

Advancements and Challenges in Molten Salt Energy Storage for Solar Thermal Power Generation

Yuxin Shi^{1*}

¹ School of Mechanical and Energy Engineering, Zhejiang University of Science and Technology, Hangzhou, Zhejiang Province, 310023, China

Abstract. Solar power, which is one of the most abundant and sustainable energy sources, has attracted a lot of attention for its clean and renewable attributes amid a growing global demand for renewable energy. Molten salt (MS) energy storage technology is an innovative and effective method of thermal energy storage. It can significantly improve CSP (concentrated solar power) systems' stability and efficiency. This review first introduces the importance of solar energy and then delves into the development and applications of MS energy storage technology. Traditional MSs (e.g., Solar Salt and Hitec Salt) face issues of thermal stability and corrosion at high temperatures, whereas improved MSs have shown significant enhancements in thermal properties. This paper summarizes research achievements in improving MS performance through the addition of alkaline substances, optimization of MS ratios, and introduction of nanoparticles to form nanofluids. Furthermore, the paper covers future research areas and challenges for MS energy storage technology. These include the creation of new MS materials, system design optimization, and cost reduction strategies. Technology utilizing MS energy storage is a promising component of energy systems of the future, as it contributes significantly to the advancement of renewable energy sources and increases energy efficiency.

1 Introduction

Solar energy, originating from solar radiation, can be captured and utilized through technologies like photovoltaic cells and solar thermal systems. Since solar energy offers a clean, sustainable, and nearly limitless energy source, its significance is indisputable. Solar energy is essential in the fight against climate change since it doesn't emit harmful emissions or contribute to environmental damage like fossil fuels do. MS energy storage is an innovative and efficient method for storing thermal energy. MSs, usually a solution of potassium and sodium nitrate, are used to absorb and retain heat at high temperatures. Electrical energy can be produced from this thermal energy that has been stored when needed, making it a vital technology for balancing supply and demand in renewable energy systems. MS storage systems offer several benefits including high energy density, extended storage

* Corresponding author: 1211440008@zust.edu.cn

capacity, and high temperature operation, which enhances the overall efficiency of energy conversion processes. This technology is particularly well-suited for solar thermal power plants, storing solar heat that is surplus during the day and releasing it at night or during times when solar radiation is low.

Countries with high solar insolation have constructed numerous solar thermal power plants integrated with MS storage systems, demonstrating the feasibility and advantages of this approach. Additionally, the goals of continuous research and development are to increase efficiency, lower expenses, and enhancing the safety of MS storage systems. As the global energy landscape continues to shift towards renewable sources, MS energy storage is essential to ensuring the reliability or stability of solar power generation.

2 Development of MS energy storage technology

MS energy storage technology is an advanced method used in solar thermal power generation systems for storing and releasing thermal energy. This approach employs MSs, typically a mixture of potassium and sodium nitrate, to transfer and store heat while remaining stable at high temperatures. With excellent thermal conductivity and high specific heat capacity (SHC), MSs can store and release large amounts of thermal energy as needed. This technology effectively addresses the intermittent nature of solar energy by providing several advantages, including stability at high temperatures, long-duration storage capacity, and high energy density.

With the need for renewable energy growing on a global scale, the installed capacity of Concentrated Solar Power (CSP) systems is rapidly increasing. CSP systems focus on solar energy to generate high-temperature thermal energy, which is then used to drive traditional power generation units. The integration of MS energy storage technology significantly enhances the stability and reliability of CSP systems, allowing continuous power generation during nighttime or cloudy conditions. In recent years, several countries have constructed large-scale CSP projects incorporating MS storage technology, driving the significant growth of global CSP installed capacity.

MS energy storage technology exhibits immense potential and a broad range of applications in practice. First of all, MS storage in solar thermal power generation systems can efficiently store excess solar heat during the day and release it at night or in overcast weather, guaranteeing steady and uninterrupted power production. Second, by storing and using waste heat, MS energy storage technology can be used in combined heat and power (CHP), district heating, and heat recovery systems of industrial waste, enhancing energy utilization efficiency. Additionally, the modular design of MS storage systems allows flexible application in various scales of energy projects, from small, distributed energy systems to large, centralized power plants, effectively fulfilling their storage roles.

In summary, as an efficient thermal energy storage method, technology for MS energy storage is essential for improving the performance of CSP systems, supporting the advancement of renewable energy sources, and increasing energy efficiency. With continuous technological advancements and expanding application fields.

3 Techniques for enhancing the performance of MSs

3.1 Basic components and improvement methods of MSs

Currently, the main components used in MS energy storage technology are conventional MSs like Solar Salt and Hitec Salt. These conventional MSs have been used extensively in thermal energy storage, but they have several serious disadvantages. Firstly, the decomposition at

high temperatures limits their thermal stability, making them prone to thermal decomposition reactions during prolonged operation. Additionally, traditional MSs can cause corrosion at high temperatures, affecting the service life of equipment. Poor thermal conductivity, hygroscopicity, and high melting points also present challenges in their practical applications. In contrast, improved MSs have shown significant enhancements in performance. This section summarizes the methods for improving MSs.

To further enhance the performance of MSs, researchers have conducted extensive studies and made improvements. Numerous techniques have been used, such as incorporating alkaline materials, adjusting the ratios of MS, and adding nanoparticles to create nanofluids. By lowering the melting point, increasing SHC, improving thermal conductivity, and improving thermal stability, these improvement techniques hope to raise the effectiveness of thermal energy storage and transfer.

3.1.1 Addition of alkaline substances and optimization of MS ratios

In the process of creating technology for MS energy storage, methods to improve MS performance primarily include the addition of alkaline substances and the optimization of MS ratios. By lowering the melting point, increasing SHC, improving thermal conductivity, and increasing thermal stability, these techniques seek to improve the dependability and efficiency of MSs in high-temperature energy storage applications. Through scientific formulation design and the addition of improved substances, the enhanced MSs exhibit superior thermal properties, meeting the high-performance material requirements of modern energy storage systems.

A novel quaternary nitrate MS was developed by adding $\text{Ca}(\text{NO}_3)_2$ to Hitec Salt. This enhancement raised the decomposition point to 628.5°C, decreased the melting point to 83.1°C, and increased the crystallization point to 163.1 °C. The new MS's operational temperature range expanded to 200-565 °C, significantly enhancing its flexibility and reliability in high-temperature applications [1].

In a different study, the proportions of sodium nitrate and sodium carbonate were changed to create three inexpensive mixed MSs. This resulted in a significant improvement in the MSs' thermal characteristics. These mixed salts have melting points of 300.7°C (Sample 3) and 281.7 °C (Sample 2), as well as a maximum decomposition temperature of 639°C (Sample 3), which increases the range of temperatures at which MSs can be applied. Sample 1 outperformed conventional MSs with a specific heat of 1.56 J/(g·K) and a thermal conductivity of 0.79 W/(m·K), respectively [2].

In summary, through the addition of alkaline substances and optimization of MS ratios, the improved MSs exhibit significant advantages in thermal stability, thermal conductivity, and operational temperature range. These advancements offer significant experience and a valuable point of reference for the future development of MS technology. They also improve the thermal properties of MSs, making them more appropriate for high-temperature energy storage applications.

3.1.2 Introduction of nanoparticles to form nanofluids

The thermal characteristics of MSs can be greatly enhanced by evenly dispersing nanoparticles in the salts to create nanofluids. This technique increases the overall thermal transfer capacity and thermal storage performance of MSs, thereby increasing their usefulness in high-temperature energy storage applications. In a study on binary nitrate MSs, the introduction of ultrasonically dispersed, highly affordable detonation nanodiamonds (NDs) with an average particle size of 10 nm, led to the development of a new type of nanofluid MS. This nanofluid MS demonstrated significant improvements in thermal

properties: the melting point decreased by 16°C, the thermal decomposition temperature increased by 35°C, the thermal conductivity increased by 93%, the volumetric heat capacity increased by 38%, and the thermal diffusivity increased by 43% [3].

A nanofluid based on molten carbonate and nano-alumina was developed for next-generation high-temperature thermal energy storage systems. A novel kind of nanofluid MS was produced by filling aluminum bottles with a mixture of 99 wt% salt and 1 wt% nanoparticles and employing a Spex Sample Prep 8000 Series Mixer/Mill for dynamic vibration fusion. This nanofluid MS had a 7% increase in SHC and a roughly 12% increase in thermal conductivity when compared to the base salt [4].

Furthermore, the thermal characteristics of the MSs were markedly enhanced by the dispersion of SiO₂ and TiO₂ nanoparticles into base salts through the use of microwave techniques. Thermal storage capacity reached 922.5 J/g, 19.4% higher than the base salt, with a 28.1% increase in SHC, a 53.7% increase in thermal conductivity, and a 0.9 weight percent increase in titanium dioxide nanoparticles added [5].

In summary, the improvement of MS energy storage technology focuses on enhancing thermal decomposition temperature, lowering the melting point, and improving SHC and thermal conductivity. By adding alkaline substances, optimizing MS ratios, and introducing nanoparticles, researchers have made significant improvements to MSs' thermal characteristics, making them more widely and efficient in high-temperature thermal energy storage and transfer. These scientific breakthroughs offer crucial theoretical underpinnings and useful direction for the advancement of MS energy storage technology, which is anticipated to become more prevalent in energy systems.

3.2 Optimizing the thermal physical properties of MS nanofluids

Research-based on nanotechnology is a mainstream direction for enhancing MS performance. Typically, this involves using traditional MSs as a base and incorporating specific nanoparticles through various methods, such as diffusion, ultrasonication, or other dispersion techniques, to create new types of MS nanofluids.

For instance, Ying Li and associates looked into how adding SiO₂ nanoparticles of various sizes and mass fractions could improve the thermal properties of MSs. They discovered that the performance enhancement of MSs was maximized when 20 nm SiO₂ nanoparticles were added at a mass fraction of 1 wt%. 1.73-1.91 J/(g·K) was the SHC, 17.8% higher than that of pure MSs [6]. Another research found that varying the heat cycling speed altered the formation speed of the samples, discovering that dendritic nanostructures were the key to enhancing the SHC of the nanofluids based on melted salt. Higher heat capacity values resulted from slower heat cycling speeds, which gave dendritic nanostructures more time to form. Conversely, faster heat cycling speeds restricted the nucleation and growth of dendritic nanostructures, resulting in fewer formations and lower heat capacity enhancement [7].

3.3 Research and development of new MS mixtures

Different MS mixtures are currently widely used in a number of fields, including chemical reactions, nuclear energy, and solar thermal power generation. Research directions include the development of low-temperature MSs by studying and selecting new salts, and additives, or adjusting salt ratios to produce mixtures with lower melting points.

For example, different kinds of MS mixtures required for thermal energy storage and heat transfer fluid applications were studied by Bernagozzi et al. By examining HITEC salt, chlorides, and nitrates with different components and additives, they developed eight new high-performance MSs [8]. The results are shown below in Figure 1.

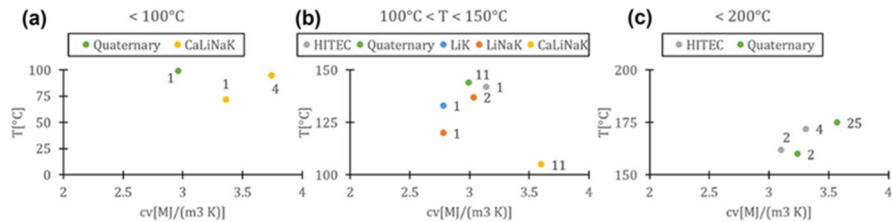


Fig. 1. Five chosen commercial starting salt mixtures and alternative new salt mixtures were tested for their experimental melting points and volumetric heat capacities in the following temperature ranges: (a) below 100°C; (b) between 100 and 150°C; and (c) below 200 °C [8].

Additionally, Cristina Prieto et al. addressed high-temperature issues in CSP by using carbonate MSs to replace traditional Solar Salt. They designed a supercritical carbon dioxide power cycle that achieved efficient, high-temperature, and long-lasting operation [9]. According to the operating parameters, the temperature was above 650 °C for over 80 hours and above 550 °C for over 318 hours. The working temperature reached 650 °C, increasing power conversion efficiency to 18.5%, a 12.12% improvement over the previous 16.5%.

3.4 Research and development of new MS mixtures

Among various MSs, carbonates, fluorides, and chlorides have become research hotspots due to their unique properties. Gowtham Mohan et al. summarized the selection of storage media for stable fluids above 600°C, including major corrosion issues related to sealing more auspicious storage liquids. They determined potential materials for storage tanks as well as methods for reducing corrosion[10]. Carbonates and fluorides have high specific heat capacities in terms of thermal performance. In terms of thermal characteristics, the LiNaK-CO₃ eutectic mixture melts at a lower temperature (397 °C) than other carbonates. The addition of hydroxides, particularly NaOH, specifically lowers the melting point of carbonates. The melting temperatures of binary and more complex salts can be significantly lower than those of single-component fluorides, which have very high melting temperatures. The NaKZn-Cl mixture has a lower melting point than other chlorides—below 200°C. Regarding expenses, chlorides are the best option.

In summary, the chemical composition of MSs primarily influences their melting point and SHC. Because hydroxides, particularly NaOH, have a negative interaction with carbonate, they have a unique effect of lowering the melting point of carbonates. Olivares et al. have successfully demonstrated this effect in LiNaK-CO₃ ternary mixtures using NaOH, KOH, and LiOH. The melting temperatures of single-component fluorides are very high, but designing binary and more complex salts can significantly lower melting temperatures. For chlorides, multi-component mixtures can maximize the reduction of melting points.

4 Application of nanoparticles in MSs

4.1 Basic characteristics of nanoparticles and their application mechanism in MSs

Nanoparticles used in MS energy storage typically range in size from tens to hundreds of nanometers. Due to their unique size effect, these particles exhibit many distinct physical and chemical properties. With their large specific surface area and a surface atomic state closer to that of gases, nanoparticles possess high reactivity. The use of nanoparticles in MSs is mainly motivated by their capacity to greatly improve the salts' thermal physical

characteristics. By changing the internal structure of the MSs, nanoparticles can improve thermal conductivity by creating more pathways for energy transfer.

Regarding the mechanism of enhanced thermal properties by nanoparticles, D. Shin et al. proposed that in MS nanofluids, the interaction between the nanoparticles causes the basic ionic compounds to form fluid nanostructures that resemble fractals. This alteration to the base fluid's structure increases SHC and thermal conductivity. Baha EI Far et al. studied different synthesis conditions of nanofluids and found that slower heating rates allowed more time for dendritic nanostructure formation, leading to higher heat capacity values. Conversely, faster heating rates limited the nucleation and growth of dendritic nanostructures, resulting in fewer formations and lower heat capacity enhancement [7]. Zhao Li et al. confirmed that the formation of dendritic structures of silicon dioxide nanoparticles is a key factor in the enhanced thermal properties of MSs. These studies provide a theoretical foundation for the widespread application of nanoparticles in MSs.

Ying Li et al.'s research found that adding a specific concentration of SiO₂ nanoparticles can greatly improve the thermal characteristics of MSs. By incorporating silicon dioxide nanoparticles into a quaternary mixed MS, Cancan Zhang et al. were able to better understand the heat transfer properties of pure MSs and achieve enhanced thermal performance. The fundamental process involves the formation of aggregates by surface adsorption of nanoparticles, which enhances the convective heat transfer coefficient, lowers the viscosity of the MS-based nanofluid, and increases the specific surface area of the MS.

4.2 Metal oxide nanoparticles on the thermal properties of MSs

SiO₂ and Al₂O₃ nanoparticles are two commonly used nanomaterials. These nanoparticles have a major effect on the thermal characteristics of MSs, according to research. For silicon dioxide particles, studies have demonstrated that adding 20 nm SiO₂ nanoparticles with a 1 weight percent mass fraction to nitrate-based MSs maximizes performance enhancement, as found by Ying Li et al.

Binjian Ma et al. looked into how various nanofluid concentrations affected the thermal characteristics of MSs in relation to aluminum oxide nanoparticles. They determined the ideal concentration conditions by applying Al₂O₃ nanoparticles at 0.5 wt%, 1.0 wt%, and 1.5 wt% concentrations using a controlled variable method. The creation of secondary nanostructures brought about by long-range ionic effects in the MS solvent and the chemical adsorption of free ions on the nanoparticle surface was responsible for the maximum 38.7% increase in SHC at a concentration of 1 weight percent [11].

4.3 Comparison of the effects of different shapes of nanoparticles

In addition to composition, the shape of nanoparticles also affects their application in MSs. Different shapes of nanoparticles exhibit varying dispersion, stability, and thermal conductivity in MSs. Generally, nanoparticles with larger specific surface areas, such as dendritic shapes, have better dispersion in MSs and can more effectively enhance their thermal properties.

D. Shin et al. proposed a novel heat storage mechanism to explain the increased SHC of MS nanofluids. They demonstrated that fractal nanostructures are significant in enhancing specific heat, distinguishing them from the specific heat mechanisms of conventional nanofluids. The researchers suggested that interactions between nanoparticles in MS nanofluids induce the formation of fluid nanostructures resembling fractals. This modification of the base fluid structure enhances both thermal conductivity and SHC.

El Far, Baha, et al. suggested that dendritic nanostructures are in charge of the increased the MSs' heat capacity. By reducing the concentration of nanoparticles to disrupt the

formation of dendritic structures, they observed a decrease in heat capacity, confirming how dendritic structures are affected. When dendritic structures were disrupted, the heat capacity enhancement dropped from the original 15% to 3%, indicating that dendritic structures are a key factor in heat capacity enhancement.

5 Future directions and challenges

MS energy storage technology holds great promise for application in Concentrated Solar Power (CSP) systems. With the global demand for renewable energy continuously growing, CSP technology, known for its stable power output, is gaining increased attention. MS energy storage, as a core component of CSP systems, offers high energy density and long-duration storage, effectively addressing the intermittency of solar power. Furthermore, systems that store excess solar heat in MS can release it at night or in cloudy conditions, providing continuous power to the grid and significantly improving the efficiency and reliability of solar power generation. Thus, there is a lot of promise for MS energy storage in the production of solar thermal power in the future.

Despite significant advancements in MS energy storage technology, several challenges remain. First, issues of thermal stability and corrosion at high temperatures in traditional MSs have not been fully resolved, limiting their long-term application under high-temperature conditions. Second, although improved MSs have shown enhanced thermal properties, their high production costs hinder large-scale applications. Additionally, MS storage systems experience heat loss during operation, necessitating further research and optimization of system design to enhance thermal efficiency.

Future research directions include: exploring and developing new MS materials with higher thermal stability and thermal conductivity to meet high-temperature storage needs; adding additives and nanoparticles to MSs to improve their thermal characteristics even more, lowering melting points, and increasing thermal decomposition temperatures; optimizing the design of MS storage systems to reduce heat loss and improve thermal efficiency, thereby enhancing overall system performance; and researching cost-effective production processes and raw materials to lower the total cost of systems for storing MS, enabling large-scale commercial application.

6 Conclusion

In conclusion, MS energy storage technology is important in improving solar thermal power generation systems, supporting the development of renewable energy, and improving energy utilization efficiency. Through the addition of alkaline substances, optimization of MS ratios, and introduction of nanoparticles, the thermal properties of MSs have been significantly improved, making them more effective. Despite notable progress, challenges remain, such as thermal stability and corrosion issues at high temperatures, high production costs, and operational heat loss. Future research should focus on developing new MS materials, optimizing system design, and reducing costs to achieve large-scale commercial applications of MS energy storage systems. As the global energy landscape continues to shift towards renewable sources, MS energy storage technology will play an increasingly vital role in ensuring the reliability and stability of solar power generation, providing strong support for global energy transition and sustainable development.

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