DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Reference herein to any social initiative (including but not limited to Diversity, Equity, and Inclusion (DEI); Community Benefits Plans (CBP); Justice 40; etc.) is made by the Author independent of any current requirement by the United States Government and does not constitute or imply endorsement, recommendation, or support by the United States Government or any agency thereof.

Final Scientific/Technical Report

High-Density, Low-Hysteresis Storage Using Hydrated Salts in Surface-Functionalized Hydrogels

Reporting Period: 10/01/2021-09/30/2024
Date of Submission of Report: Mar 10, 2025

Federal Agency/ Organization Element:	DOE/EERE/ Buildings Technology Office (BTO)
Award Number:	DE-EE0009680
Project Title:	High-Density, Low-Hysteresis Storage Using Hydrated Salts in Surface-Functionalized Hydrogels
Project Period:	10/01/2021 – 09/30/2024
Recipient Organization:	University of Illinois 1910 S. First Street, Suite A Champaign, IL 61820-7406
DUNS Number:	041544081
Principal Investigator	Sanjiv Sinha; 217-244-1891; sanjiv@illinois.edu
Business Contact:	Melanie Kuehn; 217-333-5815; spapreaward@illinois.edu
Partners:	A.O. Smith Corp.
DOE Technology Manager:	Sven C. Mumme; sven.mumme@ee.doe.gov
DOE Project Officer:	Coriana Fitz, 412-386-5538, coriana.fitz@netl.doe.gov
DOE Contract Official:	Carla Winaught, 304-285-4530; carla.winaught@netl.doe.gov
Submitting Official:	Sanjiv Sinha, 217-244-1891; sanjiv@illinois.edu

---

Disclaimer

Abstract

Nearly 70 years ago, Glauber's salt was identified as a leading phase change material (PCM) in terms of its heat storage density (~2x paraffin), thermal conductivity (~1W/m·K), safety, availability and cost (~$100/ton). However, the complex issues of supercooling and incongruent melting due to phase separation have prevented realization of the promise. The addition of thickeners and nucleating agents such as borax solve these issues but only over few cycles. This work aims to (**a**) resolve long-standing challenges with Glauber's salt as a thermal storage material through a unique materials approach, (**b**) to characterize the new material's properties that are relevant to performance and (**c**) to explore its incorporation into commercial water heaters. The materials concept involves encapsulating the salt in custom-designed, large-mesh hydrogels that enable breakthrough advances. Specifically, (**1**) the choice of mesh size and polymer chemistry control diffusion of salt/water and help to eliminate phase segregation. With the hydrogel itself occupying <10% volume, there is little loss in storage density compared to another encapsulation. (**2**) Specific nucleation centers that covalently tether to the hydrogel trigger heterogeneous nucleation, eliminating supercooling-associated hysteresis losses. The fact that they are spatially tethered, prevents the loss in performance over multiple freeze/thaw cycles (>100). We report extensive characterization of the hydrogel complex in terms of its storage density, freezing/melting temperature, cycling losses, rheological properties, aging and thermal conductivity. The novel material developed in this work is a significant advancement over the state-of-art. Finally, we investigate its potential as a thermal storage material for commercial/residential water heating and identify scenarios in which its deployment is advantageous.

1. Summary of Project Activities

1.1. Introduction

Thermal storage can potentially enable grid-integrated peak load shaving by utilizing energy production in off-peak hours. Several scenarios for using thermal storage in building applications are under investigation but are primarily restricted to water/ice as the storage material in the near-term. Beyond water/ice, a candidate material for cost-effective storage that combines higher storage density with high thermal conductivity, low hysteresis loss and low corrosion potential is still unclear. Nearly 70 years ago, Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) was identified as a leading phase change material (PCM) in terms of its heat storage density (~2x paraffin), thermal conductivity (~1W/m·K), safety, availability and cost (~\$100/ton). However, the complex issues of supercooling and incongruent melting due to phase separation have prevented realization of the promise. The addition of thickeners and nucleating agents such as borax solve these issues but only over few cycles.

The goal of the project is to (**a**) resolve long-standing challenges with Glauber's salt as a thermal storage material through a unique materials approach, (**b**) to characterize the new material's properties that are relevant to performance and (**c**) to explore its incorporation into commercial water heaters. The materials concept involves encapsulating the salt in custom-designed, large-mesh hydrogels that will enable breakthrough advances. Specifically, (**1**) the choice of mesh size and polymer chemistry control diffusion of salt/water and help to eliminate phase segregation. With the hydrogel itself occupying <10% volume, there is little loss in storage density compared to another encapsulation. (**2**) Specific polymer sequences chosen in the hydrogel act directly as nucleation centers or alternately sequences that covalently tether nucleating inorganic nanoparticles, serve indirectly as nucleation centers. These centers trigger heterogeneous nucleation, eliminating supercooling-associated hysteresis losses. The fact that they are spatially tethered, prevents the loss in performance over multiple freeze/thaw cycles encountered with untethered, nucleating additives. (**3**) Thermal transport is locally enhanced by trapping high conductivity nanoparticles inside the hydrogel complex. This enhances the crystallization rate and enables faster discharging, a key system parameter. Taken together, within a single materials system, these advances represent unprecedented engineering of a phase change material. Providing all functionalities within the hydrogel (low mass) has the potential to save production costs of the system when compared to the use of additives and thickeners.

In Section 1.2, we summarize materials development surrounding the hydrogel and nucleation agent for Glauber's salt. Characterization techniques developed as part of the work are described in detail in Section 1.2, along with key data. We report thermal cyclability characterization results from 100 cycles of T-history and 300 cycles of DSC. The rheology measurements help to explain the hydrogel performance. Isothermal titration calorimetry is used to understand the effect of [REDACTED] in the sample. The thermal conductivity of the hydrogel is measured using the bi-directional 3-omega method. Section 1.3

investigates the performance of the salt-hydrogel for thermal storage in commercial water heater applications. A cost analysis is discussed in Section 1.4.

1.2. Materials Development

A. Understanding of supercooling of sodium sulfate decahydrate

[REDACTED]

Figure 1. (a) Basic set-up for measuring supercooling temperature. (b) A schematic of surface functionalization by [REDACTED] layer on Au. (c) Temperature profile of Au substrate in the system and measured supercooling on functionalized Au (black line) and bare Au (green line)

We first investigated the supercooling (difference of melting and freezing temperature) of Glauber's salt ($Na_2SO_4 \cdot 10\ H_2O$, sodium sulfate decahydrate, SSD) to establish benchmark data. To accurately characterize supercooling, we built a rig for measuring the supercooling temperature. As shown in **Figure 1a**, the system includes a hot stage and controller (Linkam), which can accurately manipulate the cooling/heating rate. Moreover, an optical microscope is also attached to observe the moment of nucleation/crystallization at the surface while the temperature is decreased. Since Glauber's salt is highly sensitive to humidity, the Au substrate (which is the nucleating platform) and a 32.3 wt.% of Glauber's salt solution are encapsulated in a membrane box. To track the temperature of Au substrate, the thermocouple is connected to the backside of Au substrate by silver paste. As preliminary concept before we synthesize functionalized hydrogel, we simply designed 2-D functionalized Au substrate to see the effect of nucleation. We utilized [REDACTED] layer. Typically, [REDACTED] on Au(111) are ordered two-dimensional arrays formed by molecules containing thiol groups and alkane chains. This thiol groups anchor the organosulfur compounds on a metal surface via a chemical bond, and the alkane chains provide an interchain van der Waals interaction among the thiol molecules, leading to a regularly packed array structure (**Figure 1b**). As a result, the nucleation starts at 17.2 ºC on functionalized Au substrate while nucleation on bare Au substrate initiates at 4.3 ºC (**Figure 1c**). After crystallization on each substrate, the samples were characterized by scanning electron microscopy (**Figure 2**). The closely packed array of self-assembled layer ([REDACTED]) acts as nucleating agent. Therefore, the Glauber's salt is conformally covered on overall Au surface. On the other hand, when this Glauber's salt are nucleated on bare Au substrate, due to their small surface energy and there is no driving force on the substrate which can adhere the Glauber's salt, as the form of small dots, Glauber's salt is nucleate on the substrate.

[REDACTED]

Figure 2. Glauber's salt formed on (a) functionalized Au substrate and (b) Bare Au substrate.

To investigate the stability Glauber's salt nucleated on functionalized Au surface, the morphology of Glauber's salt was observed by optical microscope after repetition of cooling/heating steps (**Figure 3**).

[REDACTED]

Figure 3. The morphology of Glauber's salt formed on functionalized Au substrate with repetition of cooling and heating steps.

In the first cycle, large crystals are formed on the substrate. However, under repetitive cycles, the morphology of Glauber's salt crystals is changed. In the 2nd cycle, the crystals are divided into small grains, meaning that the driving force of crystal growth from the substrate are deteriorate and the grains themselves connect to each other. This trend continues to 3rd and 4th cycles, the size of grain is increased, implying that the surface-driven nucleation is weakened. However, on 5th cycles, the grains are disordered with random sizes because incongruent melting affects the nucleation process.

[REDACTED]

Figure 4. (a) OM and (b) SEM images of the Glauber's salt crystal (c) Averaged grain size and nucleation temperature under repetitive cycles.

Interestingly, large crystals are composed of small particles (**Figures 4a and b**). Therefore, the average grain size as a function of the cycle is in good agreement with the results that repeated cycles of cooling/heating can exacerbate surface-driven nucleation (**Figure 4c**). In addition, the nucleation temperature also decreases as surface-driven nucleation weakens over the cycle.

B. New Nucleation Agent for GS

The sodium sulfate and water have intermolecular attractions such as strong electrostatic attractions, ion-ion attractions between Na^+ and SO_4^{2-}. However, sodium sulfate decahydrate has a weaker electrostatic attraction; ion-dipole attractions between Na+ and $_{\delta-}\text{O-H}_{\delta+}$ bond dipoles in water and ion-dipole attractions between SO_4^{2-} and $_{\delta+}\text{H-O}_{\delta-}$ bond dipoles in water.

We found that [REDACTED] is an effective nucleating agent for sodium sulfate decahydrate. [REDACTED] is a cost-effective amino acid that contains both an amino group ([REDACTED]) and a carboxylic acid group ([REDACTED]). Thus, when [REDACTED] dissolves into water, the hydrogen from the carboxylic acid is de-protonated and the amine group is protonated, and then [REDACTED] is formed as a [REDACTED], having both positive and negative charges [1]. More importantly, [REDACTED] can closely interact with water molecules and form a water-[REDACTED] cluster, which is beneficial for the nucleating behavior of sodium sulfate decahydrate. We simply tested the effect of [REDACTED] using DSC and T-history method (details will be discussed in section 1.2).

[REDACTED]

Figure 5. (a) DSC exothermic up scans with repetition of heating-cooling cycles of [REDACTED]-nucleated sodium sulfate decahydrate. (b) Temperature monitoring of each sodium sulfate decahydrate with different nucleating agents (Black line: Borax and Bule line: [REDACTED]) and references for monitoring (red line, water) (c) Summary of reduced supercooling by functionalized agents with different measurement methods.

First, [REDACTED] was added to a solution of sodium sulfate (32.3 wt.%) and DI water, and the overall solution was homogeneously mixed on a hot plate at 50 °C for 30 min. After that, the solution was cooled down to room temperature. Here, we adopted DSC and T-history method for characterization, and these techniques will be introduced in the next section. [REDACTED]-nucleated crystals were taken and measured in differential scanning calorimetry (DSC). As shown in **Figure 5a**, interestingly, [REDACTED] effectively reduced supercooling of sodium sulfate decahydrate, and their on-set temperature from liquid to solid is about 26 °C, indicating that their supercooling is only 7~8 °C. More importantly, onset temperature was maintained over the 8th cycle of cooling/heating, meaning that the [REDACTED] acts as a barrier, covering the sodium sulfate particles and resulting in strong electrostatic interaction. Therefore, this reduced the setting rate of the sodium sulfate particles, thereby improving thermal cycling stability. Furthermore, for characterizing a large mass of PCM, the crystals nucleated by each [REDACTED] and borax were heated to 50 °C and transferred to the long glass test tube. Then, the glass test tube filled with samples was moved to the environmental chamber. As a reference, the temperature of water in the glass tube was also monitored (red line, **Figure 5b**). The temperature of the chamber was decreased as 0.7 °C/min. The on-set temperature of each [REDACTED]-nucleated and borax-nucleated showed 26.7 °C and 17.5 °C, respectively (**Figure 5b**). This is good agreement with DSC data and indicates that the effect of [REDACTED] as a chemical stabilizer and nucleating agents are reliable and extended to bulk-size sample. For summary (**Figure 5c**), the [REDACTED]-nucleated sodium sulfate decahydrate showed reduced supercooling and maintained their thermal cyclic stability over several cycles while borax-nucleated one was degraded easily over cycles.

C. Morphological study of [REDACTED]-nucleated Glauber's salt

Optical microscopy was utilized for characterizing particles in the molten samples. In **Figure 6**, the optical images of samples without a nucleating agent, with borax and various weight percent of [REDACTED] showed significant morphology differences. When a nucleating agent is not added, large crystals are precipitated, submerging down and causing phase separation when re-solidifying. Likewise, borax as a nucleating agent helps to reduce the size of crystals, but crystals are randomly distributed and aggregated with the large void (**Figures 6a and b**). As shown in **Figures 6c and d**, [REDACTED] acted as a physical barrier encapsulating small particles, thereby separating undissolved crystals, and preventing them from forming large aggregates The reduced size of the sample and uniformity were responsible for the high thermal cycling stability of the [REDACTED] added samples.

[REDACTED]

Figure 6. Optical images of samples (a) without nucleating agent, with (b) 2 wt.% of borax, (c) 1 wt.% of [REDACTED] and (d) 2 wt.% of [REDACTED]

However, [REDACTED]-nucleated SSD shows only 10 cycles of thermal cyclic stability in our experiment. Therefore, to improve thermal cyclic stability, we investigated the effect of [REDACTED] by varying the pH of sodium sulfate solution after adding [REDACTED]. The high or low pH environments make single charged [REDACTED]-dominant environments (low pH (acid environment is favorable for cation-form of [REDACTED], vice-versa). SSD by single charged [REDACTED] has the irregular shape of grain size and is randomly distributed (**Figures 7a and b**), indicating that this SSD has large supercooling behavior with low thermal cyclic stabilities. On the other hand, The SSD from pH 7 obviously showed well-distributed, smaller grains. Further, the crystals from the pH 8 of [REDACTED]-Sodium sulfate-water solution show small and uniform crystals, in much long-range order, which is beneficial for thermal cyclic stability and nucleation behavior as well.

[REDACTED]

Figure 7. pH dependency of [REDACTED]-nucleated sodium sulfate decahydrate. The pH of Overall solution of Sodium sulfate (32.3 wt.%) in Water before the crystallization: (a) pH 4 (cation-form of [REDACTED] dominant), (b) pH 9 (anion-form of [REDACTED] dominant), (c) pH 7 ([REDACTED]-form of [REDACTED] dominant) and (d) pH 8 ([REDACTED]-form of [REDACTED] dominant environment with small portion of anion-form of [REDACTED]) (scale bar: 500 μm)

Strong electrostatic attraction causes hydration shell around ions, hindering the SSD system from nucleation. Anion form of [REDACTED] effectively reduce hydration shell from water clusters bounded strongly with SO_4^{-2}. Moreover, Zwitter-ion of [REDACTED] act as effective nucleating agent in the solution. Therefore, [REDACTED] nucleated SSD from pH 8 (**Figure 8a**) maintained their reduced supercooling for 20 cycles (previously, 10 cycles), and which is much superior to borax-nucleated SSD (**Figure 8b**). With [REDACTED]-nucleated SSD, on-set temperature from liquid to solid is about 27 ºC, which is much superior to borax over all thermal cycles while on-set temperature of borax-nucleated SSD from liquid to solid is decreased and fluctuated with repetition of cycles, meaning they have significant phase separation during cycling.

[REDACTED]

Figure 8. (a) DSC exothermic up scans with repetition of heating-cooling cycles of [REDACTED]-nucleated sodium sulfate decahydrate from pH 8 solution. (b) Summary of reduced supercooling by [REDACTED] (yellow) and borax (purple).

In addition, the [REDACTED] nucleation SSD has a high proportion of mirabilite, an active material for thermal storage. Compared to commercially available sodium sulfate decahydrate, [REDACTED] nucleation SSDs are much more likely to be mirabilite, but commercial SSDs have a higher proportion of thenardite, indicating that [REDACTED] nucleation SSDs have higher thermal storage performance than commercial SSDs. (**Figures 9a and 9b**)

[REDACTED]

Figure 9. XRD spectrum of (a) commercial SSD and (b) [REDACTED]-nucleated SSD

D. Long-term Thermal Cyclic Stability of [REDACTED]-nucleation Versus Inorganic Nucleating Agents

[REDACTED]

Figure 10. Morphology analysis of cycled [REDACTED]-nucleated sodium sulfate decahydrate: (a) after 10 cycles, (b) 15 cycles and (c) 25 cycles. (d) averaged grain size and nucleation temperature as function of cycles.

Since [REDACTED]-nucleated SSD maintained their reduced supercooling until only 20 cycles, we analyzed the mechanism and morphologies after cycling. As shown in **Figure 10**, until 15 cycles, the SSD remains their grain size and distribution, and accordingly, their nucleation temperature is around 28 ºC, which is supercooling of 5 ºC. However, after 25 cycles, the grain size has increased tremendously, indicating that the SSD is not grown from the nucleating agents and thus they showed high supercooling. The clustering effect between water to [REDACTED] is weakened, and neutral species are more dominant, so they are suffering from degradation of nucleating behaviors. We will continuously optimize and improve thermal stability and reduce supercooling by [REDACTED] as nucleating agent and stabilizer. But, as backup, we also tried a new nucleating agent, which is [REDACTED] nanoparticles. When using [REDACTED] nanoparticles as a nucleating agent, [REDACTED] nanoparticles themselves provide nucleation sites in the SSD solution and mechanically active the nucleation. So, they maintained their reduced supercooling up to 30 cycles. Correspondingly, they sustained their morphologies with uniform distribution (**Figure 11**).

[REDACTED]

Figure 11. (a) DSC Exo-up of [REDACTED]-nucleated SSD. (b) Their morphologies after cycling.

E. Chemistry Screening for Synthesis of Glauber's Salt-based Hydrogel

The chemistry aspect of project aims at employing hydrogels to house nucleating agents to control the formation of Glauber's salt. By incorporating nucleating agents in the hydrogel chemistry, we will control nucleation inside the pores of hydrogel. This approach is chosen in order to suppress supercooling and incongruent melting. The hydrogel would be completely immersed in Glauber's salt solution during thermal storage application and hence the hydrogel polymer must be able to withstand high salt concentrations (at least 30% salt concentration). Subsequently, the hydrogel must also be stable under multiple heating-cooling cycles (25 to 50 °C). Salts are known to collapse polymers, due to introduction of polarity from the salt ions. This results in shrinkage of polymer volume and possible phase separation. This can be observed by inspection of the polymer after the salt solution has diffused inside the hydrogel network. Hence, our approach begins with shortlisting hydrogels that have salt tolerance. A method was developed to assess the salt compatibility of hydrogel at elevated temperatures. The major parameter of control in hydrogel is the pore size and hence two pore sizes will be explored in parallel. Small mesh (nano-scale) hydrogels are synthesized using classic synthetic approaches of polar polymers such as [REDACTED], [REDACTED] and [REDACTED]. Large mesh (micron-scale) hydrogels are synthesized by incorporating macromolecules such as collagen, gelatin, fibrin, that cellulose that will form a framework with large pore sizes. Initially, [REDACTED] and [REDACTED] were explored for salt tolerance. The polymer content in hydrogel was aimed between 10% to 20% to maximize Glauber's salt content. Hydrogels of 1 mm thickness were synthesized and tested for salt tolerance. Different [REDACTED] hydrogels were synthesized with varying monomer to crosslinker ratio and subsequently tested for volume change. They showed a volume change for 50% (from 704 mm^2 to 322 mm^2), indicating their susceptibility to salt concentration. A similar approach will be followed for [REDACTED], [REDACTED] and various large mesh hydrogels.

F. Synthesis of Hydrogels

In our system, hydrogels will act as a scaffold matrix that will house Glauber's salt and improve the cyclability of its phase transition by suppressing incongruent melting and supercooling. To determine the type of hydrogel that would improve phase change cyclability, we developed a screening protocol that we used to determine the compatibility of potential hydrogel candidates with melted Glauber's Salt solutions. In our screening approach, we loaded polymers into a melted Glauber's salt solution and performed a temperature cycle (20 – 40 ºC) on the mixture to test if the polymer remained soluble in this solution (i.e., does not phase separate). We tested a variety of polymers using this screening approach (e.g., [REDACTED], [REDACTED], [REDACTED], and [REDACTED]) and found that of the candidates tested, [REDACTED] hydrogels showed the best compatibility. We also explored other polymer candidates, targeting polymer's that are known to have good salt compatibility. Of note are a series of Anti-Hoffmeister polymers, which we are in the process of synthesizing and testing, but initial results show promising compatibility with melted Glauber's salt solutions. With the [REDACTED] we formulated hydrogels that had a polymer content of 25% by weight. This formulation, decreased in volume by 15% when heated to 40 ºC and submerged in salt solution, but held its structural integrity and was translucent upon the uptake of salt. The translucent appearance of the gel indicates that the polymer maintained its nanoporous structure (i.e., did not phase separate), and will allow the use of characterization by polarized optical microscopy to observe crystal formation.

We studied the cyclic nature of the Glauber's salt crystallization and melting within the hydrogel, by cycling the temperature of the hydrogel and observing its behavior using a custom heating/cooling stage that can be integrated with a microscope. Using this set-up, we were able to track the crystal formation and melting of Glauber's salt as a function of temperature (**Figure. 12**). In this experiment we see crystallization occur as the temperature is dropped 40 ºC to 0 ºC (**Figure. 12**, panels 1-4), with an onset crystallization temperature of around 5 ºC. A travelling phase boundary can be seen between the crystallized salt (coarse region) and salt dissolved in solution (clear region). Such behavior was observed over all the three cycles. As we then increased the temperature, we see the crystallized solution begin to melt and the solution return to its initial transparent state (**Figure. 12**, panels 5-8). We will continue to optimize the thermal analysis of hydrogel-salt system, as it is crucial in understanding the role that the polymer network has in the phase change of Glauber's salt.

[REDACTED]

Figure 12. Microscope images of the gel under cycling. (Images 1 to 4 are a set of images taken during the cooling phase and panels 5 to 8 shows the heating phase that completes the temperature cycle.

We also measured the crystallization and melting temperature of the hydrogel/Glauber's salt system using DSC in order to verify our custom microscope characterization platform. In DSC, we measured a crystallization onset temperature of 5 ºC, when our cooling rate was 1 ºC/min. We note that when we measured crystallization temperature in DSC using higher cooling rates, we saw a large variation in our data. Our initial results, show a need to standardize our phase change characterization procedures across our different systems. We have observed that varying sample size, sample dimensions, and heating/cooling rates will affect the performance (i.e., supercooling and cyclability) of our system. Hence standardizing testing conditions is essential for subsequent studies.

In our system, we will use a specifically formulated hydrogel to encase Glauber's salt in order to improve the cyclability of its phase transition by suppressing incongruent melting and supercooling. The meshed structure of the hydrogel will ensure that the nucleating agent stays well dispersed in the Glauber's salt over the course of thousands of melting/freezing cycles. With such applicability in mind, we screen hydrogels based on the following four criteria: a) hydrogel possess stable mesh size in the presence of high salt concentrations and temperature, b) the overall polymer content in the final system is below 30%, and c) the hydrogel polymer can be modified with potential nucleating agents. The initial selected candidate was [REDACTED] which was able to meet most of the criteria, but a major limitation of this polymer was that it needed have a polymer content of 30% for the system to remain stable in the high salt environment. We then explored several other polymer candidates and mixtures to be used as a hydrogel in our system, and we found that [REDACTED] had the most ideal properties for our application. Thermogravimetric analysis (TGA) was used to measure the composition of the [REDACTED] hydrogel after synthesis (**Figure 13a**) and after the melted Glauber salt solution uptake (**Figure 13b**). TGA analysis showed that the final polymer content was 7 % and salt present in the hydrogel was 27%, which is a substantial portion of the total system weight, indicating optimal energy storage efficiency.

[REDACTED]

Figure 13. Thermogravimetric analysis of [REDACTED] hydrogel upon synthesis (a) and after soaking in melted Glauber's salt solution (b). In both (a) and (b), all the water present in the system was evaporated by 150 ºC leaving behind polymer and salt. All the polymer was degraded by 800ºC via two degradation steps, 375ºC and 700 ºC. After 800 ºC, only salt is present which can be seen in (b) and not in (a).

Since we were able to synthesize a hydrogel with promising salt storage capacity, we then started to assess the stability of the [REDACTED] hydrogel under multiple freeze-thaw cycles. For this purpose, we fabricated a custom laboratory setup to cycle the temperature and record the size of the hydrogel-Glauber's salt system over multiple freeze-thaw cycles (**Figure. 14**). Using this setup, we cycled the gel to a total of 100 freeze-thaw cycles and captured and analyzed the area of the gel across each cycle (**Figure.**

15) We observe that as the temperature of the gel is varied over 100 cycles from 40 ºC to 20 ºC (i.e., the approximate temperature range of 1 freeze-thaw cycle), the area of the gel remains constant, approximately 223 mm^2, indicating that our synthesized [REDACTED] hydrogel will maintain its structural integrity under the desired application conditions.

[REDACTED]

Figure 14. A developed setup to test the hydrogel's stability over multiple freeze-thaw cycles. A camera above the setup was used to capture images of the gel at intervals of 4 min. The gel was placed between two glass slides and encased in an airtight [REDACTED] mold to trap moisture within, and weights were placed above to seal in the moisture. Thermocouples were placed at strategic locations to measure the temperature of gel. The heating/cooling stage was used to subject the gel over 100 freeze-thaw cycles.

[REDACTED]

Figure 15. (a) Plot of area of the gel and temperature of the gel as a function of time. (b) Images of the gel at the start of cycle 1 and at the end of cycle 100.

We have shown that the [REDACTED] hydrogel can be synthesized to have a low polymer content and that, by itself, it is stable over 100 freeze-thaw cycles. Next, we wanted to demonstrate the [REDACTED] hydrogel can be modified with potential nucleating agents and still maintain its properties. Towards this end we synthesized the [REDACTED] hydrogel to contain 5 wt.% of suspended nucleating agents (e.g., [REDACTED] nanoparticles and [REDACTED]). We found that the gel was able to successfully incorporate the external agents, without much affect to its ability to uptake and cycle melted Glauber's Salt solutions. We assessed the effect of adding nucleating agents to the Glauber's salt-[REDACTED] hydrogel system using Differential scanning calorimetry (DSC). Herein we soaked melted Glauber's salt solution into the hydrogel system containing the nucleating agent and measured the heat flow as the system's temperature was cycled between 30 ºC and 0 ºC (**Figure. 16**). We found that in the presence of the nucleating agents (e.g., [REDACTED] and [REDACTED] NP) nucleation occurred at higher temperatures compared to the [REDACTED] hydrogel without any nucleating agent. We also observe that there is no shift in the nucleating temperature of the [REDACTED] incorporated hydrogel over the 5 cycles tested. In the hydrogel with [REDACTED] nanoparticle nucleating agents, we did not observe sharp nucleating peaks, which we think could be an outcome of possible agglomeration of nanoparticles in the gel, which is hindering the nucleation of Glauber's salt within the hydrogel. We are working on creating more stable dispersions of the nucleating agent within the hydrogel, which we think will help the performance of the [REDACTED] nanoparticle nucleating agents. We have used DSC as a method to tests preliminarily, the effect of the nucleating agents in the gels. we tested these gels using the T-history method, which will be covered in the next section a more in-depth analysis of the nucleating agent for cycles.

[REDACTED]

Figure 16. DSC plots of hydrogels soaked in salt solution intended for comparative analysis of different nucleating agents and their ability to enhance Glauber's salt nucleation, over 5 cycles.

The systematic study of shortlisting suitable candidates for latent heat thermal storage systems led to the use of [REDACTED] and vinyl- based free radical polymerization to make high salt concentration stable hydrogels. The previously conducted thermogravimetric analysis showed that the total polymer content in the final, swelled system is 7 % by weight, which was a good indication of an efficient system having a majority content comprising of a PCM. The initial test to assess the structural integrity of [REDACTED] gel over a heating/cooling stage (**Figure 14**) was conducted over 30 cycles, which showed no signs of deformation. The gel was subsequently subjected to 100 heating/cooling cycles ranging from 40 ºC to 20 ºC. The gel maintained its structural integrity over 100 cycles with a constant area of approximately 223 mm^2 (**Figure 15**). [REDACTED] showed good nucleation ability in DSC and T-History ability, after being dissolved in sodium sulfate solution. Hence the next step in the development of latent heat storage system involved conducting nucleation experiments of [REDACTED] incorporated in [REDACTED] gels. Hence a T-History experiment was conducted to compare three samples; namely [REDACTED], [REDACTED] + Borax, and [REDACTED] + [REDACTED]. The aim of this experiment is to compare the efficiency of [REDACTED] to house nucleating agents whilst undergoing phase change of Glauber's salt, and the compatibility of nucleating agents with [REDACTED] polymer chemistry. **Figure 17** shows the T-History cooling curves for all three samples. A change in the trend of cooling of sample with respect to that for water is an indication of onset of nucleation, where a rise in temperature indicates crystallization. **Figure 17a** shows the onset of nucleation for [REDACTED] system to be at approximately 11 ºC, which is to be expected since this sample does not contain any nucleating agents to promote crystallization. Addition of borax into this system considerably improves the onset of nucleation to a temperature of 26ºC since borax is a known nucleating agent. However, presence of [REDACTED] has an unexpected effect on Glauber's salt nucleation in hydrogel system. The onset of nucleation reduces to 9.8ºC when [REDACTED] is added to the system. Such comparison between Borax and [REDACTED] in [REDACTED] system reveals a selective action of [REDACTED] as a nucleating agent. We hypothesize that the presence of [REDACTED] is hindering the nucleating ability of [REDACTED]. To support our hypothesis and further the development of latent heat storage system, we propose to explore the workings of nucleation action of [REDACTED]. A clearer understanding of [REDACTED]'s nucleating action would enable us to better incorporate it into our system and subsequently help in developing other nucleating agents. For this purpose, we would begin to explore the interactions between [REDACTED] and sodium sulfate under different conditions of nucleation.

[REDACTED]

Figure 17. T-History plots of first cooling cycle for [REDACTED] (a), [REDACTED] + Borax (b), and [REDACTED] + [REDACTED] (c). All three samples are cooked in 32 wt.% sodium sulfate solution. The onset of nucleation is determined at the point where the plot starts to rise instead of dropping like that of water. Onset for nucleation for [REDACTED], [REDACTED] + Borax, and [REDACTED] + [REDACTED] are 11 ºC, 26 ºC, and 9.8 ºC respectively.

To aid in our study of how the nucleating agents added hydrogels were affecting the nucleation of Glauber's salt, we used Polarized optical microscopy (POM) to image crystals in the gels with and without nucleating agents as they were cooled to room temperature. The images had distinct differences in the crystals, particularly in their size, distribution and rate of formation (**Figure 18**). When we analyzed the [REDACTED] gel with no nucleating agent present, we observed fewer crystals that were typically larger and more unevenly distributed in size and formation. For the [REDACTED] gel containing [REDACTED], we observed a higher density of crystals that formed within the gel that were smaller and more uniform in size and distribution. The [REDACTED] gel containing the [REDACTED] NPs had a distinct red tint to the gel, which was caused by the presence of the NP (**Figure 18c**). The darker regions within the gel are aggregated NPs, but the presence of Glauber's Salt crystals is still visible, with a size and distribution similar to that of the [REDACTED] loaded gels. These distinct differences in crystal structure across the three types of gels indicates that the nucleating agent is still functional inside the hydrogel, which is a major milestone in the development of our system.

[REDACTED]

Figure 18. POM image of crystals formed in blank [REDACTED] gel (a), [REDACTED] gel with 5 wt.% [REDACTED] (b), and [REDACTED] gel with 5 wt.& [REDACTED] particles.

The results shown here, provide evidence that the [REDACTED] gel is compatible in our thermal energy storage system as it fulfilled our targeted criteria.

So far, we could see [REDACTED] gel with [REDACTED] can work but the supercooling of the [REDACTED] gel is still huge and cannot work with [REDACTED]. To resolve this, we found a promising hydrogel candidate, [REDACTED], which is a hydrophilic colloidal natural [REDACTED], consisting of a long chains of carbohydrate molecules, extracted from cell walls of brown [REDACTED]. The carboxylic acid groups attribute negative charges to [REDACTED] and thus are able to interact electrostatically with the positively charged molecules to form gels. We thought the [REDACTED] can be physically crosslinked forming large mesh gel and demonstrated excellent nucleation ability with [REDACTED].

Therefore, we investigated a new hydrogel, an [REDACTED] hydrogel, combining with [REDACTED]. As shown in **Figure 19a**, [REDACTED] is a linear copolymer with homopolymeric blocks of linked [REDACTED] and [REDACTED]. Therefore, the networks based on large meshes are expected to function effectively as scaffolds for PCM materials. We found that incorporating [REDACTED] inside the hydrogel mesh still reduced supercooling of sodium sulfate decahydrate. The on-set temperature from liquid to solid is about 22 ºC, indicating that their supercooling is only 10 ºC. More importantly, onset temperature was maintained over the 20th cycle. Considering that reduced supercooling by [REDACTED] alone is 6~7 ºC, [REDACTED] hydrogel is very promising without hindering nucleating behavior. Moreover, it provides excellent thermal cyclic stability.

[REDACTED]

Figure 19. (a) Chemical structure of [REDACTED] polymer. (b) DSC exothermic up and endothermic down scans with repetition of heating-cooling cycles of [REDACTED]-[REDACTED]-sodium sulfate decahydrate. (blue line: 1st cycle, black line: 20th cycle, and red line: the heating curve in an average of every cycle).

[REDACTED]

Figure 20. SEM image on [REDACTED]- [REDACTED]-SSD hydrogel (left) and energy dispersive X-ray spectrometer analysis (right).

SEM image clearly showed interconnected 3d networks acting as scaffolds and encapsulation of SSD crystals (**Figure 20**). The networks are mainly composed of Carbon, indicating presence of "[REDACTED]", and inner structure shows Sodium, implying SSD.

This sodium sulfate hydrate (SSD) combined with [REDACTED] and [REDACTED] exhibited low supercooling temperature in the bulk as well. The 10g of the hydrogel-SSD composite was prepared in the 7 mm diameter borosilicate tubes. Comparing **Figures 21a and 21b**, there is no phase separation in the [REDACTED]-based sample while the other samples are experiencing severe phase separation. This agrees well with thermometry data as a function of time. The onset nucleation temperature of [REDACTED]-[REDACTED]-SSD is 26.13 ºC at 1st cycle and 26.59 ºC at 10 th cycle, maintaining their supercooling temperature of 5~6 ºC.

[REDACTED]

Figure 21. Optical images of T- history samples (a) at initial stage and (b) after 10th cycle. (c,d) Cooling curves of [REDACTED]-SSD, [REDACTED]-SSD, and [REDACTED]-SSD-[REDACTED] measured by T-history method.

The thermal energy storage material is composed of [REDACTED], [REDACTED], sodium sulfate solution in water, and sodium sulfate decahydrate (SSD). The theoretical mass fractions of each component in the hydrogel were derived from the phase diagram of the SSD using lever rule (**Figure 22**) [2]. We used 32.3 wt.% of sodium sulfate to the water in salt hydrate complex (hydrogel or solution synthesis). We prepared the sample at room temperature and the weight percentage of SSD can be determined at room temperature by the lever rule,

$$wt_{SSD} = \frac{(32.3 - 14.69)}{(44.1 - 14.69)} = 59.8\%$$

Therefore, the mass of SSD is 59.8% of total mass of the hydrogel (or solution). The mass of sodium sulfate and excess water in solution can be derived from the phase diagram.

[REDACTED]

Figure 22. Partial phase diagram of SSD extracted and reproduced from literature [2].

1.3. Materials Characterization and Further Refinements

A differential scanning calorimetry (DSC) and the temperature-history method (T-history) are employed for thermal characterization of the samples; SSD, [REDACTED]-sodium sulfate solution ([REDACTED]-SS solution), [REDACTED]-SSD crystal ([REDACTED]-SSD crystal), [REDACTED]-SSD hydrogel ([REDACTED]-SSD), [REDACTED]-[REDACTED]-SSD hydrogel ([REDACTED]-[REDACTED]-SSD). The rheological characteristics of the [REDACTED]-[REDACTED]-SSD hydrogel was measured by to understand the thermo-cyclic strength of the hydrogel. An isothermal titration calorimetry (ITC) was employed to investigate the effect of [REDACTED] on reduction of the supercooling of the hydrogel. The thermal conductivity of the hydrogel was measured by the bi-directional 3-omega method.

A. Thermal characteristics of the sample by DSC

The DSC heat flow data of [REDACTED]-[REDACTED]-SSD hydrogel during melting (dot-line) and freezing over 50 cycles is shown in **Figure 23**. The measured melting and freezing temperatures are around 31 and 25 °C respectively. The degree of supercooling is a difference between the melting and freezing temperature and turns out of 6 °C. Over 50 cycles, the phase transition temperatures are consistent (high cyclability).

[REDACTED]

Figure 23. DSC heat flow data for [REDACTED]-SSD.

B. Thermal characteristics of the sample by T-history experiment

Temperature-history experiments are being developed to measure phase change temperature, supercooling and latent heat of the bulk sample [3]. **Figure 24** shows the experimental design and setup. In order to extract the proper phase transition temperature and enthalpy using a lumped capacitance assumption, Biot number (Bi) should be less than 0.1. A wind shield was applied for a low Bi by limiting a forced convection, and the glass tubes (10 mm diameter, 178 mm long Norell Standard Series NMR) containing about 10 g of samples (around 150 mm height) are placed in an environmental chamber (LabEvent, Weisstechnik) for cycling (15 – 45 °C with 4 °C/min for most of the samples, 5 – 45 °C with 4 °C/min for SSD). **Figure 24c** shows the samples after cycling ([REDACTED]-SSD hydrogel, [REDACTED]-SS solution, and [REDACTED]-[REDACTED]-SSD hydrogel: cycled of 100, [REDACTED]-SSD crystal: cycled of 69). Distilled water was used for a reference and a rubber stopper sealed the glass tube to minimize the moisture loss during the cycling. The thermocouple probes (K-type, 0.04 in. diameter and 6 in. long) measured the temperature of the samples, and a data logger (PICO TC-08) recorded temperatures. After preheating the tubes (45 °C), the cycling was conducted with the holding time of 3 and 4 hours in melting and freezing respectively.

In **Figure 24d**, the temperature of the chamber is controlled according to a protocol. While the temperature of the liquid water decreases accordingly without changing phase, the [REDACTED]-[REDACTED]-SSD hydrogel undergoes nucleates and releases heat to the ambient.

The 4 cycles T-history experiment on SSD result is in **Figure 25**. From the temperature-time curve, the phase transition temperature is measured by applying the inflection point method [4]. The 1st melting plot shows constant melting temperature during melting at 32.4 °C. From the 2nd melting, the melting temperature shows lower and does not constant during melting because of phase segregation of salt after the 1st melting. The precipitated sodium sulfate after the 1st melting could not participate in hydration process in the freezing. Therefore, sodium sulfate in the solution, which turns to the crystal, has lower weight percentage and the melting temperature is lowering based on the phase diagram (**Figure 22**). The freezing temperature does not show any trend for cycles. Overall freezing temperature over 4 cycles is lower than the melting temperature due to supercooling. The enthalpy is extracted from the temperature-time curve based on the lumped capacitance assumption [3, 5]. The enthalpy change during phase change is called the energy storage density, J/g.

[REDACTED]

Figure 24. (a) T-history experimental setup (b) Temperature measurement for the PCM, air, and water in the environmental chamber (c) Samples used for thermo-cyclic T-history experiment (d) representative T-history T-t result plot on [REDACTED]-[REDACTED]-SSD hydrogel.

[REDACTED]

Figure 25. 4 cycled T-history experimental results on SSD.

[REDACTED]

Figure 26. Temperature-time curves from the 100 cycled T-history experiment on [REDACTED]-SSD hydrogel, [REDACTED]-SS solution, [REDACTED]-[REDACTED]-SSD hydrogel, and [REDACTED]-SSD (69 cycles).

The temperature-time curves for other samples are illustrated in **Figure 26**. [REDACTED]-SSD hydrogel does not show phase change after the 1st cycle while a high performance of [REDACTED]-SSD hydrogel is reported in [6]. This suggests that the sample source and synthesis procedure can influence the thermal energy storage system. [REDACTED]-SS solution shows consistent onset melting and freezing temperature. However, the graph shape changes for cycles. The curvature of the plot is vanishing, which means the phase change is diminishing for cycles. [REDACTED]-SSD crystal shows similar trend to [REDACTED]-SS solution result. However, [REDACTED]-[REDACTED]-SSD hydrogel shows consistent graph over 100 cycles in both melting and freezing and it can keep store the thermal energy consistently.

The enthalpy-temperature curve (**Figure 27**) is computed from the temperature-time curve [3]. [REDACTED]-SSD hydrogel does not show enthalpy change for temperature after the 1st cycle. This means the sample is supercooled after the 1st freezing and it never nucleates for cycles. Rather, [REDACTED]-SSD hydrogel keeps its liquid phase over 100 cycles. Other materials show abrupt enthalpy change along the phase transition. The enthalpy of [REDACTED]-SS solution and [REDACTED]-SSD crystal shows show high enthalpy initially, but decreases over 100 cycles due to phase segregation for cycles. However, [REDACTED]-[REDACTED]-SSD hydrogel shows well overlapped enthalpy data for 100 cycles because of [REDACTED] acting as thickener. The viscous effect of [REDACTED] prevents phase segregation and makes reliable and stable for cycle. We will discuss this later in rheologic characteristic measurement section.

[REDACTED]

Figure 27. Enthalpy-temperature curves from the 100 cycled T-history experiment on [REDACTED]-SSD hydrogel, [REDACTED]-SS solution, [REDACTED]-[REDACTED]-SSD hydrogel, and [REDACTED]-SSD (69 cycles).

[REDACTED]

Figure 28. Phase change temperature of the samples in (a) melting and (b) freezing for cycles. (c) The degree of supercooling of the samples for cycles.

The melting and freezing temperature of different samples are extracted over cycles (**Figure 28a and b**). The pure SSD shows abrupt reduction of melting and freezing temperature due to phase segregation. Other materials show consistent phase transition temperature over cycles due to the [REDACTED] acting as nucleation agent. The degree of supercooling of our samples (**Figure 28c**) is much lower than the pure SSD and is well maintained over 100 cycles. We investigated the energy storage performance by comparing the volumetric energy storage density,

$$\begin{aligned}&Volumetric\ energy\ storage\ density\ \left(\frac{kWh}{m^3}\right)\\&\quad= Enthalpy\ change\ during\ phase\ change\ \left(\frac{J}{kg}\right)\times Density\ \left(\frac{kg}{m^3}\right)\times\frac{10^{-3}}{3600}\left(\frac{kWh}{J}\right)\end{aligned}$$

The density of the sample is

$$Density\ of\ the\ sample=\frac{m_{sample}}{\pi {R_{sample}}^2 L_{sample}-\pi {R_{TC\ probe}}^2 L_{sample}}.$$

The density of the SSD is reported to be 1460 kg/m^3 [7, 8]. The obtained volumetric energy storage density for different samples over cycles is plotted for melting and freezing respectively (**Figure 29**).

[REDACTED]

Figure 29. Energy storage density of the samples in (a) melting and (b) freezing for cycles.

For all samples, the melting energy storage density is higher than the freezing energy storage density except for the case of [REDACTED]-SS solution after 10 cycles. The highest energy storage density was around 78 kWh/m^3 from the 1st melting of SSD. However, SSD shows poor cyclability because of lack of a nucleation agent and thickener. With the nucleation agent ([REDACTED]), the energy storage performance in melting has been reduced slightly. However, the performance in freezing is much better than pure SSD because [REDACTED] helps nucleation. Even though the freezing energy storage density of [REDACTED]-SS solution and [REDACTED]-SSD crystal is higher than the one of pure SSD, they are ineligible for long-term cycle. They underwent phase segregation as shown in **Figure 24c**. [REDACTED]-

[REDACTED]-SSD hydrogel shows reliable and robust cyclability over 100 cycles preventing phase segregation. The detail energy storage density of [REDACTED]-[REDACTED]-SSD hydrogel over 100 cycles is in **Table 1**. The energy storage density has two forms. The gravimetric energy storage density is extracted from the enthalpy-temperature curve (J/g) and can be converted to the volumetric energy storage density by applying the density.

Table 1. Gravimetric/Volumetric energy storage density of [REDACTED]-[REDACTED]-SSD hydrogel over 100 cycles.

[REDACTED]

[REDACTED]

Figure 30. DSC and T-history comparison for the [REDACTED]-[REDACTED]-SSD hydrogel in (a) phase change temperature and (b) energy storage density.

The temperature and energy storage density of [REDACTED]-[REDACTED]-SSD hydrogel over long-term cycles (**Figure 30**) are plotted for different measurement technique (DSC: 300 cycles, T-history: 100 cycles). Both results show a small degree of supercooling and high cyclability of the hydrogel. Therefore, we selected [REDACTED]-[REDACTED]-SSD hydrogel as a thermal energy storage material in this project. In practical application, the pure SSD hardly stores the latent heat when the sample goes through cycles due to a phase segregation [8]. As we discussed, our [REDACTED]-[REDACTED]-SSD hydrogel prevents the phase segregation to maintain the high thermal energy storage ability for 300 cycles.

We investigated how the thermal energy is stored in the hydrogel and why the energy storage density lowers compared to pure SSD. The hydrogel is composed of [REDACTED], [REDACTED], sodium sulfate solution (SS+water), and sodium sulfate decahydrate (SSD). We found that [REDACTED]-[REDACTED]-SSD hydrogel contains 40.9 wt.% of sodium sulfate (even though we synthesized 32.3 wt.% of SS in the water for sample preparation. The detail procedure how to find this will be covered in the next section, optimization of the hydrogel). By the lever rule, the mass of SSD is around 77% of total mass of the hydrogel and the mass of sodium sulfate and excess water in solution can be derived with the phase diagram [2]. The energy storage of the hydrogel is the sum of latent heat and sensible heat of the components. The [REDACTED], [REDACTED], sodium sulfate, and water store thermal energy as a sensible.

$$E_{total} = LH_{SSD} + SH_{SS} + SH_{water} + SH_{\text{[REDACTED]}} + SH_{\text{[REDACTED]}} = m_{total} * (H_{end} - H_{onset})$$

where E_{total}, LH_{SSD}, SH_{SS}, SH_{water}, $SH_{[REDACTED]}$, $SH_{[REDACTED]}$, m_{total}, H_{end}, H_{onset} are total stored thermal energy, latent heat portion by SSD, sensible heat portion by SS, water, [REDACTED], and [REDACTED], and the sample mass, enthalpy at end of phase change, and enthalpy at onset of phase change. The sensible heat is computed by

$$SH_{water} = m_{water}C_{p,water}(T_{end} - T_{onset})$$

where m_{water}, $C_{p,\ water}$, T_{end}, T_{onset} are water mass, specific heat of water, end and onset of phase change temperature of the hydrogel. The latent heat portion was extracted from the total energy storage by subtracting the sensible heat. We analyzed how much thermal energy was stored in each component. The thermodynamic analysis for the hydrogel's energy storage revealed that most of the thermal energy was stored as a latent heat by sodium sulfate decahydrate. Around 98~99 % thermal energy was stored in SSD as a latent heat, and the rest of heat was stored in water and other components as a sensible heat. However, the mass of the water in the hydrogel is around 8 % of the total mass, and the mass of the [REDACTED] in the hydrogel is around 10 % as shown in **Figure 31**. The large mass portion of them in the hydrogel reduces the total energy storage density because of their low sensible heat contribution for thermal energy storage. Therefore, reducing mass content of water and [REDACTED] in the hydrogel with increasing the salt fraction at the same time can be a way to enhance the total energy storage density. Thus, we synthesized different hydrogels with different composition and check their energy storage density as well as the cyclic stability.

[REDACTED]

Figure 31. Mass fraction in the [REDACTED]-[REDACTED]-SSD hydrogel, (e) Stored energy during melting, (f) Stored energy during freezing of the hydrogel over 100 cycles.

Table 2. Summary of 100 T-history freezing cycles of [REDACTED]-[REDACTED]-SSD hydrogel in average value. The mass fraction is determined by the phase diagram using lever rule. The energy is computed by multiplying the specific energy to the mass.

[REDACTED]

C. Optimization of the hydrogel by T-history experiment

[REDACTED]

Figure 32. TGA analysis of [REDACTED]-[REDACTED]-SSD gel.

To enhance the current energy storage capacity, it's essential to accurately analyze the proportion of the active material, SSD, in the hydrogel and the proportion of water in it. The TGA (**Figure 32**) shows that water makes up about 51%, which is different from the actual ratio of water used in the material synthesis (approximately 58%). The given ratios for the materials are: [REDACTED]: 1.2g, [REDACTED]: 0.4g, Water: 6.77g, Sodium sulfate: 3.23g. The discrepancy arises because during the synthesis of the material, unnecessary water evaporates after the hydrogel network undergoes the gelation step and intakes the solution.

After synthesizing the hydrogels (32.3 wt.% of sodium sulfate), the exact weight percentage of sodium sulfate and water in the hydrogel was measured by dehydration method incorporated with DSC [9]. We ran the DSC technique for melting and freezing (**Figure 33)**. The DSC analysis of this hydrogel, from -40°C to 40°C, provides information on the quantitative composition of the hydrogel and describes how water exists within it. The gel, influenced by the effect of [REDACTED], exhibits reduced supercooling and shows on-set nucleation at 24°C. The associated enthalpy for this is around 114 J/g. At a colder temperature, approximately -20°C, another peak is observed, which is attributed to the enthalpy produced by freezable water – essentially the water that has not bonded with the SSD.

During freezing of the hydrogels, we measured the enthalpy change, and decomposed it to crystallizable (forming SSD around 30 C) and freezable water (excessive water to ice at 0 C). Some portion of water can be bounded with the sodium sulfate called as the crystallizable water. The crystallizable water's weight percentage is

$$Crystallizable\ water\ weight = \frac{\Delta H_{crystallizable}}{\Delta H_{total}} = \frac{\Delta H_{crystallizable}}{\Delta H_{crystallizable} + \Delta H_{freezable\ water}}$$

where $\Delta H_{crystallizable}$ is the enthalpy of water freezing as indicated in the DSC curve, and ΔH_{total} represents the sum of all freezing enthalpies during the cooling cycle, $\Delta H_{crystallizable}+\Delta H_{freezable}$ [6]. The freezable water means pure water phase transition to ice. Then, the lid of the DSC cup was removed, and the sample was exposed to dry air to dehydrate the water from the sample. Once all the water is evaporated from the sample, the rest of the sample is only composed of sodium sulfate, [REDACTED], and [REDACTED]. Therefore, the amount of water in the hydrogel (m_{water}) is determined by the difference of mass between the initial and the dehydrated sample. Then, the mass of water crystallizable is obtained according to the crystallizable water weight.

[REDACTED]

Figure 33. DSC heat flow data for [REDACTED]-[REDACTED]-SSD hydrogel.

Basing on this, when the DSC pan is reopened and the water is evaporated, the mass comparison is as follows: Original sample mass: 7.33 mg (Water mass: 3.73 mg, Dry sample mass: 3.60 mg ([REDACTED]: 0.758 mg, [REDACTED]: 0.252 mg and Sodium sulfate: 2.59 mg). Furthermore, importantly, the ratio of the two enthalpies (from SSD and water) suggests that a significant amount of water is bound with [REDACTED]. In conclusion, the weight percentage of SS in the current gel is approximately 41%, which is close to the SSD's weight percentage of 44.1 wt.%. This suggests that it's approaching a practical limit. To enhance the energy storage capacity, it is necessary to reduce the weight of the inactive material, [REDACTED], and the freezable water. Therefore, exploring new synthesis methods or alternative hydrogel materials becomes crucial.

Phase diagram of sodium sulfate hydrate (SSD), following the equilibrium relationship between sodium sulfate and water. The diagram indicates that a composition of 44.1 wt.% sodium sulfate is required to form a pure SSD, which is hypothesized to maximize energy storage capacity (**Figure 34**). This concentration corresponds to the peak energy storage potential as it allows for complete crystallization without excess water or sodium sulfate, thereby leveraging the full latent heat of the SSD during phase change. The diagram is instrumental in determining the ideal SSD concentration for enhanced thermal energy storage in Phase Change Material (PCM) applications, ensuring optimal performance.

[REDACTED]

Figure 34. Phase diagram of sodium sulfate and water [2].

The analytical method encompassed measuring the mass of the samples post-synthesis, followed by dehydration to ascertain water content. The water's mass was determined by subtracting the dry weight from the initial wet weight (**Figure 35**). Additionally, considering the quantities of [REDACTED] and [REDACTED] added, we back-calculated the mass of sodium sulfate. **Figure 36** delves into the intriguing aspects of the concentration of salt and the salt/bound water ratio in various sodium sulfate hydrate (SSD) formulations, including commercial crystals and those synthesized in our lab. Notably, the concentration of salt in commercial SSD crystals aligns closely with the 44.1 wt.% mark indicated in the phase diagram. Our synthesized samples, [REDACTED] SSD 1 and [REDACTED] SSD 2, exhibit actual sodium sulfate concentrations of 43.1 wt.% and 39.8 wt.%, respectively. However, a critical factor here is the salt to bound water ratio, previously outlined in our methodology. For commercial SSDs, the observed ratio of 6.62 suggests a predominance of heptahydrate forms or a significant proportion of anhydrates salt, as opposed to the expected decahydrate structure. In contrast, our [REDACTED] SSD 2 sample, synthesized with a recipe concentration of 44.1 wt.% sodium sulfate, shows a higher ratio of 8.78, indicating a composition closer to the true decahydrate form. Our analysis reveals that the addition of [REDACTED] significantly impacts the water-binding dynamics within the SSD structure. Specifically, [REDACTED] SSD samples demonstrate higher salt to bound water ratios compared to their counterparts without [REDACTED]. For gels, it underscores the critical importance of [REDACTED] gel in the context of PCM formulations, particularly in influencing the salt to water ratio. [REDACTED], a key component in forming the gel matrix, inherently requires a substantial amount of water for its structure. Therefore, adding a significant volume of water during the synthesis of [REDACTED] gels is essential. This matrix structure plays a pivotal role in isolating SSD crystals, effectively preventing the loss of bound water to free space. As a result, [REDACTED] gel-based PCMs exhibit higher salt to water ratios, indicating a more efficient and stable hydration state. Notably, our results show that in gels containing 7% [REDACTED], the salt to water ratio approaches 10, suggesting an exceptionally stable and efficient PCM material. This figure presents a comparative analysis of salt to water ratios in SSD systems with varying [REDACTED] concentrations, highlighting how [REDACTED] gel contributes to creating more effective and reliable PCM materials. By encapsulating SSD in the [REDACTED] matrix, we observe a marked improvement in maintaining the desired hydration state, crucial for the long-term performance and efficacy of PCM systems in thermal energy storage applications.

[REDACTED]

Figure 35. Compositional analysis of synthesized SSD crystals and gels.

[REDACTED]

Figure 36. Composition of salt concentration and salt/bound water ratio in SSD formulations.

Now, we focus on a sodium sulfate-based hydrogel incorporated with [REDACTED] and [REDACTED] to obtain high energy storage density, low supercooling and stability. We found that the weight percentage of sodium sulfate and water influences the energy storage performance because the latent heat of SSD takes majority of thermal energy storage in the hydrogel. Thus, we studied the effect of composition experimentally (T-history method). Three different hydrogels, [REDACTED]-[REDACTED]-SSD Gel 1, 2, and 3 (**Figure 35, 36 and 37**) were synthesized and tested by T-history experiment to show the effect of weight percentage of component.

[REDACTED]

Figure 36. Hydrogels image and mass fraction.

Because of different weight percentage of water, different ratio of salt-water bound according to gels was expected (**Figure 36**). By the dehydration-DSC method, we revealed that gel 2 contains the largest amount of water followed by gel 1 and gel 3. Subsequentially, we can find the sodium sulfate-water bound ratio ($m_{crystallizable,water}/ m_{sodium\ sulfate}$) for three different hydrogels (**Figure 37**). Ideally, the ratio should be 10 to form SSD. The gel 2 has the largest amount of water content leading the highest salt/bounded water ratio and closer ratio to the theoretical SSD. The ratio of gel 1 and gel 3 are 9.18 and 7.27 respectively due to lack of water content according to **Figure 37**. Especially, the amount of water in gel 3 is severely lacking leading residue of sodium sulfate that cannot form decahydrate. We expected it shows the highest energy storage density and followed by gel 1 and 3.

[REDACTED]

Figure 37. Salt/Bound water ratio in SSD formulations for different gels.

We investigated the energy storage performance of three hydrogels using the T-history experiment that was performed independently. **Figure 38** shows the temperature-time curves of the hydrogels overlapped for cycles. The gel 1 ([REDACTED]-[REDACTED]-SSD hydrogel, 100 cycles) result is already reported in the previous section. Gel 2 and 3 were cycled for 10.

The gel 1 and 2 show well-overlapped curves for cycles with stable melting and freezing temperature. However, the gel 3 shows changes in melting and freezing temperature as well as the shape of the plot. Even though the gel 3 contains a higher wt.% of [REDACTED], the nucleation does not happen properly. The effect of [REDACTED] to the hydrogel as a nucleation agent is still mysterious, and we will discuss this later in ITC technique section. Also, the gel 2 showed the lowest degree of supercooling as shown in **Figure 39**. The gel 2 showed the lowest averaged supercooling for cycles of 3.72 °C followed by gel 1 with 5.17 °C and gel 3 with 12.5 °C. The lower supercooling of gel 2 could improve the energy storage density.

[REDACTED]

Figure 38. Temperature-time curves of (a) Gel 1 in melting and (b) freezing for 100 cycles, (c) Gel 2 in melting and (d) freezing (e) Gel 3 in melting and (f) freezing for 10 cycles.

[REDACTED]

Figure 39. Degree of supercooling (=T_m-T_f) of different gels for cycles.

The enthalpy-temperature plots for cycles show the same trend (**Figure 40**). The gel 2 showed almost identical enthalpy graphs while the gel 3 showed decrease of enthalpy values for the first few cycles. The water content played a role for hydrogel structure. Even though the gel 2 and 3 have almost same weight percentage of [REDACTED], the water content of the gel 2 is significantly lower and the hydrogel cannot sustain its original form because the [REDACTED] requires some water to form the cross-link as we discussed in **Figure 35-36**. Therefore, suppressing the amount of water can have a negative effect on the formation of hydrogel and cause a decrease in cycling performance.

Also, the gel 3 shows the lowest enthalpy. This lower enthalpy is originated from small salt/bounded water ratio leading small amount of SSD in the hydrogel. For freezing, the higher supercooling of the gel, the lower enthalpy.

The energy storage density of the hydrogels for cycles is plotted in **Figure 41**. The gel 2 shows the highest energy storage density and the gel 3 shows the lowest value for all cycles. We averaged the energy storage density for cycles on the three hydrogels and compared the energy storage performance. The gel 2 showed the highest averaged volumetric energy density of 38.6 and 38.1 kWh/m^3 for melting and freezing respectively. The gel 1 showed 36.9 and 33.4 kWh/m^3 for melting and freezing respectively. The gel 3 showed 23.4 and 15.5 kWh/m^3 for melting and freezing respectively. Surprisingly, the volumetric energy density trend is similar with the salt/bounded water ratio. Therefore, the salt/bounded water ratio is proportionally related to the energy storage density of the hydrogel.

In conclusion, we synthesized three different hydrogels with different weight percentage of component of sodium sulfate, water, [REDACTED], and [REDACTED] as gel 1, gel 2, and gel 3. The different weight percentage of component led different salt/bounded water ratio. The energy storage density of the hydrogels follows the salt/bounded water ratio. For cyclability, proper water content is required to activate the [REDACTED] as a thickener.

[REDACTED]

Figure 40. Enthalpy-temperature curves of (a) Gel 1 in melting and (b) freezing for 100 cycles, (c) Gel 2 in melting and (d) freezing (e) Gel 3 in melting and (f) freezing for 10 cycles.

[REDACTED]

Figure 41. Energy storage density for difference gels over cycles. Volumetric energy density averaged in cycles for different gels.

D. Rheological Characteristics of the Hydrogel

We showed that the hydrogel composed of [REDACTED]-[REDACTED]-sodium sulfate decahydrate ([REDACTED]-[REDACTED] SSD) have significantly high thermal cyclic stability without any degradation on nucleation temperature and energy density. The mechanical and rheological characteristics of the hydrogel ([REDACTED]-[REDACTED] SSD) and [REDACTED]-sodium sulfate decahydrate ([REDACTED]-SSD) are studied in this section. **Figure 42a** shows the storage and loss modulus (G' and G'') of [REDACTED]-SSD (pink line) and [REDACTED]-[REDACTED]-SSD (blue line). Irreversible deformation occurs if the fluid is deformed larger than a certain strain. The blue G' curve of [REDACTED]-[REDACTED]-SSD shows a sharp downturn, indicating brittle fracturing behavior. This means that the gel under shear does not break homogeneously but rather into larger pieces. In contrast, the pink G' curve of [REDACTED]-SSD drops continuously, indicating a gradual breakdown of the superstructure. This explains the creamy behavior of [REDACTED]-SSD. More importantly, when comparing two samples after melting with increasing the temperature to 45 °C, it clearly showed the origin of high thermal stability of hydrogel. In case of [REDACTED]-SSD without SSD, it exhibited ~10^5 Pa.s. of complex viscosity at 1 Hz while its viscosity decreased to ~10^4 Pa.s after melting (**Figure 42b**), indicating that the [REDACTED]-SSD easily lost their water from SSD when melting. Therefore, this irreversibly losing water cause phase separation and deteriorate thermo-cylic stability. In the contrary, [REDACTED]-[REDACTED]-SSD maintained their viscosity after melting (**Figure 42c**), implying that liquid water is confined into the 3D network of hydrogel and it is re-used when solidifying as SSD. Therefore, [REDACTED] acts as strongly binder for [REDACTED] and SSD as well as functions nucleating agent.

[REDACTED]

Figure 42. Mechanical and Rheological characteristics of the hydrogel (a) Complex viscosity as function of strain to hydrogel and [REDACTED]-SSD. (b,c) Measured complex viscosity of (b) [REDACTED]-SSD and (c) [REDACTED]-[REDACTED]-SSD with frequency sweep.

[REDACTED]

Figure 43. Thermo-Rheological characteristics of the hydrogel (a,b) Storage modulus of [REDACTED]-SSD upon repetition of cycle (45°C ⇔ 15°C) and (c,d) Storage modulus of [REDACTED]-[REDACTED]-SSD upon repetition of cycle (45°C ⇔ 15°C)

We explore the thermal cyclic stability and thermo-rheological characteristics of hydrogels composed of [REDACTED]-[REDACTED]-Sodium Sulfate Decahydrate ([REDACTED]-[REDACTED] SSD) and [REDACTED]-Sodium Sulfate Decahydrate ([REDACTED]-SSD). We observed that the [REDACTED]-SSD hydrogel did not recover its modulus after a cycle, indicating that the hydrogel underwent permanent damage upon cycling (**Figure 43a and b**). This lack of recovery could be attributed to the absence of nucleation sites for crystal growth, which inhibited the formation and growth of Sodium Sulfate Decahydrate (SSD) crystals during the recovery phase. In contrast, the [REDACTED]-[REDACTED] SSD hydrogel exhibited excellent thermal cyclic stability, with no degradation in nucleation temperature or energy density after multiple cycles (**Figure 43c and d**). We found that the presence of [REDACTED] in [REDACTED]-[REDACTED] SSD hydrogels played a crucial role in maintaining their structural integrity during thermal cycling. [REDACTED] is a [REDACTED]ic amino acid that contains both positively charged amino group ([REDACTED]) and negatively charged carboxyl group ([REDACTED]) at neutral pH. These charged groups can participate in chemical reactions with other functional groups, such as those found in the crosslinking agent and the polymer matrix of the hydrogel. The strong network provided by [REDACTED] can hold the liquid phase of SSD, minimizing the decrease in modulus when compared to a hydrogel without [REDACTED]. This property helps to maintain the structural robustness of the [REDACTED]-[REDACTED] SSD hydrogel by preventing the loss of the liquid phase during thermal cycling. Additionally, [REDACTED] acts as a nucleating agent for SSD crystals, promoting crystal formation and aiding in the recovery of the hydrogel's modulus after a cycle. The presence of [REDACTED] provides nucleation sites for the formation of SSD crystals during the recovery phase, which facilitates the efficient growth of crystals and leads to the recovery of the hydrogel's modulus. In summary, our study highlights the importance of [REDACTED] in enhancing the thermal cyclic stability and mechanical properties of [REDACTED]-[REDACTED] SSD hydrogels. The absence of [REDACTED] in [REDACTED]-SSD hydrogels results in irreversible damage upon cycling, whereas [REDACTED]-[REDACTED] SSD hydrogels exhibit beautiful cycling behavior.

[REDACTED]

Figure 44. Thermo-Rheological characteristics of the hydrogel under harsh temperature.

The [REDACTED]-[REDACTED]-Sodium Sulfate Decahydrate ([REDACTED]-[REDACTED] SSD) hydrogel exhibits exceptional thermal stability with a recovery phase observed at 60°C, 70°C, and 80°C, during which there is no degradation (**Figure 44**). Despite exposure to these elevated temperatures, the hydrogel maintains its structural integrity, and its mechanical properties remain intact after the heating and cooling cycles. This outstanding behavior can be attributed to a combination of factors, including the nucleation-promoting effect of [REDACTED], the strong network structure of the hydrogel, and the stable crosslinking interactions between its constituents. These properties make the [REDACTED]-[REDACTED] SSD hydrogel a promising candidate for applications.

One of the key factors contributing to the hydrogel's high stability at elevated temperatures is the presence of [REDACTED], a [REDACTED]ic amino acid. [REDACTED]'s molecular structure, with both a positively charged amino group ([REDACTED]) and a negatively charged carboxyl group ([REDACTED]) at neutral pH, facilitates its interaction with other functional groups in the hydrogel. This enables [REDACTED] to act as a nucleating agent for SSD crystals. During the cooling phase after exposure to high temperatures, the [REDACTED]-mediated nucleation promotes efficient crystal formation and growth, aiding in the hydrogel's recovery and maintaining its mechanical properties. Moreover, the [REDACTED]-[REDACTED] SSD hydrogel possesses a strong and resilient network structure due to crosslinking interactions between [REDACTED], [REDACTED], and sodium sulfate decahydrate. These crosslinks provide stability and prevent the structural degradation of the hydrogel during thermal stress. Even at high temperatures, the crosslinking within the hydrogel matrix maintains its structural integrity, allowing it to withstand repeated heating and cooling cycles without breaking down. More importantly, Another crucial aspect contributing to the hydrogel's stability at high temperatures is the role of [REDACTED] in holding the liquid phase of Sodium Sulfate Decahydrate. While exposure to elevated temperatures may lead to the melting of SSD in the hydrogel, the strong network provided by [REDACTED] helps in retaining the liquid phase. This minimizes the reduction in modulus and prevents complete structural failure, allowing the hydrogel to recover its mechanical properties during the cooling phase. In addition, the [REDACTED]-[REDACTED] SSD hydrogel demonstrates excellent chemical stability, ensuring that its molecular structure remains intact during thermal cycling. The stable crosslinking between [REDACTED] and [REDACTED], along with the interactions between these components and sodium sulfate decahydrate, prevents chemical degradation and ensures the hydrogel's resilience to temperature changes.

E. Isothermal Titration Calorimetry (ITC) to Investigate the Effect of [REDACTED]

For more than a decade, researchers have explored the use of nucleating agents to trigger phase change in PCM for latent heat storage. Throughout this time, they have investigated a diverse array of inorganic and organic nucleating agents applied to various salt hydrates. Despite extensive research into different nucleating agents, the underlying science behind the nucleation mechanism of these additives remains unexplored. We believe that by conducting a more scientific and rigorous analysis of the nucleation mechanism, it will become feasible to systematically evaluate potential nucleating agents. Therefore, our exploration has commenced, focusing on techniques to study the interaction between nucleating agents and salt ions.

Isothermal titration calorimetry (ITC) is a powerful calorimetric technique used to monitor the thermal effects of molecular interactions by measuring the temperature response when one molecule is titrated into another. ITC provides both thermodynamic and kinetic parameters of molecular interactions under different experimental conditions such as temperature, pH, and concentration. Each ITC experiment is conducted at a constant temperature and the instrument monitors any temperature fluctuations of the sample cell when each titration is conducted, with respect to a reference cell. As seen in **Figure 45**, multiple titrations are conducted to obtain a Heat flow vs. time plot with equidistant spikes corresponding to individual titrations. The area under each spike provides the energy associated with the binding energy of the interacting species with respect to the molar ratio of titration. Such enthalpy vs. injection plots provide a interaction energy profile across a range of molar ratio depending on the choosen titration concentrations and injection volumes. In our experiment, we aimed to understand the nucleation mechansim of [REDACTED] and hence we conducted three sets of experiments at 15°C, 25°C, and 35°C. A comparision is done between the energy profile of sodium sulfate titrated in water and sodium sulfate titrated in [REDACTED].

As seen in the **Figure 46**, at 35°C both the profiles overlap exactly which indicates that at 35°C the presence of [REDACTED] has no immpact on the sodium and sulfate ions. At 25°C, one can observe a difference in the energy profiles of the two titrations which indicates that [REDACTED] has some energetic interactions with sodium and sulfate ions at 25°C. This interaction increases at 15°C as seen by the increase in the difference between the two titrations in the 15°C plot.

Parallels are drawn to the case of borax as well, which is a know nucleating agent. One can see no such trend in the Borax titrations (**Figure 47**) going from 35°C to 15°C, indicating that borax does not have a temperature dependent interaction with sodium sulfate, and hence confirms that borax use a templated crystal structure nuceation mechansim to nucleate Glauber's salt.

Our subsequent analysis involves varying parameters such as pH to better understand the nucleation mechanism of [REDACTED]. This use of this characterization tool can also be extrapolated to other salt hydrates and can be used to screen nucleating agents.

[REDACTED]

Figure 45. Heat flow profiles (top) and energy profiles (bottom) of sodium sulfate in [REDACTED] (left) and in water (right).

[REDACTED]

Figure 46. Energy profile trends of sodium sulfate titration in [REDACTED] at different temperatures.

[REDACTED]

Figure 47. Energy profile trends of sodium sulfate titration in borax at different temperatures.

The nucleation of Glauber's salt (GS) in our PCM system is assisted by the presence of nucleating agent, [REDACTED]. The field of thermal energy storage has seen much research on understanding the nucleation mechanism of inorganic nucleating agents, where the molecule assists in nucleation due to a matching crystal lattice with the salt hydrate. However, there is still a lack of understanding on how organic nucleating agents interact with the salt hydrate to promote phase change. [REDACTED] is an organic amino acid with a [REDACTED]ic structure (both charges present on the structure), where either of the two charge becomes dominant as pH of the system changes (**Figure 48**). We demonstrated that both positive and negative charges on [REDACTED] are needed for successful nucleation of SSD, and when either of the two charges become dominant results in hindered nucleation (**Figure 48**). We further proceeded with exploring this effect of [REDACTED] using ITC that allowed us to monitor molecular scale interactions between the [REDACTED] and Na^+ and SO_4^{2-} at different temperature and pH conditions. A typical titration curve conducted at pH 7 and 25°C is shown in **Figure 49**, where sodium sulfate solution is titrated into [REDACTED] solution. Multiple such titrations were conducted at pH 2, 7 and 10, and at temperature 35°C, 25°C and 15°C. The analysis of this data revealed a trend in [REDACTED] - salt ion interaction energy at different pH across the temperature range. At a neutral pH (**Figure 50a**) we see an increase in the interaction enthalpy between the interacting molecules as temperature is reduced, a pattern favorable for nucleation. For basic pH of 10 (**Figure 50b**), the dependence of enthalpy of interaction on temperature is not distinctly evident which would explain why nucleation was hindered for this sample in the T-History experiments. At an acidic pH of 2 (**Figure 50c**), titration isotherms have positive enthalpy values, indicating repulsive forces between [REDACTED] and salt ions, which explains the absence of nucleation in the pH

2 scenario. Further replicates of these titrations would be conducted to obtain better accuracy of the quantitative interaction energies between [REDACTED] and SSD. We are also interested in analyzing the presence of [REDACTED] in the actual crystal lattice of SSD, for which subsequent experiments would involve crystallographic characterizations.

[REDACTED]

Figure 48. pKa of [REDACTED]. Effect of pH on the charge of [REDACTED]

[REDACTED]

Figure 49. T-History of [REDACTED] and SSD at different pH

[REDACTED]

Figure 50. ITC titration curve and isotherm (integration of peaks from titration curve) for sodium sulfate titration into [REDACTED] at pH 7 and 25°C

[REDACTED]

Figure 51. Interaction enthalpy between [REDACTED] and sodium sulfate at (a) pH 7 and (b) pH 10. (c) ITC isotherm at pH 2

F. Thermal conductivity measurement

The thermal conductivity of salt-hydrogel samples is measured by the bi-directional 3-omega method which measures heat penetrating upward to the sample and downward to the substrate. The bi-directional 3-omega method has a high accuracy for low thermal conductivity and slippery materials [10]. In the bi-directional 3-omega method, a sample is placed on a micron-scale metal line patterned on a substrate. This method measures the thermal conductivity of the substrate first using conventional 3-omega method, and then measures the thermal conductivity of the sample placed on the substrate. Heat from a metal heater diffuses upward into the sample and downward into the substrate. **Figure 52a** shows the measurement setup. We used the lock-in amplifier and humidity chamber (**Figure 52b**) to prevent moisture loss from the hydrogel. We tested the humidity effect on the hydrogel (**Figure 52d**), and humidity significantly affects hydrogel samples; they lose water rapidly when exposed to dry air. To reduce water evaporation from samples during measurement, an acrylic humidity chamber with a screw-on clamp and O-ring seal was built as shown in **Figure 52b**. **Figure 52d** shows that when hydrogel samples are in this chamber, the hydrogel shrinks to 80% of its weight over two days and ~95% over hours, enough time for thermal conductivity measurement. Therefore, hydrogels will be placed inside the chamber when their thermal conductivity is measured.

The side view of the chip carrier with the test sample is shown in **Figure 52b**. The microfabricated metal heater/sensor on the glass substrate is on the carrier (**Figure 52c**). The 3-omega experiment was conducted by the electric connection (**Figure 52e**) after the sensor is calibrated (**Figure 52f**). We employed the common-mode subtraction-(CMS) to cancel out the 1-omega voltage during 3-omega measurement to enhance measurement accuracy.

[REDACTED]

Figure 52. (a) Thermal conductivity measurement setup (b) Humidity chamber built for hydrogel thermal conductivity measurement and side view of carrier with test sample (c) Microfabricated metal heaters on glass sample on carrier (d) Humidity effect on the hydrogel exposed to air and inside chamber with high humidity (e) Electric circuit composition (f) Calibration of the sensor.

[REDACTED]

Figure 53. Best fit line of the sensor.

Sinusoidally-varying current at increasing frequencies is passed through the metal pattern and voltage between the straight line is measured at the third harmonic. The measured voltage output is converted to a temperature oscillation and the thermal conductivity is computed from the slope of the temperature oscillation according to frequency. The thermal conductivity of the substrate alone is measured according to equation (slope method [10, 11], **Figure 53**).

$$k = -\frac{I^2 R_0}{2\pi L}\left(\frac{\partial \Delta T}{\partial \log{(2\omega)}}\right)$$

Next, the measurement is repeated with the sample. By subtracting the thermal conductivity of the substrate from the apparent total thermal conductivity, the thermal conductivity of the sample can be deduced. The thermal conductivity of the glass substrate without a sample was computed as 1.1–1.2 W/m·K. This matches the known value for borosilicate glass at room temperature, 1.1 W/m·K [12].

Since slight uncertainties in slope computation cause large changes in the result, computational simulations of the experimental setup are being performed to further understand and complement analysis. The configuration of the COMSOL simulation is shown in **Figure 54a**. Both frequency-domain simulations, which are fast and convenient for changing only frequency, as well as transient simulations at fixed frequencies, are performed in this research. **Figure 54b** shows the result of a transient simulation with induced Joule heating at a fixed frequency; the peak value of the temperature perturbation is compared with the frequency domain simulation result, theoretical curve, and experimental result in **Figure 54c**. When the corresponding heat power and electric current from experiment are applied for both numerical approaches, the simulation results have shown good agreement with the experimental result and with each other. Thus, the frequency domain simulation provides equivalent results that can be used in 3-omega analysis.

[REDACTED]

Figure 54. (a) COMSOL simulation for the glass substrate (b) Temperature oscillation in transient simulation (c) Validation of COMSOL simulation for the glass substrate of a chip with 2b=25 µm.

Deionized (DI) water is used for checking the sensor's measurement performance. We expand the numerical analysis for a DI water droplet based on the frequency domain. The thermal conductivity of the glass is measured as 1.17 W/m·K which is close to the literature value, 1.1 W/m·K. After measuring the thermal conductivity of the glass, DI water's thermal conductivity is measured as 0.66 W/m·K from the slope of the measurement by subtracting the apparent thermal conductivity from the glass thermal conductivity.

We conducted COMSOL simulation for the bi-diectional 3omega case as well. **Figure 55a** shows a temperature oscillation of the water droplet on the metal sensor. The shape and volume of the water droplet are similar to the experimental study. **Figure 55b** is a cross-section view of the temperature. The isothermal lines show that the heat is spreading well through the glass than the DI water because the water has a lower thermal conductivity than the glass substrate. Also, the cross-section view suggests that the size of the water droplet is sufficient so that it is working well to accommodate the thermal penetration wave to measure thermal conductivity.

[REDACTED]

Figure 55. (a) COMSOL simulation for DI water droplet fully covering the metal sensor (b) Cross sectional view for the droplet showing lines of constant temperature (c) Simulations performed for DI water not fully covering the metal sensor (d) Coverage effect for the temperature oscillation.

Numerical simulation allows analysis of the effect of subtle factors in the measurement. **Figure 55c,d** shows that the thermal conductivity of the DI water should be measured when the droplet covers the metal sensor fully, because when DI water only partially covers the metal line, the slope's magnitude increases and the effect of the polymer layer is larger than the other. During DI water measurement, water evaporates and the volume of the water shrinks. The water droplet size decreases with time and part of the metal heater become exposed to air, which has lower thermal conductivity than water. If the metal sensor measures the water droplet and air simultaneously, the measured thermal conductivity is relatively lower. The partial coverage causes the metal sensor to measure the insulation layer's thermal conductivity in addition to the sample's thermal conductivity. Other possible conditions such as different moisture air diffusivity conditions, evaporation rate, and humid initial conditions should be studied more in the future.

A promising sample of a thermal storage material, [REDACTED]-[REDACTED]-SSD hydrogel is measured with a working glass sensor. This sample composed of [REDACTED], [REDACTED], and sodium sulfate with water is carefully placed on the sensor and measured continuously seven times in 1 to 100 Hz frequency range over a six-hour period. **Figure 56a** shows that the slope of the temperature oscillation (of the metal heater) is changing with each measurement. Sample pictures before and after the experiments are shown in **Figure 56b**; the sample is exposed to a dry air at room temperature, and the thermal conductivity has reduced continuously according to loss of water. **Figure 56c** quantifies the reduction of thermal conductivity for each measurement in 1 to 50 Hz frequency range selection. When the sample is applied on the sensor at first, the measured thermal conductivity is 0.7 W/m·K. After every water is evaporated from the hydrogel, the thermal conductivity converges to 0.2 W/m·K. Instability in the measurement of current means that there may be significant uncertainty in this measurement, at most 20%. Therefore, the setup will be modified to control current and to measure inside a preexisting humidity chamber to maintain high humidity of samples.

[REDACTED]

Figure 56. (a) Temperature oscillation for the [REDACTED]-[REDACTED]-sodium sulfate sample on the glass substrate (b) Sample sensitivity to humidity causes it to dry out (c) Measured thermal conductivity of the sample

The project deliverable is to increase the thermal conductivity of a phase change composite above 0.75 W/m-K. A key finding is that thermal conductivity depends strongly on moisture content. Our data show that gels with >95% water by mass in their liquid state have thermal conductivity of 0.62 W/m-K, equivalent to liquid water on the same sensor. Also, thermal conductivity decreases to ~0.4 W/m-K as the mass of water in the hydrogels decreases to ~30%.

To better control and understand what is going on, we have begun measuring the [REDACTED] hydrogel with [REDACTED] and sodium sulfate decahydrate with our 3-omega method. We had difficulty pressing the solidified gel onto the sensor, as it was not soft enough to conform to the metal pattern and absorb heat. Thus, we have established a technique to immerse a calibrated 3-omega sensor with its wires into the hydrogel. This is done at the precise time before it is hardened, before the last step of the synthesis recipe. We have shown that signals can still be extracted from the sensor despite being frozen inside the hydrogel. For the measurement itself, we are working on other aspects.

A key outcome for this report is that a physical hydrogel containing [REDACTED], [REDACTED] and sodium sulfate has thermal conductivity above 0.7 W/m-K in the solid state. Along with the bi-directional 3-omega method, we also employed a commercially purchased meter [13] (TEMPOS from METER Group), which employs the transient hot-wire method [14] (ASTM D5334-22, 2022) to verify our measurement correctness. **Figure 57** shows the schematic of the meter and data from this sample. A metal-sheathed probe containing a heater and thermocouple was embedded into a hydrogel in its synthesis beaker. The beaker was sealed to limit moisture loss and immersed in a temperature-controlled bath. The temperature was fixed at each point for at least two hours and the average of three measurements spaced apart by twenty minutes was reported. In **Figure 57b**, Red points indicate data taken during heating and blue points indicate data taken while cooling the sample. Dashed lines indicate the perceived temperature at which thermal conductivity sharply changed. We are still working on repeating these results to understand why thermal conductivity increases to ~0.9 W/m-K as temperature increases towards the melting temperature. However, we believe the thermal conductivity of the solidified gel is at least 0.7 W/m-K and that the liquid thermal conductivity is 0.55 W/m-K. The fact that the gel in solid state has higher thermal conductivity than its liquid state is another key finding. These findings will help guide research towards the effect on the rate of system energy storage, how to enhance the liquid state properties, and modeling the solid thermal conductivity with available theories.

[REDACTED]

Figure 57. (a) Transient hot-wire method to measure the thermal conductivity of the hydrogel (b) Thermal conductivity of composite containing [REDACTED], [REDACTED] and sodium sulfate decahydrate measured above and below its solid-liquid transition.

Upon heating this material near its melting point (~28 C), the thermal conductivity κ appears to increase to 1 W/m-K, then decreases to that of the hydrogel in its unfrozen state, 0.56 W/m-K. Increased thermal conductivity near the phase transition for PCMs has been observed by other groups, for example paraffins using a suspended wire 3ω method [15]. Since thermal conductivity is proportional to specific heat, the increase in κ was thought to be due to increased volumetric heat capacity near the phase transition. Other researchers have suggested that if the rate of microscopic transformation is fast compared to the rate of transport of heat, heat capacity increases but thermal diffusivity decreases, and thermal conductivity changes smoothly at phase transitions [16]. We offer a third explanation, that phase change materials absorb heat input by the sensor and melt during the transient measurement. The absorption of heat is recorded by the sensor and interpreted as effectively higher thermal conductivity though not from the same microscopic origin, like conductivity enhanced by convection in liquids.

Here we present data for [REDACTED] hydrogels with dispersed [REDACTED] particles which are moderately hydrophilic and have high thermal conductivity (~120 W/m-K). **Figure 58a** shows thermal conductivity for [REDACTED] hydrogels as a function of water content in the gel on a volumetric basis. Hydrogels with added [REDACTED] show enhanced thermal conductivity above the hydrogel alone with a maximum measured value of 0.7 W/m-K. We think that greater enhancements could be measured if the particles were manipulated to be in complete thermal contact and if particles had higher aspect ratio. **Figure 58 b,c** show the hydrogel appears black under optical microscopy and we cannot distinguish individual particles. The morphology of the particles is roughly spherical with 10 µm diameter. No attempt was made to control the distribution of the particles, but they were visually confirmed to be well-dispersed by ultrasonication in an aqueous solution before being poured into the polymer solution, shaken, and poured into molds for overnight gelation.

[REDACTED]

Figure 58. (a) Thermal conductivity of [REDACTED] hydrogels without and with [REDACTED] particles (2% on a weight basis) as a function of the volume of water in the hydrogel. Measurements were made with the 3ω method. (b) Edge of dried hydrogel under optical microscope, hydrogel containing 2 wt.% [REDACTED] under 5X magnification. (c) 20X magnification.

[REDACTED]

Figure 59. (a) Thermal conductivity of paraffin wax as a function of temperature measured with 3-omega method. (b) Thermal conductivity of [REDACTED] [REDACTED] sodium sulfate decahydrate ([REDACTED]-[REDACTED]-SSD) by 3-omega method.

Accurate measurements of thermal conductivity of phase change materials (PCMs) near their phase transition is helpful in modeling their performance in real systems. The measured thermal conductivity (κ) of [REDACTED] [REDACTED] sodium sulfate decahydrate hydrogels ([REDACTED]-[REDACTED]-SSD) from this method do not show a peak in κ as the solidified [REDACTED]-[REDACTED]-SSD becomes unfrozen. To further validate our data, we have recently measured thermal conductivity of paraffin wax by the 3-omega method near its phase transition. We used prior experience with mounting [REDACTED]-[REDACTED]-SSD to first heat the wax to liquid state, then pour and solidify it in contact with the sensor. Results were analyzed in the same manner as any material and assumed no heat generation occurred in the material.

Figure 59a shows the trend of κ_{wax} for temperatures at which the solidified wax becomes liquid. Results showed $\kappa_{wax,solid}$=0.22 W m^{-1} K^{-1}, increasing to 0.29 W m^{-1} K^{-1} at 50 C, and $\kappa_{wax,liquid}$=0.15 W m^{-1} K^{-1}. We observed a peak in the change of thermal conductivity of wax with temperature but did not observe a peak for [REDACTED]-[REDACTED]-SSD (**Figure 59b**), for the same measurement method. We have not investigated whether this occurs for solidifying of PCMs, only for melting PCMs, and data quality could be improved with an automated cancellation circuit. Whatever the cause of the peak, phase change material heat absorption was not accounted for in the data analysis. In fact, phase change material heat absorption is not usually a factor in thermal conductivity analysis, and measurements near the phase transition by ~1 C are not reported or not discussed in the literature.

Therefore, we are developing a theory to account for the heat release during 3-omega measurements. Heat diffusion in a material which is changing phase, where the location of the interface is not known *a priori*, was first studied by J. Stefan with regards to ice formation in the polar seas. Stefan problems are nonlinear due to the energy interface balance at the solid-liquid interface. The specific Stefan problem we face also has a periodic heat flux boundary condition:

$$-\kappa_l \left.\frac{\partial T}{\partial r}\right|_{r=0} = q_0''(1+\cos(4\pi f t)),$$

where κl is the liquid phase thermal conductivity assuming the solid is melting, T is temperature, r is the radial coordinate, q_0'' is a constant heat flux, f is the frequency of the input current and t is time. The fact that this boundary condition is time-dependent, along with the nonlinear boundary condition between the solid and liquid, means that there is no exact analytical solution. We are seeking an approximate analytical solution to the temperature of the PCM $T(r=0,t)$ as a function of thermal conductivity κl as well as interface location $s(t)$ and heating frequency f. Given $s(t)$, this solution can be inverted as a nonlinear least-squares problem to find an optimal value of κl.

[REDACTED]

Figure 60. (a) Schematic of cylindrical geometry of simulation. Dimensions not to scale. (b) Temperature of paraffin wax at time of 0.1 seconds for initial temperature 0.1 C below melting temperature.

To validate the theory, we are also conducting simulations of heating wax and the [REDACTED]-complex from a 3-omega sensor. The simulations are done in ANSYS Fluent with its solidification physics module. Figure 10a shows a schematic of our heat transfer problem as implemented in software. **Figure 60b** shows example results for a wax bead heated by our 3-omega sensor at an initial temperature 0.1 C below melting temperature. The simulations report temperature $T(r=0,t)$ and interface location $s(t)$ which can be fed into the theory. We anticipate that this will improve accuracy of our results and improve our understanding of behavior near the phase transition relevant for building envelopes and indoor thermal energy storage.

1.4. Applications to Water Heating

A. Thermal storage modeling in a water heater system

For a performance assessment of hydrogels as thermal storage materials, thermal modeling of industrial application is required. Here, thermal and fluid modeling of both water and phase change material in water heater system is conducted using COMSOL Multiphysics. **Figure 61** shows the geometry of the system and boundary conditions. The 2D-axisymmetric water heating-cooling system is built with laminar water flow inside the 1/2-inch diameter tube at the center. The tube wall material is aluminum, with extended surfaces in radial direction. Phase change material (PCM) is filled between adjacent extended walls. The wall thickness, width and PCM thickness are arbitrarily given as 10, 100, and 40 mm, respectively, and to be optimized later. The melting temperature of PCM is 32°C, and initial temperature of PCM is 40°C for all simulations.

[REDACTED]

Figure 61. 2D-Axisymmetric water heater system. (a) 3D-modeled water heater system (onset) and simulation domain. (b) resultant transient phase state of PCM.

First, to analyze the effect of supercooling on heat exchanging effectiveness, the average heat transfer rate as a function of supercooling temperature is obtained. The simulated supercooling temperature ranges from 0°C to 20°C, with three different water inlet temperatures of 0, 5, 10°C. **Figure 62** shows the resultant average heat transfer rate as a function of supercooling temperatures. This shows that the average heat transfer rate exceeds up to four times higher without supercooling, compared to the case with 16~20°C supercooling temperatures. This is because when supercooling occurs, PCM takes longer time to fully solidify than PCM without supercooling.

[REDACTED]

Figure 62. Average heat transfer rate as a function of supercooling temperature.

Next, the spatial variations of phase change behavior is studied. For the top and bottom PCM blocks, six points in horizontal direction and 4 points in vertical direction are picked as depicted in **Figure 63**. For a given water inlet temperature of 10°C, local temperature changing rates during phase change are recorded and calculated for different supercooling temperatures.

[REDACTED]

Figure 63. Local points picked to calculate temperature change rates for spatial variation study. (a) Six points spaced in horizontal direction, (b, c) four points spaced in vertical direction. Top block and bottom block have different points for temperature sensing.

Figure 64 shows that the temperature change rates vary as a function of location and supercooling temperature. Specifically, for horizontal spatial variations, the inner part of PCM (nearer to the water pipe wall, #2 from **Figure 63a** have 1.5 times faster temperature change than outer part of PCM (#6 from **Figure 63a** for top PCM block. For the bottom block, the temperature change rate is 3 times faster. Vertical variations show more distinctive increase, which was 4 times faster for top block, and 3 times for bottom block. However, these increases happen more stiff when the supercooling temperature is less, but analysis in depth is needed because temperature change itself is too low to directly compare with higher supercooling cases.

[REDACTED]

Figure 64. Temperature change rate during phase change (solidification) as a function of onset temperature, for different locations on PCM. (a) two points from **Figure 63a** (b) two points from **Figure 63b, c**.

So far, heat transfer performance of PCM in water heater application is evaluated for different supercooling temperatures. To design a model using PCM in this project, extensive calculation will be continued to simulate tradeoffs between geometric parameters and material properties of PCM. In addition, 1-D model from AO Smith for water heater applications will be integrated with simulation results.

COMSOL simulation does not present an inbuilt supercooling model for phase change materials, hence we incorporated our own phase change model to mimic supercooling as seen in the system. In our previous model, we set T_{melt} to a fixed value of 31.67°C and varied ΔT_{pc} as degree of supercooling (0°C, 6°C, 12°C). Upon further analysis of our results, we realized that due to numerical error of the simulation, the 0°C supercooling case did not incorporate any latent heat contribution during phase change (as seen in **Figure 66**). Both 6°C and 12°C supercooling cases showed equal contribution of latent heat (~101 J/g) in their phase change, however 0°C only had sensible heat across its entire freezing run.

[REDACTED]

Figure 65. Phase change model applied in COMSOL simulation [17].

[REDACTED]

Figure 66. Latent heat contribution for the three cases of supercooling. Both 6°C and 12°C show equal release of latent heat and 0°C supercooling case shows only sensible heat contributions and no latent heat.

We modified our model to resolve this error by changing the way degree of supercooling was defined in our simulation (other condition: entire system initialized at 45°C, and water at different inlet temperatures ranging from 10°C to 25°C allowed to flow through the heat exchanger). We set ΔT_{pc} to a fixed value of 6.7°C and varied T_{melt} to 31.67°C (0°C supercooling), 25.67°C (6°C supercooling), and 19.67°C (12°C supercooling). This allowed us to rectify the issue of no latent heat release at 0°C supercooling case. As seen in **Figure 68**, we see latent heat contributions across all degrees of supercooling and all water inlet temperatures where phase change is observed (**Figure 67**). This analysis confirmed that the updated model of supercooling is an improvement and is a better description of the real scenario compared to the previous model.

[REDACTED]

Figure 66. Change in enthalpy release and phase across the PCM temperature drop for different degrees of supercooling [(a) 0°C, (b) 6°C, (c) 12°C] and different inlet temperatures.

[REDACTED]

Figure 68. Latent heat distribution across the operating temperature of PCM for different inlet temperatures of water.

The effect of supercooling on the efficiency of HX is illustrated in **Figure 69**, where the latent heat extracted from simulating phase change is plotted against inlet temperatures for different degrees of supercooling. As undercooling in the system increases, we are restricted by the allowed inlet water temperature before we start to hinder system efficiency by not extracting all the available latent heat in the [REDACTED]-[REDACTED]-SSD system. Total heat transfer rate for different scenarios was further calculated from inlet and outlet temperatures of water, plots of which are shown in **Figure 70**. This data was utilized by AO Smith for efficiency determinations and applications in real world scenarios across different climate zones.

[REDACTED]

Figure 69. A correlation between the degree of supercooling and inlet temperature, and its effect on the available latent heat obtained during phase transition.

[REDACTED]

Figure 70. The outlet temperature (a) and corresponding heat transfer rate (b) obtained when running water, at different inlet temperatures, through [REDACTED]-[REDACTED]-SSD water heater HX.

We also show the effect of thermal conductivity enhancements on both melting and solidification processes (**Figure 71**). The baseline thermal conductivity was chosen as 0.4824 W/m-K. In general, higher thermal conductivity will result in higher heat transfer rate. With higher thermal conductivity (up to 300% enhancement), the fully solidified/melted time can be reduced up to 20% compared to baseline case. Larger temperature differences between inlet water and melting temperature will further minimize the fully melted/solidified time.

[REDACTED]

Figure 71. Effects of thermal conductivity enhancements on (a) melting (b) solidification processes.

Besides the enhancements of thermal conductivity, we also simulated a potential PCM candidate, [REDACTED], which has a higher melting temperature at 58°C. We investigated this material and the results will be covered in section 1.5. **Figure 72** shows the heat transfer rate change with different supercooling (SC) values. The water inlet was kept at 20°C with an initial PCM temperature at 65°C. Higher SC will lead to lower heat transfer rate due to lower temperature differences.

[REDACTED]

Figure 72. Effects of supercooling (SC) on heat transfer rate for [REDACTED] solidification.

For performance assessment of thermal storage in a real application, we integrated our phase change material (PCM) thermal storage model (COMSOL) into a hot water heater model developed by A.O. Smith. The PCM thermal storage model has been illustrated above. It consists of a water flow channel in the center attached with ten aluminum fins and PCM is stored between fins. The size of the thermal storage section is set at 0.5m in height and 0.25m in diameter, which is reasonable for a regular size water heater. **Figure 73a** shows the schematics of a PCM integrated water heater. A PCM section is adjunct to a 1-D water heater model. The water heater model is developed by A.O. Smith. It consists of 12 nodes, where node#0 is for hot water drawn and node#11 is for cold water refilling. A PCM section is set between node#3 and node#9. When charging and discharging the PCM section, water flows out from node#3, goes through the PCM section and gets back to node#9. The heat transfer process between PCM and the water was simulated and calculated by COMSOL Multiphysics as shown in **Figure 73b**. The heat transfer data was then imported into A.O. Smith's water heater model. We use Uniform Energy Factor (UEF) test (**Figure 73c**) to evaluate the water heater. The UEF test is a standard testing procedure for water heater suggested by the Department of Energy. It simulates the water usage condition in a 3-day period for residential use. Our baseline is a heat pump water heater (HPWH) without PCM section.

[REDACTED]

Figure 73. (a) Schematics of the model (b) Heat transfer data from COMSOL simulation (c) UEF test.

Figure 74 shows the results of water heater simulation in UEF tests. Both **Figure 74a** and **Figure 74b** present three plots. The first plot shows the temperature changes from node#0 to node#11. When drawing hot water, the temperature nodes will drop almost vertically in the plot. This is due to the relatively short hot water drawing time (tens of minutes) compared to a large time scale (3-day) of the entire test. The second plot shows both the instantaneous energy use throughout the simulation and the cumulative energy efficiency of the system. The third plot shows the cumulative energy use split by heating element and heat pump (HP). Comparing **Figure 74a** and **Figure 74b**, we can find that with PCM storage section, heat pump is more preferred to be used for heat generation. This is because the PCM storage section can serve as a partial heating element for supplementary heating power. When in high demand, we can reduce the usage of heating element due to the supply from PCM section. In low demand, the heat pump can gradually charge the PCM section for next high-demand usage. Since the heat pump has intrinsic high energy efficiency with coefficient of performance (COP) larger than 1, the energy is saved by using more heat pump instead of heating element. In a 3-day period, the total energy usage has been saved for 1.27 kWh, the COP increased to 2.817 from 2.519, the unsatisfied demand minutes reduced 28%.

[REDACTED]

Figure 74. (a) Results of a HPWH without PCM (b) Results of a HPWH without PCM.

Different connections between PCM section and water heater are also tested. Previously we used node#3 to import hot water and node#9 for cold water. **Figure 75** shows results of using different nodes for transporting water. For this test, the cold startup time was expanded to 19 hours to make sure the water heater really was stabilized before starting the test. The first row in figure 8 shows the baseline case without PCM section. From the table, we can see by using node#3 as hot node and node#9 as cold node, it has the highest system COP and lowest unsatisfied minutes. While using node#4 and node#9 as hot and cold nodes, more energy (1.7kWh) can be saved with higher unsatisfied minutes.

[REDACTED]

Figure 75. Different combinations of connections between PCM section and water heater.

1.5. Cost Analysis

We analyzed the cost of these three different hydrogels; gel 1, 2, and 3. The cost per mass for each material is based on private communication and various suppliers' information. For 1-ton minimum order requirement, the sodium [REDACTED] is estimated at around \$0.3/kg [18], the [REDACTED] can be supplied at \$1/kg [19], and the sodium sulfate is provided at \$0.1/kg [20]. Also, we estimate the water price at \$0.6/kg [21]. These prices do not include the shipping and delivery. We multiply each component cost value by individual gel weight percentage and the cost in the gel for each component can be evaluated.

$$wt\% = \frac{mass\ of\ the\ component\ in\ the\ gel}{Total\ mass\ of\ the\ gel}$$

$$Cost\ of\ material\left(\frac{\$}{kg_{material}}\right) * wt\% = Cost\ in\ gel_{Component}\ \left(\frac{\$}{kg_{Component\ in\ gel}}\right)$$

The calculated cost of the gel for individual component is in **Table 3**. Finally, the total sum of each cost in the gel is the final cost of the gel per kg. Gel 1, 2, and 3 are \$0.406/kg, \$0.436/kg, and \$0.394/kg respectively.

Table 3. Cost analysis for hydrogels

[REDACTED]

According to **Figure 41** and **Table 3**, gel 2 shows the best energy storage performance, lowest supercooling, and cost-effectiveness compared to the other two hydrogels. We compared the cost of each hydrogel to other salt hydrates and PCMs. According to the literature, the materials cost of the various PCMs is evaluated. The sodium sulfate decahydrate is estimated at \$0.11/kg, the calcium chloride hexahydrate is \$0.39/kg, and the zinc nitrate hexahydrate is \$0.6/kg. Also, the lithium chlorate trihydrate and potassium fluoride tetrahydrate show much higher cost requirements at \$5.21/kg and \$4.85/kg respectively [22]. The comparison of the cost of the PCMs is in **Figure 76**. Moreover, gel 2 shows a comparable cost to the eicosane (Latent heat=239.9 J/g, melting temperature=33 °C, \$6/kg [23]).

We computed the material energy cost of our hydrogels and compared it with other materials. The material energy cost is

$$Material\ energy\ cost\left(\frac{\$}{kWh}\right) = \frac{Cost\ of\ gel\ \left(\frac{\$}{kg}\right)}{Energy\ storage\ density\left(\frac{kJ}{kg}\right)} * \frac{3600\ kJ}{1\ kWh}$$

High material energy cost means that the material requires a much higher cost to store 1 kWh of thermal energy. Therefore, the lower material energy cost is preferable, and our hydrogels show low material energy cost compared to other salt hydrates.

[REDACTED]

Figure 76. (a) Cost ($/kg) for hydrogels based on Table 1. (b) Material energy cost ($/kWh) and cost($/kg) comparison in various salt hydrates.

[REDACTED]

Figure 77. Material energy cost versus melting temperature plot for salt hydrates, paraffins, and hydrogels

We adopt the cost analysis for salt hydrates and paraffins from the literature [5] and compare our gels' cost with them as shown in **Figure 77**. The material energy cost for different materials is plotted in terms of melting temperature. We also put our hydrogel data and compared it with other materials. In a temperature range of 25-35 °C, our hydrogel shows fairly good material energy cost compared to n-Octadecane. The manganese(II) nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) and Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) seems promising rather than our hydrogels. However, $Mn(NO_3)_2 \cdot 6H_2O$ is considered as moderate hazardous chemical. Also, $CaCl_2 \cdot 6H_2O$ and $Na_2SO_4 \cdot 10H_2O$ have a critical drawback, phase segregation. On the other hands, our hydrogels are non-toxic and do not show phase segregation for repeated long-term cycles. The high stability of the hydrogels is overwhelming other salt hydrates by the long-term utility perspective. Therefore, despite the higher material energy cost of our hydrogels to some salt hydrates, we expect the long-term cost of the hydrogels will be more cost-effective than other salt hydrates.

References

1. [REDACTED]

2. Biswas DR (1977) Thermal energy storage using sodium sulfate decahydrate and water. *Solar Energy*, 19(1):99–100. https://doi.org/10.1016/0038-092X(77)90094-9

3. Yinping Z, Yi J, Yi J (1999) A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measurement Science and Technology*, 10(3):201–205. https://doi.org/10.1088/0957-0233/10/3/015

4. Hong H, Kim SK, Kim Y-S (2004) Accuracy improvement of T-history method for measuring heat of fusion of various materials. *International Journal of Refrigeration*, 27(4):360–366. https://doi.org/10.1016/j.ijrefrig.2003.12.006

5. Marín JM, Zalba B, Cabeza LF, Mehling H (2003) Determination of enthalpy temperature curves of phase change materials with the temperature-history method: improvement to temperature dependent properties. *Measurement Science and Technology*, 14(2):184–189. https://doi.org/10.1088/0957-0233/14/2/305

6. [REDACTED]

7. Gawron K, Schröder J (1977) Properties of some salt hydrates for latent heat storage. *International Journal of Energy Research*, 1(4):351–363. https://doi.org/10.1002/er.4440010407

8. Kauffman K, Pan Y-C (1972) Thermal energy storage in sodium sulfate decahydrate mixtures.

9. [REDACTED]

10. Lubner SD, Choi J, Wehmeyer G, Waag B, Mishra V, Natesan H, Bischof JC, Dames C (2015) Reusable bi-directional 3 ω sensor to measure thermal conductivity of 100- μ m thick biological tissues. *Review of Scientific Instruments*, 86(1):014905. https://doi.org/10.1063/1.4905680

11. Cahill DG (1990) Thermal conductivity measurement from 30 to 750 K: the 3ω method. *Review of Scientific Instruments*, 61(2):802–808. https://doi.org/10.1063/1.1141498

12. SCHOTT Technical Glass Solutions GmbH BOROFLOAT® 33 – Thermal Properties. https://www.schott.com/en-us/products/borofloat-p1000314/downloads

13. METER Group Inc TEMPOS Tech Specs. https://www.metergroup.com/en/meter-environment/products/tempos/tempos-tech-specs

14. Standard Test Method for Determination of Thermal Conductivity of Soil and Rock by Thermal Needle Probe Procedure. https://doi.org/10.1520/D5334-22A.

15. Zhao G, Xu X, Qiu L, Zheng X, Tang D (2013) Study on the heat conduction of phase-change material microcapsules. *Journal of Thermal Science*, 22(3):257–260. https://doi.org/10.1007/s11630-013-0621-2

16. Agne MT, Voorhees PW, Snyder GJ (2019) Phase Transformation Contributions to Heat Capacity and Impact on Thermal Diffusivity, Thermal Conductivity, and Thermoelectric Performance. *Advanced Materials*, 31(35):1902980. https://doi.org/10.1002/adma.201902980

17. (2018) Theory for the Heat Transfer Module. *Heat Transfer Module User's Guide*, :174–177.

18. [REDACTED].

19. [REDACTED]

20. High Quality Anhydrous Sodium Sulfate White Powder. https://www.goldsupplier.com/provide/p172226047.html

21. DeIonized Water. https://www.chemworld.com/DeIonized-Water-s/2622.htm

22. Hirschey J, Gluesenkamp KR, Mallow A, Graham S (2018) Review of Inorganic Salt Hydrates with Phase Change Temperature in Range of 5°C to 60°C and Material Cost Comparison with Common Waxes. :10.

23. Hásl T, Jiříček I, Jeremiáš M, Farták J, Pohořelý M (2019) Cost/Performance Analysis of Commercial-Grade Organic Phase-Change Materials for Low-Temperature Heat Storage. *Energies*, 13(1):5. https://doi.org/10.3390/en13010005

Acknowledgment

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the award number DE-EE0009680.