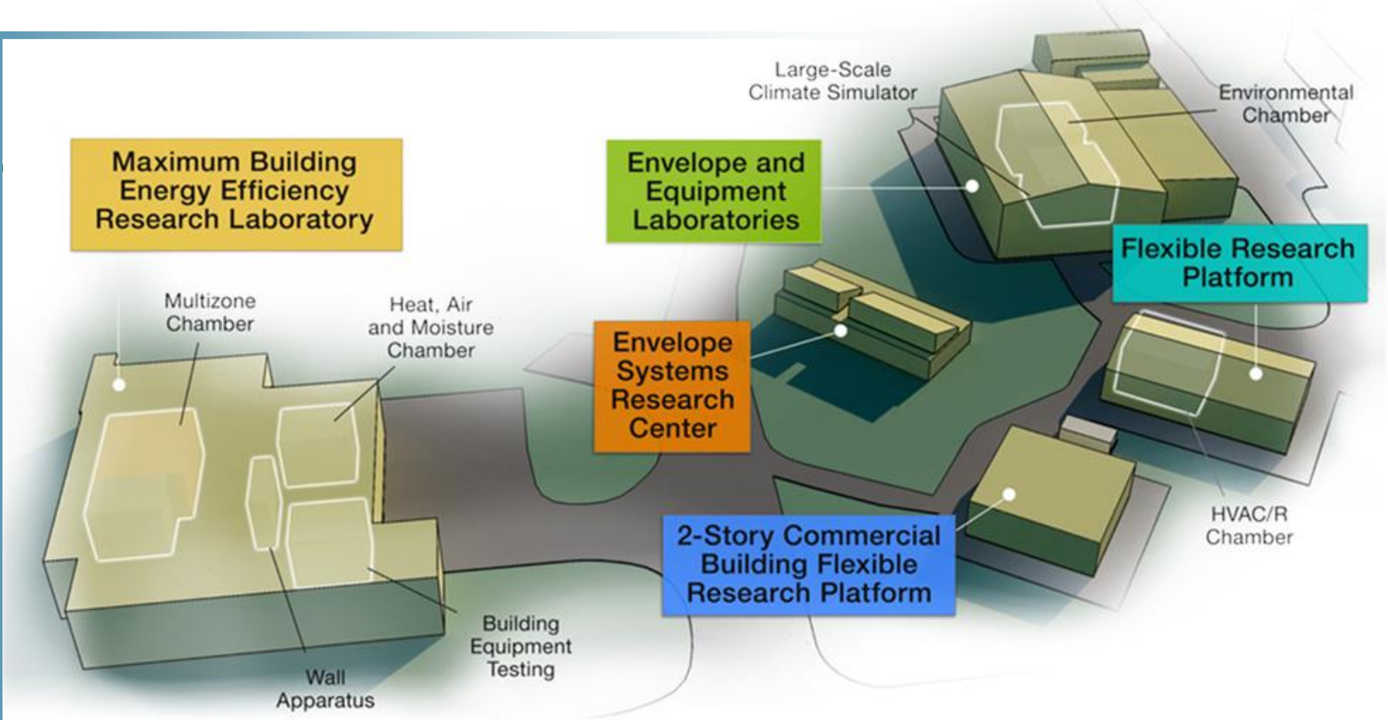


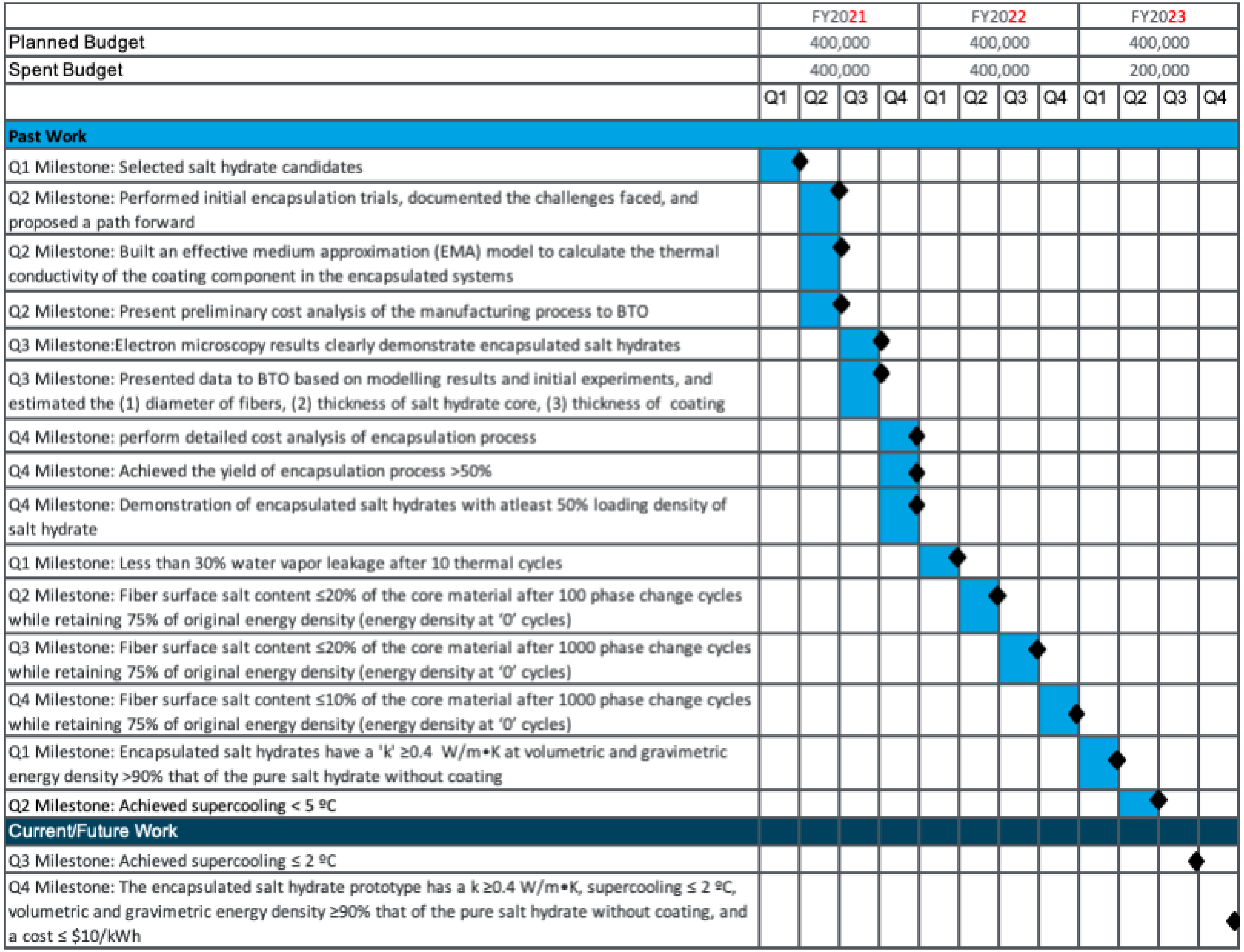
ORNL’s Building Technologies Research and Integration Center (BTRIC) has supported DOE BTO since 1993. BTRIC is comprised of 60,000+ ft^2 of lab facilities conducting RD&D to support the DOE mission to equitably transition America to a carbon pollution-free electricity sector by 2035 and carbon free economy by 2050.

Scientific and Economic Results
236 publications in FY22
125 industry partners
54 university partners
13 R&D 100 awards
52 active CRADAs

BTRIC is a DOE-Designated National User Facility

REFERENCE SLIDES

Project Execution



	FY2021				FY2022				FY2023			
Planned Budget	400,000				400,000				400,000			
Spent Budget	400,000				400,000				200,000			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Past Work												
Q1 Milestone: Selected salt hydrate candidates	🟦◆											
Q2 Milestone: Performed initial encapsulation trials, documented the challenges faced, and proposed a path forward		🟦◆										
Q2 Milestone: Built an effective medium approximation (EMA) model to calculate the thermal conductivity of the coating component in the encapsulated systems		🟦◆										
Q2 Milestone: Present preliminary cost analysis of the manufacturing process to BTO		🟦◆										
Q3 Milestone:Electron microscopy results clearly demonstrate encapsulated salt hydrates			🟦◆									
Q3 Milestone: Presented data to BTO based on modelling results and initial experiments, and estimated the (1) diameter of fibers, (2) thickness of salt hydrate core, (3) thickness of coating			🟦◆									
Q4 Milestone: perform detailed cost analysis of encapsulation process				🟦◆								
Q4 Milestone: Achieved the yield of encapsulation process >50%				🟦◆								
Q4 Milestone: Demonstration of encapsulated salt hydrates with atleast 50% loading density of salt hydrate				🟦◆								
Q1 Milestone: Less than 30% water vapor leakage after 10 thermal cycles					🟦◆							
Q2 Milestone: Fiber surface salt content ≤20% of the core material after 100 phase change cycles while retaining 75% of original energy density (energy density at '0' cycles)						🟦◆						
Q3 Milestone: Fiber surface salt content ≤20% of the core material after 1000 phase change cycles while retaining 75% of original energy density (energy density at '0' cycles)							🟦◆					
Q4 Milestone: Fiber surface salt content ≤10% of the core material after 1000 phase change cycles while retaining 75% of original energy density (energy density at '0' cycles)								🟦◆				
Q1 Milestone: Encapsulated salt hydrates have a 'k' ≥0.4 W/m•K at volumetric and gravimetric energy density >90% that of the pure salt hydrate without coating									🟦◆			
Q2 Milestone: Achieved supercooling < 5 ºC										🟦◆		
Current/Future Work												
Q3 Milestone: Achieved supercooling ≤ 2 ºC											◆	
Q4 Milestone: The encapsulated salt hydrate prototype has a k ≥0.4 W/m•K, supercooling ≤ 2 ºC, volumetric and gravimetric energy density ≥90% that of the pure salt hydrate without coating, and a cost ≤ $10/kWh												◆

EERE/BTO goals

The nation’s ambitious climate mitigation goals

Greenhouse gas emissions reductions

50-52% reduction by 2030 vs. 2005 levels

Net-zero emissions economy by 2050

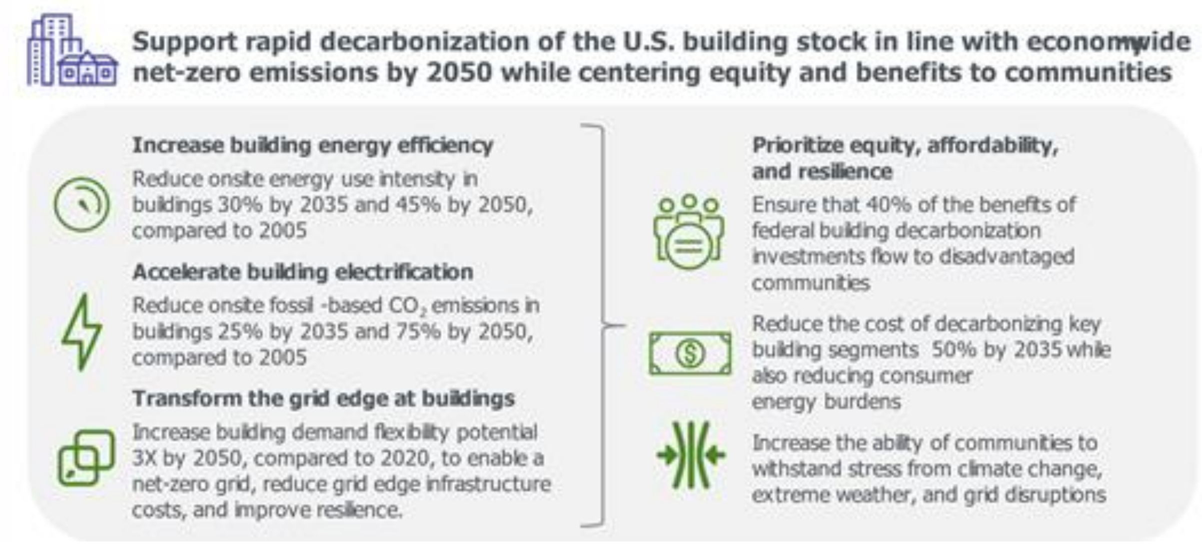
Power system decarbonization

100% carbon pollution-free electricity by 2035

Energy justice

40% of benefits from federal climate and clean energy investments flow to disadvantaged communities

EERE/BTO’s vision for a net-zero U.S. building sector by 2050



Support rapid decarbonization of the U.S. building stock in line with economywide net-zero emissions by 2050 while centering equity and benefits to communities

Increase building energy efficiency

Reduce onsite energy use intensity in buildings 30% by 2035 and 45% by 2050, compared to 2005

Accelerate building electrification

Reduce onsite fossil-based CO_2 emissions in buildings 25% by 2035 and 75% by 2050, compared to 2005

Transform the grid edge at buildings

Increase building demand flexibility potential 3X by 2050, compared to 2020, to enable a net-zero grid, reduce grid edge infrastructure costs, and improve resilience.

Prioritize equity, affordability, and resilience

Ensure that 40% of the benefits of federal building decarbonization investments flow to disadvantaged communities

Reduce the cost of decarbonizing key building segments 50% by 2035 while also reducing consumer energy burdens

Increase the ability of communities to withstand stress from climate change, extreme weather, and grid disruptions

Key Team Members

ORNL

Encapsulation

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Encapsulation

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DSC

Nihal Kanbargi

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Diana Hun

Guidance

André Desjarlais

Modelling

Som Shrestha

PCES

Testing & product development

Reyad Sawafta

Anne McClean

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Kyle Gluesenkamp