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Molten Salt Thermal Energy Storage Technology: A Review of Material Performance Optimization and Applications

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ABSTRACT
The utilization of new energy sources such as solar and wind energy is restricted by natural conditions and exhibits obvious intermittency. This characteristic has made the research, development, and application of energy storage technologies a focus of the industry. Among various energy storage technologies, thermal energy storage is a key link to improve energy utilization efficiency. As a core thermal energy storage technology in high-temperature environments, molten salt thermal energy storage is playing an irreplaceable role. This paper first introduces the two main thermal energy storage methods of molten salts, then summarizes several approaches to enhance the performance of molten salts, subsequently lists the common applications of molten salt materials, and finally concludes with an outlook on future development directions.

KEYWORDS
Molten salt thermal energy storage; Performance enhancement methods; Molten salt applications

1 Introduction

Energy serves as the cornerstone of the survival and development of human society, and it is also crucial to national economy, people's livelihood, and national security. New energy sources such as solar energy and wind energy exhibit intermittent and unstable characteristics during utilization, thus requiring the deployment of energy storage systems. The 14th Five-Year Plan for the Development of New Energy Storage jointly issued by the National Development and Reform Commission and the National Energy Administration on February 10, 2022, points out that new energy storage is a vital technology and basic equipment for constructing a new power system, as well as a key support for achieving the "dual carbon" goals [1]. Molten salts are ideal energy storage media, boasting advantages such as strong thermal stability, high heat storage density, low cost, and high safety. They have been widely applied in fields including concentrated solar power (CSP), molten salt reactors, heating, and waste heat recovery, presenting broad application prospects [2]. Molten salt materials are cost-effective, with the service life of thermal energy storage systems reaching over 10 years, and their long-term operational economy outperforms that of most battery energy storage technologies. Additionally, molten salt materials possess strong chemical stability and higher safety.

Existing literature in the field of molten salt performance enhancement primarily covers three aspects: research progress on technologies for single-aspect improvement of molten salt performance; methods for enhancing specific molten salt materials; and overviews of technologies for improving molten salt performance focusing on specific application scenarios. Therefore, this paper aims to summarize various feasible methods for enhancing molten salt performance, providing references for research and practical applications.

2 Thermal Energy Storage Methods of Molten Salts

Currently, the main thermal energy storage methods for molten salts are sensible heat storage and latent heat storage.

2.1 Sensible Heat Storage

Sensible heat storage achieves the storage and release of heat through temperature changes of the heat storage medium. Its advantages include relatively simple integration of the heat storage system and low energy storage cost; however, it has low energy storage density, resulting in a large system volume and significant heat loss during heat absorption/release processes [3].

2.2 Latent Heat Storage

Latent heat storage realizes heat storage and release by leveraging the phase change process of the heat storage medium. It offers higher energy storage density compared to sensible heat storage, leading to a relatively smaller required system volume. Nevertheless, the heat storage medium has poor thermal stability, suffers from high-temperature corrosion, and exhibits low compatibility with heat storage containers [3].

Up to now, sensible heat storage technology has achieved full development, while latent heat storage technology is gradually maturing, progressing from the laboratory verification stage to the commercial demonstration stage [3]. Among numerous heat storage materials, molten salts are extensively studied and applied. They can function both as latent heat storage materials and sensible heat materials in CSP, possessing unique characteristics that many other heat storage materials lack.

3 Methods for Enhancing the Thermal Properties of Molten Salts

Thermal properties mainly include thermal conductivity, specific heat capacity, and thermal stability. Enhancing these properties can expand the application scope of materials and improve their reliability and utilization efficiency. Molten salt materials already have relatively good thermal properties, but there are still approaches to further enhance some of their thermal properties, thereby improving heat storage efficiency.

3.1 Utilization of Nanomaterials

The concept of nanofluids was initially proposed by Choi in 1995. By dispersing metal nanoparticles into a base solution, they observed a significant increase in thermal conductivity. Since then, an increasing number of researchers have dedicated themselves to the study of nanofluids. Common nanomaterials include SiO_2, Al_2O_3, CuO, carbon nanotubes, and graphene [4]. Nanomaterials can significantly enhance the application potential of molten salts in the field of thermal energy storage by regulating key parameters such as the melting point, viscosity, and thermal conductivity of molten salts.

The main methods for preparing nanofluids are the "one-step method" and the "two-step method". The "one-step method" demonstrates numerous advantages and excellent results in terms of nanoparticle dispersion and size control. However, this process typically requires specialized equipment, so it has not been widely used for the preparation of molten salt-based nanofluids. In contrast, the "two-step method" has lower equipment requirements and is widely employed in the preparation of molten salt-based nanofluids [5].

A study by Wei Xiaolan et al [6]. found that when nano-SiO_2 fluid is added to nitrate molten salts, the specific heat capacity of the molten salt fluid first increases and then decreases, and there exists an optimal addition amount of nano-SiO_2. Qiu Lixiang et al [7]. discovered that adding nano-SiO_2 to solar salt can enhance its thermal conductivity, and aggregated nanofluids exhibit a better improvement effect on thermal conductivity. They also analyzed the underlying reasons through experiments. Yuan Hongyue et al [8]. added nano-Al_2O_3 to the (LiCl-NaCl-KCl) ternary eutectic molten salt. Experiments confirmed that within the temperature range of 673–1073 K, the density, viscosity, and thermal conductivity of both the molten salt and its nanofluid decrease with increasing temperature. However, the addition of nanoparticles increases the density, viscosity, and thermal conductivity of the molten salt. There are also other nanomaterials. For instance, Wang Chen et al [9]. used NaCl, KCl, and $CaCl_2$ as phase change materials, MgO as a carrier material, and nano-Bi_2O_3 as a thermal conductivity enhancer to prepare chloride/magnesium oxide-based composite phase change thermal storage materials via a mixing and sintering method. This material exhibits significantly improved specific heat capacity and thermal conductivity, along with good thermal stability at high temperatures.

The understanding of the properties of nanofluids remains incomplete, and the mechanism research on the enhancement of thermal physical parameters (such as specific heat capacity) of molten salts by nanoparticles is still insufficient. Although the combination of some nanomaterials with molten salts can reduce their corrosiveness, a general rule has not been established yet. Therefore, attention must still be paid to the impact of the corrosiveness of thermal storage materials on containers [5].

3.2 Optimization of Composite Molten Salt Proportioning

Optimization of composite molten salt proportioning is a method to improve molten salt performance by adjusting the proportions of various components in the mixed system to achieve the optimal combination of specific properties, thereby meeting the requirements of practical application scenarios. The performance of composite molten salts is jointly determined by their components and proportioning. Single-component molten salts often have limitations, while mixing them can complement their advantages. Common components of composite molten salts include nitrates, carbonates, and chlorides. He Cong et al [10]. found that when the molar ratio of the ternary system molten salt ($NaNO_3$∶NaCl∶Na_2CO_3) is 0.92∶0.064∶0.016, it exhibits good eutectic properties, a low melting point, and a large latent heat. This makes it suitable for application in heat transfer and thermal storage systems, and it also has great potential in the preparation of composite phase change thermal storage materials. Wu Yuting et al [11]. experimentally explored the appropriate proportion of the ternary mixed carbonate molten salt. Through comparative experiments, they concluded that when the ratio of lithium, sodium, and potassium is 3∶2∶5, the molten salt has a high specific heat capacity and low viscosity.

3.3 Composite with Non-Salt Substances

Composite with other non-salt substances is one of the current research hotspots in the performance optimization of molten salt thermal energy storage. Typically, non-salt substances are added to the composite molten salts with optimized proportioning. This approach not only retains the original core advantages of molten salts but also makes up for their shortcomings, further optimizing their performance. It is an important way to improve the performance of molten salt materials and has unlimited development potential.

Xiao Junbing et al [12]. studied the performance of the NaCl-KCl-CaCl $_2$/CLSF composite molten salt. The maximum decrease in melting enthalpy was 27.09%, the maximum increase in thermal conductivity was 60.03%, and the heating time and cooling time within the same temperature range were reduced by a maximum of 62.50% and 39.13%, respectively. These results confirm that this material has excellent thermal conductivity, thermal stability, and thermal storage performance, along with broad application prospects. Argyrios Anagnostopoulos et al [13]. investigated composite phase change materials prepared by mixing red mud and solar salt, and improved the material performance by adjusting the proportioning. Experiments showed that an appropriate proportion can slightly change the thermal conductivity of the material, and when the solar salt (SS) content is 60%, the latent heat reaches the optimal value of 58 J/g.

3.4 Appropriate Adjustment of Purity

Purity also has an impact on the performance of molten salts, which may be related to impurities contained within them. High-purity molten salts can maintain stable chemical properties at high temperatures. Impurities may act as "catalysts" or "reactants" in chemical reactions, accelerating the decomposition of molten salts, corroding equipment, or generating harmful products. However, the higher the purity, the lower the thermal conductivity, specific heat capacity, and viscosity of nitrate molten salts, and these properties further decrease with increasing temperature [14]. Therefore, the control of purity cannot be ignored, and at the same time, the interference of impurities on molten salts must be prevented.

4 Practical Applications of Molten Salt Thermal Energy Storage

Owing to their excellent thermochemical properties, molten salt materials have been widely applied in various energy storage and thermal storage fields, such as solar power generation, waste heat recovery, molten salt nuclear reactors, and molten salt electrochemical metallurgy. The application of molten salt materials can improve factory efficiency and reduce costs, presenting extremely high practical value.

4.1 Solar Power Generation Field

Molten salt materials hold irreplaceable significance in solar power generation, particularly in the field of CSP. They address the core issue of intermittency and instability of solar energy, promoting the development of solar power generation towards high efficiency, stability, and dispatchability.

Currently, more than half of the CSP facilities in operation in Europe and North America are equipped with thermal energy storage systems, mainly based on molten salt sensible heat storage media [15]. In the field of pure solar power generation, power plants equipped with thermal energy storage systems demonstrate significantly better performance than those without. Specifically, the annual total power generation of the system is increased by 68 GW·h, and the annual capacity factor of the system is increased by 16% [16].

4.2 Waste Heat Recovery Field

Waste heat recovery is an important application for energy reuse, enabling efficient capture of low-grade heat. Through the closed loop of "efficient heat absorption – stable heat storage – flexible heat release", molten salt materials solve core issues in waste heat recovery, such as "asynchrony between supply and demand" and "low utilization efficiency", and they are one of the key technologies for promoting industrial energy conservation.

At present, most high-temperature flue gas waste heat recovery in copper smelting enterprises adopts the form of waste heat boilers to produce high-temperature steam. The steam, as a heat carrier, can be used for heating, power generation, daily life, etc. However, the fluctuation of flue gas leads to low-quality steam production and low waste heat utilization efficiency, which only reaches 30% of the total flue gas heat. The economic benefits generated by generating electricity using the heat stored in molten salts according to peak, flat, and valley periods are far higher than those of direct waste heat recovery using flue gas waste heat boilers [17].

4.3 Molten Salt Nuclear Reactor Field

A molten salt nuclear reactor is a type of fourth-generation nuclear reactor that uses molten salts as coolants. The operating environment of molten salt reactors can avoid high-pressure constraints. Operating under near-atmospheric pressure not only reduces the manufacturing and welding costs of pressure vessels and system pipelines but also improves the safety of the reactor. Additionally, molten salt reactors have high thermal efficiency [18].

The molten salt materials used in nuclear reactors are mainly fluorides, which feature low ambient pressure and high thermal efficiency. However, fluorides have extremely strong corrosiveness, posing a significant challenge to the corrosion resistance of containers.

4.4 Molten Salt Electrochemical Metallurgy Field

Molten salt electrochemical metallurgy is a technology that utilizes molten salts as electrolytes to achieve metal extraction, purification, or alloy preparation through electrochemical reactions, and it holds important significance in the metallurgical industry. Compared with aqueous electrolytes, molten salt electrolytes have a wide electrochemical window and good chemical stability, which is the primary reason for their widespread application.

The solid-state molten salt electrolysis technology jointly developed by the University of Science and Technology Beijing and Tohoku University (Japan) enables efficient impurity separation through electrolysis at 500°C (lower than the melting point of waste aluminum). This technology increases the purity of aluminum from 90% to 99.9%, with a recovery rate of 96%, and impurities such as silicon and copper are concentrated in the anode slime [19].

5 Conclusion and Outlook

This paper mainly focuses on the methods for enhancing the performance of molten salts, including the utilization of nanomaterials, optimization of composite molten salt proportioning, composite with non-salt substances, and appropriate adjustment of purity. Meanwhile, it also introduces the four practical applications of molten salt thermal energy storage, namely solar power generation, waste heat recovery, nuclear reactors, and the metallurgical field.

With the rapid development of artificial intelligence, it is expected that AI will assist in the proportioning of composite molten salts in the future to explore proportioning combinations with more excellent performance. Chlorides and fluorides have stable chemical properties and will become key research objects in the field of molten salt materials. However, both of them have strong corrosiveness, so the fields of corrosion-resistant alloys and corrosion-resistant coatings are of great research value.

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