Enhancement of Specific Heat Capacity of Binary Carbonate Salt Using CuO and ZnO Nanoparticles

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Abstract

Despite how attractive solar power systems may seem, their low energy efficiency is the biggest barrier to development. The energy efficiency is greatly increased when a thermal energy storage is integrated into the entire energy extraction process. For solar thermal power, nanofluids of birnary carbonate have shown to be a viable option for thermal energy storage at high temperature and transmission medium. The increase in specific heat capacity (Cp) for the binary carbonate, Na2CO3-K2CO3 (60:40 mass ratio), using CuO and ZnO nanoparticles was up to 32.4% at 540°C. This research offers insights into how the use of two nanoparticles can significantly increase the Cp value of the binary carbonate salt. Moreover, it focuses on determining whether utilizing these nanoparticles has any negative consequences on the fusion's onset and offset temperatures. This reasearch shows that the addition of nanoparticles has no adverse impact on the target temperatures.

Keywords

Binary carbonate Salt, Specific Heat Capacity, CuO and ZnO nanoparticle, DSC.

1.Introduction

Renewable energy technologies using solar power has provided one of many ways for balancing the demand and supply of energy in recent times. The storage of available solar power has grown a major concern due the uncertain nature of the energy's availability. On the quest of exploring several alternatives available to serve the concern, thermal

energy storage (TES) systems have proven to be one of the best options (Pelay et al. 2017, Cac 2013). Though various heat transfer fluids have been researched and implemented to bring out the best performance out of a storage system, use of different molten salts have been brought to light in recent times for their advantageous thermophysical properties than other available options (González et al. 2017, Gal & Caballero 2021). The only hindrance in the implementation of these salts are their extremely low heat capacity (below 2 J/g K on average) (Araki et al. 1988)– (Zhu et al. 2020); on which researchers from around the world are working effortlessly.

1.1 Objectives

The mediums of energy storage lack a considerable value of heat capacity as thermal energy storage application despite of having high thermal stability, small vapor pressure, less viscosity, high thermal conductivity, nonflammability, nontoxicity. So, the prime objectives of this study are:

- To observe the onset as well as offset temperature of fusion of two samples.
- To determine the C_p value of two samples and compare them.

2. Literature Review

Among all the other attempts, mixing of different salts and addition of nanoparticles has put satisfactory display in performance enhancement. Researchers have incorporated different types of nanoparticles to observe their effect on Cp enhancement (Sang and Tiu, 2017). Most commonly used nanoparticle was SiO2. Shin et al. (2013) used 1.5% mass concentration of SiO2 nanoparticles as a dopant for lithium carbonate (Li2CO3)/potassium carbonate(K2CO3) eutectic mixture (62:38 molar ratio) and got 118-124 percent Cp enhancement in liquid phase. Tiznobaik et al. (2013) on the other hand used 1% mass concentration of SiO2 and found an overall enhancement of 25%. B.E.Farr et al.(2020) also conducted similar study using spherical SiO2 with same concentration, which resulted in 19 percent Cp enhancement. L.Sang et al. (2019) and W.Ai et al. (2019) doped ternary carbonate (K2CO3-Li2CO3-Na2CO3, mass ratio of 4:4:2) with 1 wt.% SiO2 at different conditions and achieved an enhancement of 113.7% and 38.5% respectively. S.M.M. Rizvi et al. (2020) used the same salt mixture and doped it with 1% Of Al2O3 nanoparticles and the nanofluidic sample that went through heating and cooling rate of 2 °C per minute exhibited the largest increase in Cp value which was 34% of enhancement on average. B. Jo et al. (2014) conducted research with graphite nanoparticle-doped binary carbonate mixtures which in liquid phase had a dramatic increase in the Cp value to 3.12 J/g K. They (2015) also investigated the effect of different chemical compositions of binary carbonate on Cp enhancement and found that at about 65 percent of lithium carbonate, the Cp value of pure carbonate mixtures and nanomaterials increased dramatically.

3. Methods

In this work, binary carbonate mixture (sodium carbonate and potassium carbonate; mass ratio of 60:40), was doped with copper oxide (CuO) and zinc oxide (ZnO) nanoparticles in 1 wt.% concentration (50:50 mass ratio) to observe the enhancement of Cp value due to the addition of nanoparticles to the base salt. A laboratory oven was implemented

for drying the samples and a differential scanning calorimeter (DSC) was implemented to determine the Cp values of the samples.

Two samples were prepared to be analyzed throughout this work: Sample-1 is a mixture of sodium carbonate and potassium carbonate with mass ratio of 60:40, and Sample-2 has the same ratio of the salts mentioned previously together with 1 percent CuO and ZnO nano particles with mass ratio of 50:50).

3.1 Sample Preparation

A digital scale was used to measure 1.2g of sodium carbonate and 0.8g of potassium carbonate for sample 1. These salts were be combined with 200ml of distilled water for three hours using a magnetic stirrer. After mixing, the solution was heated at 300°C until all of the water had evaporated. This procedure took about 80 minutes. After drying in an electric oven at 90°C for one hour, the salt mixture is going to be cooled to room temperature and kept in an airtight container. The second sample was prepared following the same procedure. 1.19g of sodium carbonate, 0.79g of potassium carbonate, 0.01g of copper oxide, and 0.01g of zinc oxide nanoparticles was weighed for sample 2 using the same scale. The evaporation step took about 76 minutes for sample-2.

3.2 Measurement of Cp Value

Setaram Evo 130 DSC was chosen to find out the Cp value of the two samples. Reference pan material used for this purpose was aluminum. The DSC machine was sapphire calibrated. The samples had been heated between 50 and 550 degrees Celsius with a 10°C/min heating rate to determine their Cp value at different temperature points. Cp value was obtained using the following equation:

Specific Heat Capacity = $\frac{\text{Heat Flow Rate} \times 60}{\text{Sample mass} \times \text{Heating Rate}}$

4. Data Collection

DSC curve of Sample-1

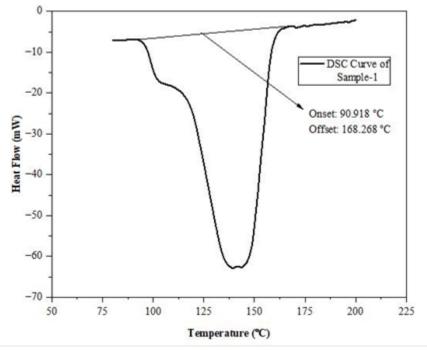


Fig. 1. Fusion temperatures of Sample-1

• DSC curve of Sample-2

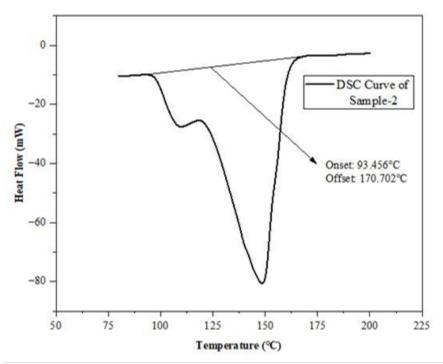


Fig. 2. Fusion temperatures of Sample-2

• Cp value of Sample-1 at chosen temperature points

Temperature	100	200	300	400	500	550
(°C)						
Cp Value of	3.0884	0.4577	0.2833	0.2281	0.1863	0.0954
Sample-1						
(J/g° C)						

• Cp value of Sample-2 at chosen temperature points

100	200	300	400	500	550
3.7724	0.6081	0.3757	0.3316	0.2201	0.1412

5.Results and Discussion

5.1 Numerical Results

Onset and offset temperatures of fusion of molten salt are vital parameters to evaluate their suitability to be used as a heat transfer fluid in a TES system. Figure 1 and Figure 2 presents a portion the DSC curve obtained for sample-1 and sample-2 respectively which shows the onset and offset temperatures of fusion for both samples. These temperatures are also listed in Table 1. From the data obtained, it is safe to express that addition of nanoparticles to the binary salt mixture has not brought out vast disparity in the values of offset and onset temperature of fusion of sample-2 than sample-1.

Table 1. Fusion Temperatures of the Samples

Sample	Fusion Temperatures (°C)		
	Onset	Offset	
Sample-1	90.918	168.268	
Sample-2	93.456	170.702	

For both samples, Cp values were calculated using the equation mentioned earlier by using data obtained from DSC analysis of these samples. All these values are listed in Table 2 and the last column of the table shows that there is increase in the Cp value of sample-2 than sample-1 for a particular temperature.

Temperature	Cp Value of	Cp Value of	Percentage Increase
(°C)	Sample-1	Sample-2	in Cp Value (%)
	$(J/g^{\circ} C)$	(J/g° C)	
100	3.0884	3.7724	18.1321
200	0.4577	0.6081	24.7254
300	0.2833	0.3757	24.6033
400	0.2281	0.3316	31.1990
500	0.1863	0.2201	15.3207
540	0.0954	0.1412	32.4272

It appears that approximately 32.427% increase in Cp of sample-2 is achieved for 540°C, which is considered as a reference temperature of comparison in many literatures.

5.2 Graphical Results

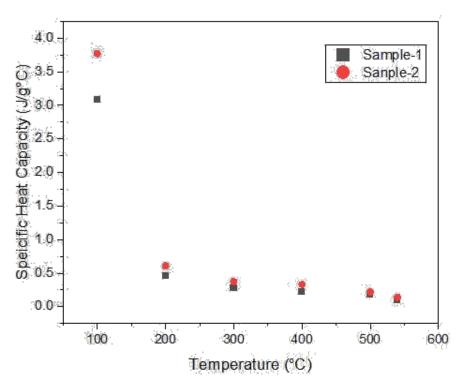


Fig. 3. Specific Heat Capacity vs. Temperature graph of Sample-1 and Sample-2

Fig. 3 presents a graph with Cp value of two samples. Where at low temperate both of the samples have highest Cp values. With the increase in temperature the drop in Cp values were gradual whereas the Cp values were always higher in sample 2.

6.Conclusion

With all the adverse effects of using fossil fuel for energy harnessing on environment, which is making the life of all the living beings difficult, it is high time to shift to any renewable energy sources possible to reduce the load over fossil fuel. With these broader aspects in mind, this research has worked on such a matter that can help in enhancing the popular renewable energy technologies. This work used nano particles as mean to increase the Cp value of a mixture of two carbonate salts, which has other excellent properties to be used as a medium for TES technologies and has succeeded to achieve an enhancement of 32.4% at 540°C. Moreover, data obtained from this work was sufficient to conclude that nano particle addition in minute concentration does not greatly affect the onset and offset temperature of fusion of the molten salts. Further research needs to be conducted to improve and modify the specific heat capacity of molten salts for usage in thermal energy storage systems more efficiently.

References

U. Pelay, L. Luo, Y. Fan, D. Stitou, and M. Rood, "Thermal energy storage systems for concentrated solar power plants," *Renew. Sustain. Energy Rev.*, vol. 79, no. January, pp. 82–100, 2017, doi: 10.1016/j.rser.2017.03.139.

G. Cac, "Concentrated solar power plants: Review and design methodology," vol. 22, pp. 466–481, 2013, doi: 10.1016/j.rser.2013.01.032.

E. González-roubaud, D. Pérez-osorio, and C. Prieto, "Review of commercial thermal energy storage in concentrated solar power plants: Steam vs. molten salts," *Renew. Sustain. Energy Rev.*, vol. 80, no. February, pp. 133–148, 2017, doi: 10.1016/j.rser.2017.05.084.

S. Gal and Á. Caballero, "Molten Salts for Sensible Thermal Energy Storage: A Review and an Energy Performance Analysis," pp. 1–15, 2021.

N. Araki, M. Matsuura, A. Makino, T. Hirata, and Y. Kato, "Measurement of thermophysical properties of molten salts: Mixtures of alkaline carbonate salts," *Int. J. Thermophys.*, vol. 9, no. 6, pp. 1071–1080, Nov. 1988, doi: 10.1007/BF01133274.

Y. Y. Chen and C. Y. Zhao, "Thermophysical properties of Ca(NO3)2-NaNO3-KNO3 mixtures for heat transfer and thermal storage," *Sol. Energy*, vol. 146, no. 3, pp. 172–179, 2017, doi: 10.1016/j.solener.2017.02.033.

K. Coscia, S. Nelle, T. Elliott, S. Mohapatra, A. Oztekin, and S. Neti, "Thermophysical properties of lino3–nano3– kno3 mixtures for use in concentrated solar power," *J. Sol. Energy Eng. Trans. ASME*, vol. 135, no. 3, pp. 1–5, 2013, doi: 10.1115/1.4024069.

C. Zhu, L. Gong, and S. N. Tie, "Influence of preparation processes on thermophysical properties of molten salt," *AIP Adv.*, vol. 10, no. 2, 2020, doi: 10.1063/1.5129609.

L. Sang and T. Liu, "Solar Energy Materials and Solar Cells The enhanced speci fi c heat capacity of ternary carbonates nano fl uids with different nanoparticles," vol. 169, no. September 2016, pp. 297–303, 2017, doi: 10.1016/j.solmat.2017.05.032.

D. Shin and D. Banerjee, "Enhanced Specific Heat Capacity of Nanomaterials Synthesized by Dispersing Silica Nanoparticles in Eutectic Mixtures," vol. 135, no. March, pp. 1–8, 2013, doi: 10.1115/1.4005163.

H. Tiznobaik and D. Shin, "International Journal of Heat and Mass Transfer Enhanced specific heat capacity of high temperature molten salt-based nanofluids," Int. J. Heat Mass Transf., vol. 57, no. 2, pp. 542–548, 2013, doi: 10.1016/j.ijheatmasstransfer.2012.10.062.

B. El Far, S. Muhammad, M. Rizvi, Y. Nayfeh, and D. Shin, "International Journal of Heat and Mass Transfer Investigation of heat capacity and viscosity enhancements of binary carbonate salt mixture with SiO2 nanoparticles," vol. 156, pp. 1–5, 2020, doi: 10.1016/j.ijheatmasstransfer.2020.119789.

L. Sang, "Insights into the specific heat capacity enhancement of ternary carbonate nano fluids with SiO2 nanoparticles: the effect of change in the," pp. 5288–5294, 2019, doi: 10.1039/c8ra10318f.

L. Sang, W. Ai, Y. Wu, and C. Ma, "Solar Energy Materials and Solar Cells SiO 2 -ternary carbonate nanofluids prepared by mechanical mixing at high temperature: Enhanced specific heat capacity and thermal conductivity," Sol. Energy Mater. Sol. Cells, vol. 203, no. September, p. 110193, 2019, doi: 10.1016/j.solmat.2019.110193.

S. Muhammad, M. Rizvi, and B. El Far, "Heat capacity and viscosity of ternary carbonate nanofluids," no. August, pp. 1–10, 2020, doi: 10.1002/er.6148.

B. Jo and D. Banerjee, "ScienceDirect Enhanced specific heat capacity of molten salt-based nanomaterials: Effects of nanoparticle dispersion and solvent material," ACTA Mater., vol. 75, pp. 80–91, 2014, doi: 10.1016/j.actamat.2014.05.005.

B. Jo and D. Banerjee, "International Journal of Thermal Sciences Effect of solvent on specific heat capacity enhancement of binary molten salt-based carbon nanotube nanomaterials for thermal energy storage," Int. J. Therm. Sci., vol. 98, pp. 219–227, 2015, doi: 10.1016/j.ijthermalsci.2015.07.020.

B. Jo and D. Banerjee, "International Journal of Thermal Sciences Effect of solvent on speci fi c heat capacity enhancement of binary molten salt-based carbon nanotube nanomaterials for thermal energy storage," Int. J. Therm. Sci., vol. 98, pp. 219–227, 2015, doi: 10.1016/j.ijthermalsci.2015.07.020.

Biographies

Shantanu Saha has freshly graduated from Chittagong University of Engineering & Technology in Mechanical Engineering. As a spirited person, he likes to explore different areas of research related to mechanical engineering. His research interest comprises of renewable energy technologies, phase change heat transfer, heat transfer enhancement with nanofluids. He is currently looking for opportunities to work with researchers with similar research interests.

Anupam Kumar Nath has completed his bachelor's in mechanical engineering from Chittagong University of Engineering and Technology in 2022. The author has an avid interest in the field of heat transfer and nanofluids. He wishes to tread further and deeper into this field as he embarks on the new journey of higher studies. The author has also been ardently involved in various extracurricular activities like business case competitions, leadership and writing among others in his earlier day.

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