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## ENHANCEMENT OF THERMAL ENERGY STORAGE USING BINARY NITRATE SALT MIXTURE VIA ADDITION OF LATENT HEAT

Sanjana Choudhary

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ENHANCEMENT OF THERMAL ENERGY STORAGE  
USING BINARY NITRATE SALT MIXTURE  
VIA ADDITION OF LATENT  
HEAT

by

SANJANA CHOUDHARY

Presented to the Faculty of the Honors College of  
The University of Texas at Arlington in Partial Fulfillment  
of the Requirements  
for the Degree of

HONORS BACHELOR OF SCIENCE IN MECHANICAL ENGINEERING

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November 15, 2019

## ABSTRACT

# ENHANCEMENT OF THERMAL ENERGY STORAGE USING BINARY NITRATE SALT MIXTURE VIA ADDITION OF LATENT HEAT

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The University of Texas at Arlington, 2020

Faculty Mentor: Sunand Santhanagopalan

Solar thermal energy is an important energy source because of its abundance. Solar thermal energy can be stored and reused in systems like concentrated solar power (CSP) plants. In addition to the sensible heat, which is associated with temperature rise, latent heat associated with the phase change can also be utilized to store heat. The study of the composition of heat transfer fluid (HTF) and the phase change material (PCM), that can survive high temperatures (above 300°C), has not been done extensively. In this work, solar salt, which is a mixture of potassium nitrate and sodium nitrate salts, has been used as the HTF, silica as the encapsulation material, and lithium carbonate-sodium nitrate as the PCM. Sol-gel method has been used to make silica. Scanning Electron Microscopy (SEM), X-ray mapping, Fourier-transform infrared spectroscopy (FTIR), and transmission electron

microscopy (TEM) have been used in the verification of the formed capsules. An increase of 40.5% high specific heat and 134.4% latent heat in the heat capacity throughout the HTF was found in the study. The results show that the microencapsulation method provides stable results and works for different types of molten salts. The findings from this research can have significant impact on the design of storage systems for solar thermal energy.

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## CHAPTER 1

### INTRODUCTION

In 2009, the burning of fossil fuels accounted for approximately 80% of the total energy production in the world [1]. Today, a looming crisis of climate change has resulted in the need of an increased reliance on renewable energy sources, such as solar and wind energy, to meet the growing population demand [2]. Figure 1.1 shows the growing trend of energy consumption over the years (2.9% increase in 2018) and the 18% increase in renewable energy consumption in 2018 [3]. This change has led to an accelerated shift towards developing energy efficient storage technologies. Various energy storage technologies – mechanical energy storage, electrical energy storage, and chemical energy storage are constantly being explored and improved for efficient energy harvesting, storage, and conversion. Amongst these, thermal energy storage (TES) is a technology that stores thermal energy, mainly solar energy, and aids in avoiding energy conversion losses. The thermal energy gained using storage is used in heating or cooling applications and power generation [4]. TES has a wide variety of applications ranging from buildings to concentrated solar power (CSP) plants. In TES, waste heat from various processes or heat from the sun, is collected from a solar collector and is stored in a storage device for future applications.

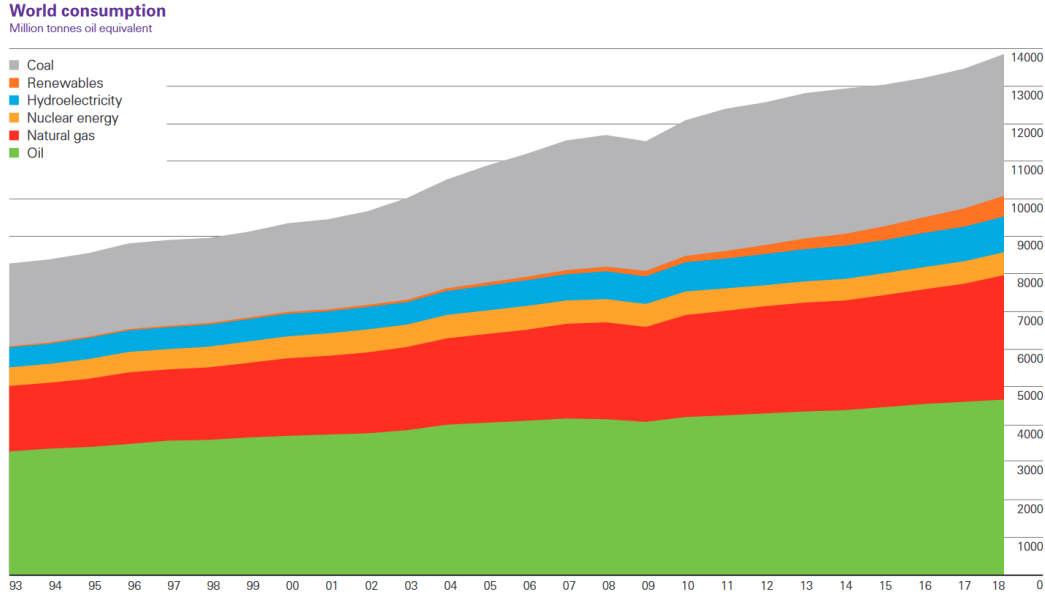


Figure 1.1: Global Energy Consumption Review by the BP Statistical Review of World Energy [3]

### 1.1 Thermal Energy Storage (TES)

TES uses the change in internal energy of a material for energy storage. Thus, it is categorized in three categories depending on the type of heat used for energy storage sensible/specific heat, latent heat, and thermochemical heat. In sensible heat storage (SHS), energy storage uses the specific heat capacity and the temperature change of the material during discharging and charging (cooling and heating) process. SHS has storage capacity ranging from 10-50 kWh/t with 50-90% efficiency [5]. The amount of heat stored using sensible heat is given by Eq. (1).

$$Q = \int_{T_i}^{T_f} mC_p dT \quad (1)$$

Latent heat storage (LHS) uses the energy dissipated or absorbed by a material undergoing a phase change. Figure 1.2 shows the latent heat and sensible heat of the material across a temperature range. LHS uses phase change materials (PCMs) that have

high latent heat capacity or high heat storage density. Figure 1.2 shows the added latent heat at the phase change temperature ( $T_{pc}$ ) increases energy. PCMs have storage capacity of 50-150 kWh/t with 75-90% efficiency. The amount of heat stored using latent heat, as a PCM is heated across its melting temperature is given by Eq. (2).

$$Q = \int_{T_i}^{T_m} mC_p dT + ma_m \Delta h_m + \int_{T_m}^{T_f} mC_p dT \quad (2)$$

Thermo-chemical energy storage (TCES) has the highest capacity of energy storage of approximately 12-250 kWh/t with 50-90% efficiency amongst the three TES systems [6]. The TCES system uses the energy involved in the breakage and formation or reformation of molecular bonds – endothermic and exothermic reactions, for storage [5].

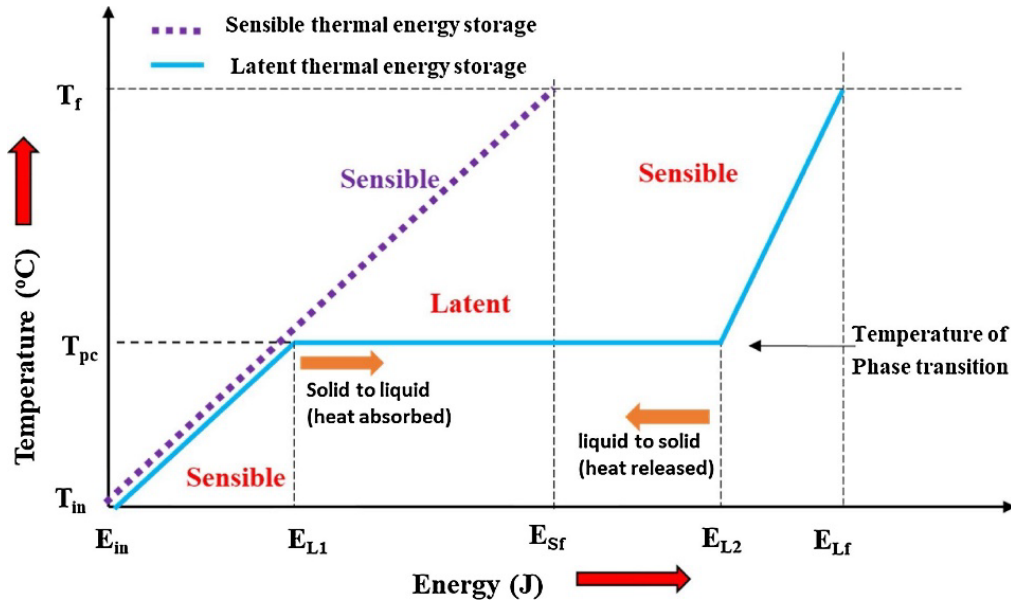


Figure 1.2: Temperature Change Profile of a Material [6]

### 1.2 Phase Change Materials

PCMs as LHS materials are attractive due to the increase in efficiency of storage system with added PCMs and the increase in heat storage capacity within a temperature

range. There are three main types of PCMs – organic PCMs, inorganic PCMs, and eutectic PCMs. Organic PCMs - paraffin wax and fatty acids are corrosion resistant and have low or no undercooling (delayed phase change). However, they are flammable and have a low thermal conductivity. Inorganic PCMs – salt hydrates and metallics have higher latent heat capacity or enthalpy of phase change than organic PCMs. Inorganic PCMs also have a high thermal conductivity. However, they are not corrosion resistant, exhibit undercooling, and lack thermal stability which results in phase segregation of the PCMs [7].

Eutectic PCMs are mixtures of two or more components at a specific concentration ratio set to optimize thermophysical properties of the mixture. They have a fixed freezing/melting point and the different compounds in the mixture do not react with each other to form a new chemical. They have higher volumetric storage density compared to organic PCMs. Currently, there are only a few eutectic mixtures known that are suitable for TES applications [6]. However, a critical application of eutectic PCM is in concentrated solar power (CSPs) plants.

### *1.2.1 Concentrated Solar Power Plants*

CSP is a power generation technology that uses solar energy or solar irradiation concentrated on a specific area. A field of mirrors or heliostats concentrate and reflect the sunlight to a receiver (usually at the top of a tower) where the heat is transferred to a thermal energy fluid carrier or the heat transfer fluid (HTF), which is also the medium for energy storage. Using a secondary heat engine system, the energy stored is converted to electricity through a turbine [8]. Figure 1.3 shows the schematic of a traditional CSP plant.

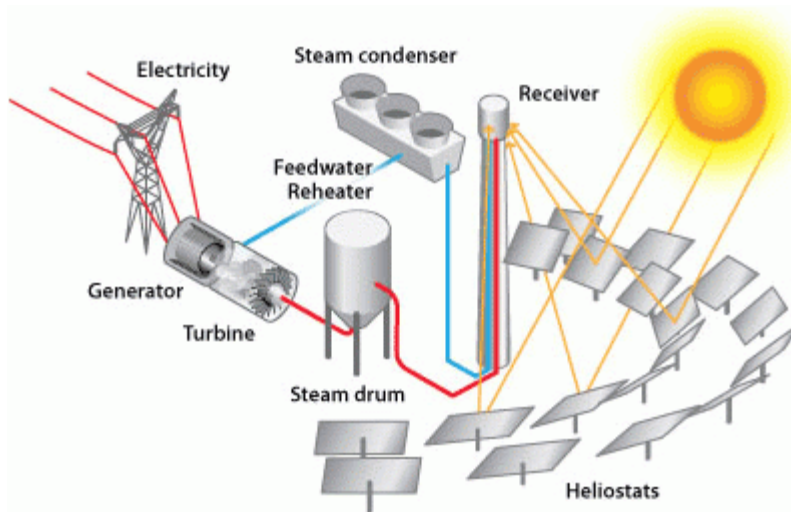


Figure 1.3: CSP Plant [9]

The HTF, which is typically Solar Salt ( $60\text{NaNO}_3\text{-}40\text{KNO}_3$ ) or HITEC Salt ( $40\text{NaNO}_2\text{-}7\text{NaNO}_3\text{-}53\text{KNO}_3$ ), gets heated to a high temperature of approximately  $500\text{ }^\circ\text{C}$  and is stored in the storage tank [10]. Subsequently, water gets heated to form steam, which runs the turbine to produce electricity. The cooler steam is then condensed to water in the condenser and it cycles back to the steam drum; while the energy in the system is stored using two tanks-cold and hot and the HTF is cycled between them. The HTF stores energy using sensible heat. Current performance enhancement strategies involve addition of micro/nanoparticles to HTF. This enables faster heat transfer rates and specific heat enhancement owing to increased surface area provided by the additives. In this work we propose the addition of phase change materials to enhance the heat capacity via incorporation of latent heat storage in the system. To prevent the interaction between the two chemical compounds and corrosion, encapsulation around phase change materials is needed. The encapsulation also increases the surface area for active heat transfer thereby increasing the rate of heat transfer and specific heat of the HTF.

## CHAPTER 2

### LITERATURE REVIEW

Macro-encapsulations with metals have been carried out by many researchers. In 2014, Zhang et al. encapsulated copper capsules as phase change materials with a chromium-nickel layer via periodic-barrel electroplating [11]. These capsules could withstand working temperatures above 1000 °C and durability of about 1000 charging and discharging cycles. They also exhibited high thermal conductivity. However, the encapsulated PCM system is not cost effective with heavy capsules that could potentially increase the pumping power and reduce the efficiency of the HTF-PCM system.

Currently, PCMs that have been implemented in high temperature applications are very rare. Nomura et al. reported a micro encapsulated PCM (MEPCM) with a stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> shell and Al-25 wt% Si core and durability up to 300 cycles of heating and cooling [12]. However, the encapsulation technique used is not compatible with other materials except for the Al-Si mixture. Also, the use of metallic compound results in significant weight increase, thus reducing overall gravimetric performance. Molten nitrate salts exhibit higher latent heat capacity along a wider temperature range, from approximately 300 °C-1000 °C [13]. They offer a good alternative to metal shells and are cost efficient [14].

Recently, our Multi-Scale Energy Systems (MuSES) laboratory at the University of Texas at Arlington, developed a novel micro-encapsulation technique for single nitrate salts [15]. Silicon dioxide as an encapsulation material offers promising results due to the high thermal and chemical stability. The silicon dioxide shell is stable at high temperature

of up to 600 °C. Additionally, the synthesis of silica- the sol-gel method, is a facile and an established technique. However, established silica synthesis methods were water based, which posed a serious limitation for encapsulation of water-soluble salt PCMs. Zhang et al. demonstrated the successful microencapsulation of KNO<sub>3</sub> (latent heat of 100 J/kg) as the PCM with silica as the shell using a modified organic solvent-based sol-gel technique [13]. The microencapsulated phase change material (MEPCM) system showed high encapsulation ratio of 95.2 % and stability through 100 thermal cycles. The melting point of the system was at a high temperature of 334 °C [15].

CHAPTER 3  
METHODOLOGY

The conventional encapsulation of silica or the Stöber process involves hydrolysis of silica alkoxide and subsequently a water condensation process. However, the inclusion of salts, that are mostly water soluble, as PCMs, limits the usage of water. Thus, Zhang et al. modified the conventional Stöber process to a water limited encapsulation process using alcohol condensation for  $\text{KNO}_3$  capsules [15]. Figure 3.1 shows the schematic of the water limited silica encapsulation process which can be replicated with  $\text{Li}_2\text{CO}_3$  (44.3) – 55.7  $\text{Na}_2\text{CO}_3$  binary mixture due to the compatibility of the process.

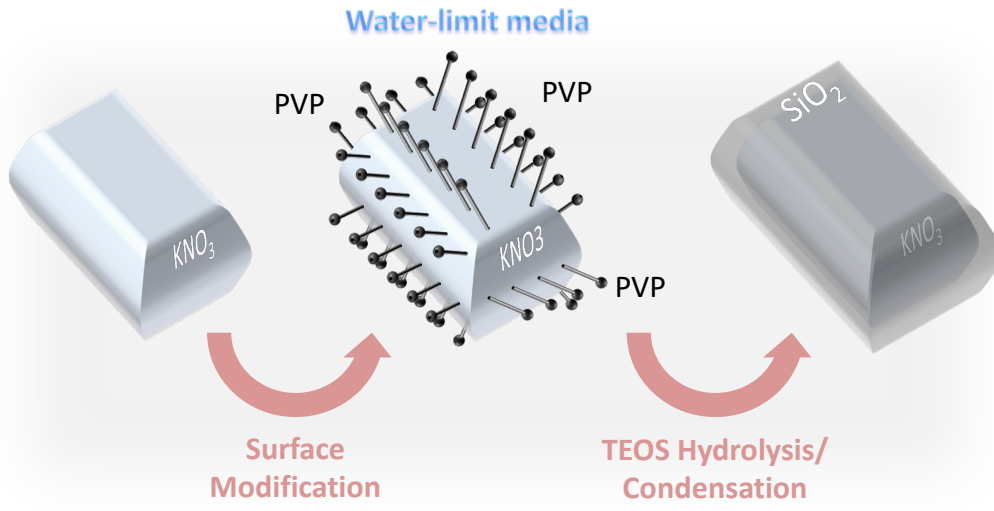
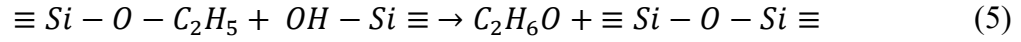
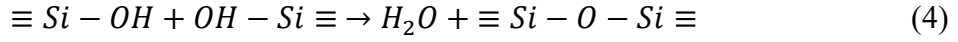
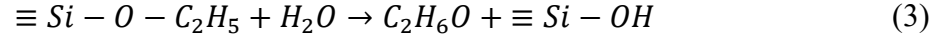


Figure 3.1: Schematic of the Fabrication Process [15]

The conventional Stöber process' chemical reaction is given by Eq. (3-4). Equation 3 is the hydrolysis reaction and Eq. 4 is the water condensation reaction. Equation 5 is the alcohol condensation process in place of the water condensation process.





Using the Stöber process, silica is then coated on the surface on the poly vinyl pyrrolidone (PVP) by drop-wise addition of tetraethyl orthosilicate (TEOS) to the PVP-Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> dispersion. Since the fabrication process is water-limited, the only source of water in the process is ammonia. Thus, the concentration of TEOS and ammonia control the rate of hydrolysis and condensation of silica on the surface of Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> capsule.

## CHAPTER 4

### DISCUSSION

#### 4.1 Characterization

Field-emission scanning electron microscopy (FESEM, Hitachi S-4800) was used to visualize the MEPCM samples at different magnifications. The particle size of the samples from SEM images is characterized using ImageJ (National Institutes of Health) software. The thickness of the shell of MEPCM was characterized using high-resolution transmission electron microscopy (HRTEM, Hitachi H-9500). The thermal analysis of the samples was carried out using differential scanning calorimetry (DSC Q20, TA Instruments).

#### 4.2 Results and Analysis

Regular hand grinding was used to reduce the size of  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  salt particles. The average particle size of the encapsulated  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  salt is  $5.1 (\pm 2.1)\mu\text{m}$ . Similar images from Figure 4.1 were obtained in this study. Figure 4.1a shows plain LiNa eutectic salt. Figure 4.1f shows the size distribution for the hand ground eutectic salt. Figure 4.1b shows the encapsulated salt, and a change in the surface roughness can be seen. Figure 4.1c-d are energy dispersive x-ray (EDX) images showing the different elements present in the sample, clearly showing the presence of Si and O. Zhang et al. reported that the encapsulation ratio for the  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  MEPCMs was 61.2%. It is hypothesized that the low encapsulation ratio, which is a result of a lower heat capacity occurs due to the evolution of carbonate in  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  to carbon-dioxide at a high temperature of above

approximately 500 °C.

From Figure 4.2-a, it is seen that there exists a significant difference between the latent heat exhibited by the pure binary salt and the encapsulated binary salt. The latent heat of the pure binary salt is higher due to the absence of the silica shell that basically adds to the weight and is an inactive protective coating. At the 100<sup>th</sup> cycle, the latent heat of the encapsulated binary carbonate salt is lower by almost over 50 J/g indicating lower heat transfer and low encapsulation ratio. From Figure 3.1-b, it can be seen that the heating curves are not aligned indicating a shift or a decrease in the heat capacity of the binary salt system. The cooling curves from the DSC are not analyzed specifically as the cooling temperature was not controlled due to equipment limitations.

Figure 4.3 shows the enhanced effective heat capacity with the inclusion of  $\text{Li}_2\text{CO}_3$ - $\text{Na}_2\text{CO}_3$  over solar salt or HTF which stores sensible heat.  $\text{LiNa@Si-1.5}$  exhibits a heat capacity of 516 J/g at a high temperature of 530 °C, which is 134.4% higher than the heat capacity of solar salt within the same temperature range.

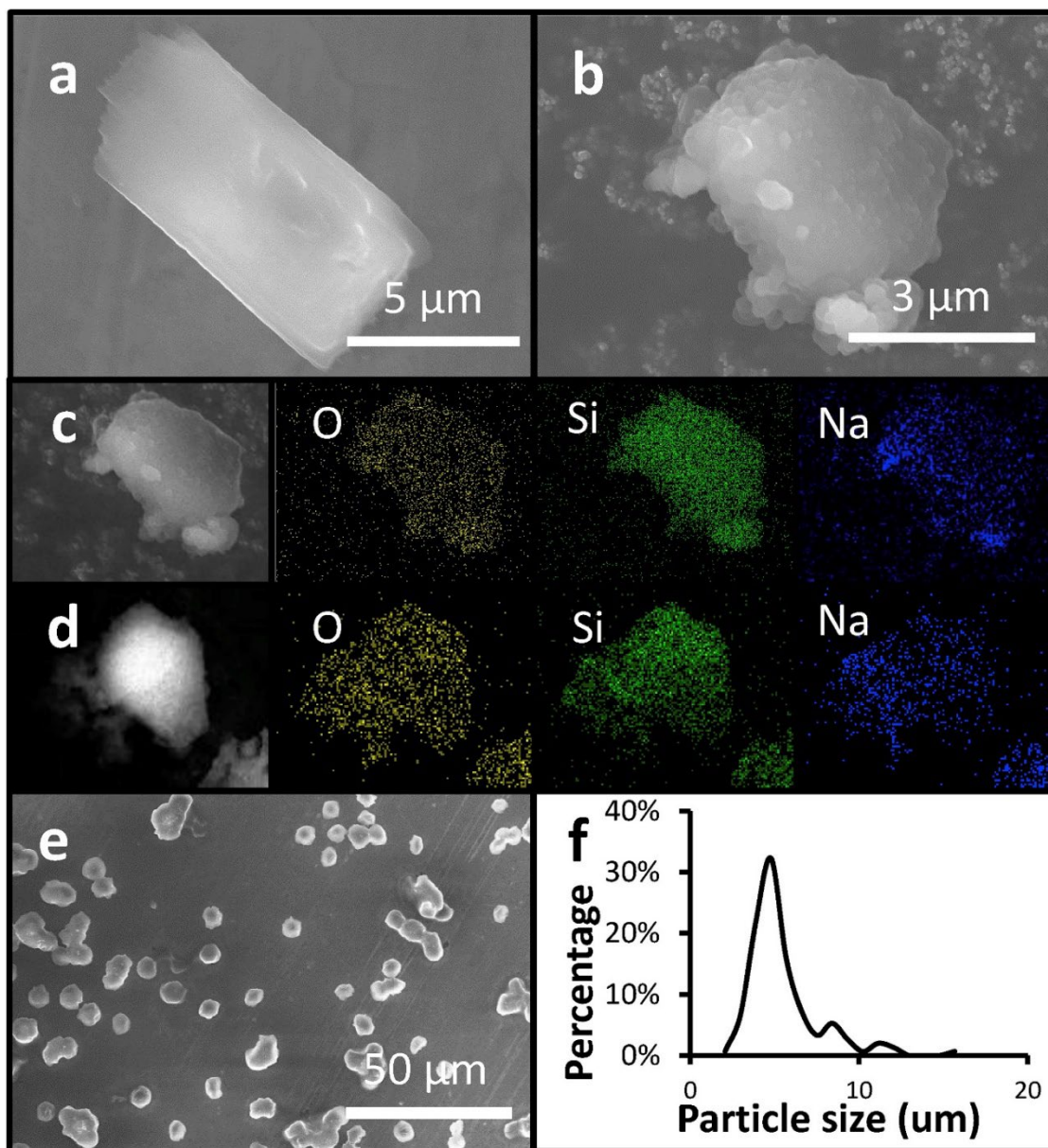


Figure 4.1: Morphology of a) Plain LiNa Eutectic Salt, b) LiNa@Si Microcapsules; c) & d) XRD of LiNa@Si and e) & f) Particle Size Distribution of LiNa@Si [16].

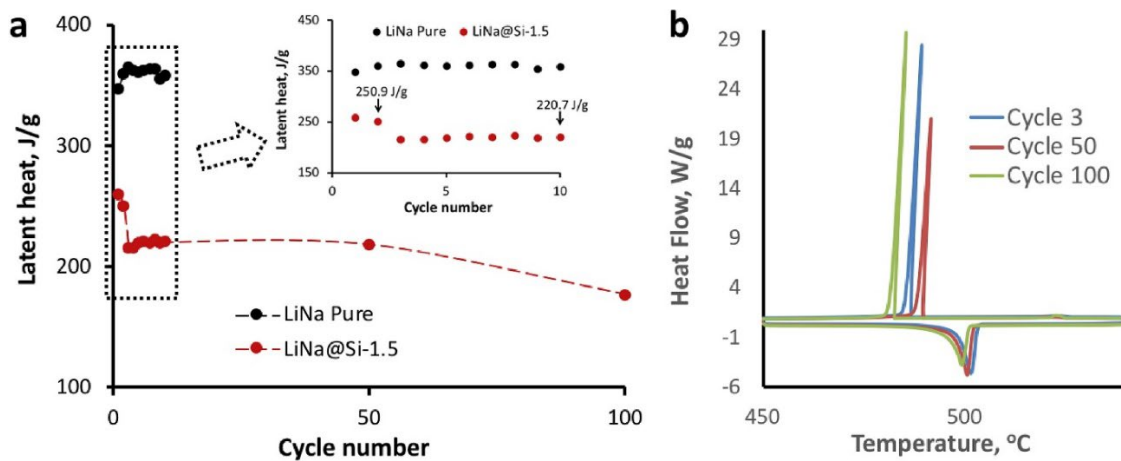


Figure 4.2: DSC Results [16]

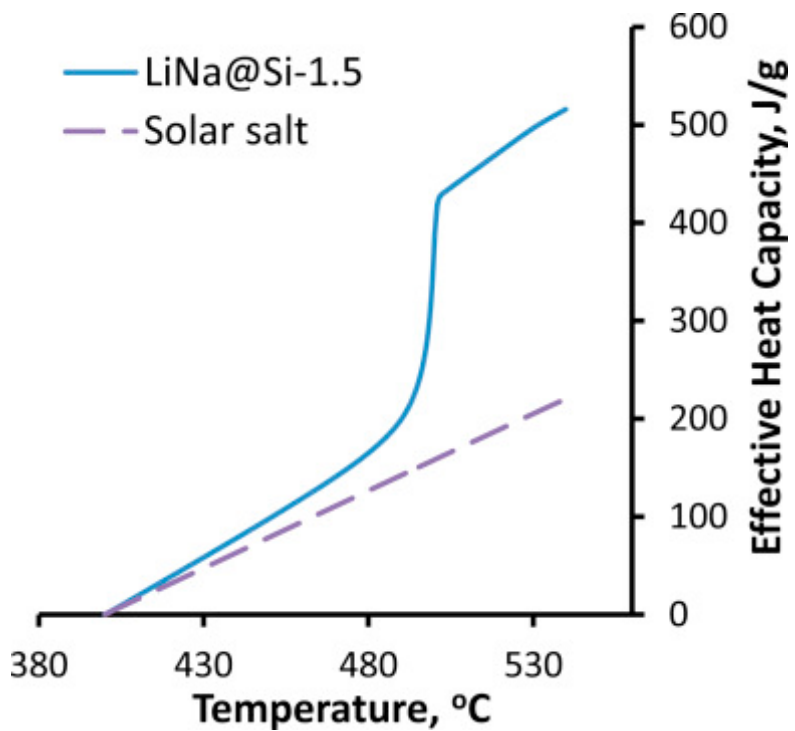


Figure 4.3: Enhancement of Effective Heat Capacity by using Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> Salt [16]

## CHAPTER 5

### CONCLUSION

The binary nitrate salt mixture was successfully encapsulated with silica with an encapsulation ratio of 61.2% and a latent heat of 220J/g at 498 °C. To the best of our knowledge this was the first such encapsulation of binary salt PCM ever demonstrated. A future study for this research work will be of conducting a rheology study of the binary encapsulated phase change materials to determine the efficiency of the MEPCMs in industry-based applications. Additionally, the microencapsulation method performed shows promising potential to be compatible with a wide variety of single, binary and even tertiary salt systems.

## REFERENCES

- [1] U. Energy, “Annual Energy Review 2009,” US, Us Energy Inf. Adm., pp. 19–53, 2010.
- [2] J. Twidell and T. Weir, *Renewable Energy Resources*, 3rd ed. London: Routledge, 2015.
- [3] B. Dudley, “BP Statistical Review of World Energy,” *BP Stat. Rev.* London, UK, vol. 68, p. 61, 2019.
- [4] N. H. S. Tay, M. Liu, M. Belusko, and F. Bruno, “Review on transportable phase change material in thermal energy storage systems,” *Renewable and Sustainable Energy Reviews*, vol. 75. pp. 264–277, 2017.
- [5] A. Sharma, V. V. Tyagi, C. R. Chen, and D. Buddhi, “Review on thermal energy storage with phase change materials and applications,” *Renew. Sustain. Energy Rev.*, vol. 13, no. 2, pp. 318–345, Feb. 2009.
- [6] K. S. Reddy, V. Mudgal, and T. K. Mallick, “Review of latent heat thermal energy storage for improved material stability and effective load management,” *J. Energy Storage*, vol. 15, pp. 205–227, Feb. 2018.
- [7] B. Zalba, J. M. Marín, L. F. Cabeza, and H. Mehling, “Review on thermal energy storage with phase change: materials, heat transfer analysis and applications,” *Appl. Therm. Eng.*, vol. 23, no. 3, pp. 251–283, Feb. 2003.

- [8] H. L. Zhang, J. Baeyens, J. Degève, and G. Cacères, “Concentrated solar power plants: Review and design methodology,” *Renew. Sustain. Energy Rev.*, vol. 22, pp. 466–481, Jun. 2013.
- [9] O. of E. E. & R. Energy, “Power Tower System Concentrating Solar Power Basics,” US Department of Energy, 2013. [Online]. Available: <https://www.energy.gov/eere/solar/articles/power-tower-system-concentrating-solar-power-basics>. [Accessed: 11-Nov-2019].
- [10] B. Iverson, J. Cordaro, and A. Kruizenga, “Thermal Property Testing of Nitrate Thermal Storage Salts in Solid-Phase,” in *ASME 2011 5th International Conference on Energy Sustainability and 9th Fuel Cell Science Engineering and Technology Conference*, 2011.
- [11] G. Zhang et al., “Encapsulation of copper-based phase change materials for high temperature thermal energy storage,” *Sol. Energy Mater. Sol. Cells*, 2014.
- [12] T. Nomura et al., “Microencapsulated phase change materials with high heat capacity and high cyclic durability for high-temperature thermal energy storage and transportation,” *Appl. Energy*, vol. 188, pp. 9–18, Feb. 2017.
- [13] M. M. Kenisarin, “High-temperature phase change materials for thermal energy storage,” *Renew. Sustain. Energy Rev.*, vol. 14, no. 3, pp. 955–970, Apr. 2010.
- [14] A. Mathur, R. Kasetty, J. Oxley, J. Mendez, and K. Nithyanandam, “Using Encapsulated Phase Change Salts for Concentrated Solar Power Plant,” *Energy Procedia*, vol. 49, pp. 908–915, Jan. 2014.



- [15] H. Zhang, A. Balram, H. Tiznobaik, D. Shin, and S. Santhanagopalan, “Microencapsulation of molten salt in stable silica shell via a water-limited sol-gel process for high temperature thermal energy storage,” *Appl. Therm. Eng.*, vol. 136, pp. 268–274, May 2018.
- [16] H. Zhang, D. Shin, and S. Santhanagopalan, “Microencapsulated binary carbonate salt mixture in silica shell with enhanced effective heat capacity for high temperature latent heat storage,” *Renew. Energy*, vol. 134, pp. 1156–1162, Apr. 2019.

## BIOGRAPHICAL INFORMATION

Sanjana Choudhary is currently pursuing an Honors Bachelor of Science in Mechanical Engineering degree. Upon the completion of undergraduate studies, she plans to attend graduate school in mechanical engineering. Apart from academics and research, Sanjana enjoys reading novels and traveling.