INFLUENCE of ELECTRIC FIELD on STRUCTURE and PROPERTIES of TERNARY CARBONATE MOLTEN SALT

ZHUCHuang1*, GONG Li2
1New Energy (Photovoltaic) Industry Research Center, Qinghai University, Xining, Qinghai, 810016, China
2Science and Technology Department, Qinghai University, Xining, Qinghai, 810016, China
*Corresponding author’s e-mail: zzccpy_22@163.com

Abstract. Molten salt is one of the important heat storage materials in the field of solar thermal utilization, and nanoparticles can improve partial thermal properties of molten salt. To investigate whether nanoparticles with charge can affect the structure of molten salt ions, the micro electric field of nanoparticles was replaced by applied electric field and the liquid Li2CO3-Na2CO3-K2CO3 was solidified in the electric field. DSC was used to determine the phase change temperatures and latent heat, and thermal stability was analyzed by TG curve. At last, the microstructures of molten salt were analyzed by SEM. Results show that the applied electric field can reduce the starting and ending temperatures of the carbonate by about 10℃ as well as the latent heat. The mass loss rates of molten salt samples at the positive and negative plates are 1.44% and 0.81% respectively at 700℃, and these samples have higher thermal stability than normal molten salt. The applied electric field can produce new microstructure of molten salt near positive and negative plates.

1. Introduction
Molten salt has been used in some solar thermal power stations [1]. To improve the properties of molten salt, extensive studies have been carried out on flow heat transfer performance [2, 3], heat storage performance, corrosion and other aspects, and research on nitrate system are abundant [4, 5]. The maximum operating temperature of nitrate phase change materials is mainly distributed between 450℃ and 550℃. As the crescent demand of energy nowadays, it is urgent to develop molten salt materials which can be applied to higher temperature ranges. Therefore, carbonate, chloride and other heat storage materials have become the new research hotspot [6, 7]. The specific heat is a very important property parameter for any kind of molten salt. The high specific heat is beneficial to increase the heat storage density and reduce the cost. Furthermore, the temperature change of molten salt with high specific capacity is more stable during the process of heat absorption and emission, which is conducive to the safe operation of the system. At last, the molten salt with high heat storage density has a longer heat release time, which enables the photothermal power station to effectively deal with the natural phenomenon of long-time sunshine shortage.

According to the research from Shin et al. [8], it was found that the specific heat of the composite molten salt increased by 32% when doping Al2O3 with a mass fraction of 1.0% and a particle size of 10nm into Li2CO3-K2CO3 eutectic salt, and a new chain structure appeared in the base salt.
Hani Tiznobaik et al. [9] found that the formation of most the special microstructure in the nano-SiO2-carbonate was prevented by adding trace NaOH, and found that the specific heat capacity was reduced from 26% to 3%, indicating that the microstructure had an important effect on the specific heat increase of the nanocomposite molten salt. By dispersing nano-SiO2 and nano-MgO into Li2CO3-K2CO3, Xiong et al. [10] found that the specific heat of binary carbonate was increased by 27.5%~34.1% and 11%~20.7%, respectively. It can be seen that some nanoparticles have a certain strengthening effect on the specific heat of molten salt, however, the microscopic mechanism is not clear at present. In order to explore this mechanism and determine whether the micro-electric field formed by charged nanoparticles has an impact on the ionic structure and properties of molten salt, an electric field was applied to Li2CO3-Na2CO3-K2CO3 ternary carbonate, and the properties and microscopic morphology of molten salt at positive and negative plates were analyzed, which could provide a reference for the in-depth study of the microscopic mechanism of specific heat strengthening by adding nanoparticles into molten salt.

2. Experiment

2.1 Sample and preparation
The potassium carbonate, sodium carbonate and lithium carbonate with analytical purity used in the experiment come from Shanghai Aladdin biochemical technology co., LTD.

K2CO3, Na2CO3 and Li2CO3 were placed in a vacuum drying box, and then dried at 120℃ for 24 hours before hermetrical saving. According to the research of Frangini et al. [11], the melting point of the ternary carbonate would be about 397℃ if the molar ratio of Li2CO3, Na2CO3 and K2CO3 is 43.5:31.5:25. In this study, three kinds of carbonates were respectively weighed according to this proportion and put into a mortar to grind evenly. To mix the molten salt well, 30g of the mixed carbonate was put into the ceramic crucible and held for 3 hours in a resistance furnace at 550℃. Then the molten salt was taken out and solidified in an external electric field, and the molten carbonate affected by the electric field was obtained. Finally, molten salt samples near the positive and negative plates of electric field were taken to analyze the microstructure and thermal properties.

2.2 Analytical instruments
STA 449F3 produced by NETZSCH in Germany was used to test samples, and the phase change temperature, latent heat and thermogravimetric loss were analyzed by DSC-TG. Nitrogen protection was used during the test, and the heating rate was set to 10℃/min. The microscopic morphology of molten salt was analyzed by scanning electron microscope with JSM-5610LV produced by JEOL in Japan, and the magnification of microscopic photos were magnified 2000 times.

3. Results and discussion

3.1 Phase change temperature and latent heat
Molten salts solidified in the electric field were taken out, and the samples near the positive plate and the negative plate were respectively taken to determine the phase change interval and latent heat, which were compared with the carbonate samples solidified in the case of no applied electric field (normal molten salt). The DSC curves of molten salt near the positive plate and normal molten salt are shown in Figure 1, and the starting and ending temperature of the phase change are listed in Table 1. The results show that the phase change starting point of molten salt near the positive plate decreases by about 11℃, and the ending point decreases by about 6.5℃, indicating that the electric field can reduce the phase change temperature interval of molten salt near the positive plate. Additionally, it is found that the latent heat of the sample at the positive plate decreased by about 17J/g compared with the normal molten salt, which indicated that less heat is needed during the melting process of the molten salt near the positive plate.
Figure 1. DSC curves of molten salt near the positive plate and normal molten salt

Table 1. Phase change temperature and latent heat of molten salt near the positive plate and normal molten salt

| Sample                      | Starting point of phase change(℃) | Ending point of phase change (℃) | Latent heat (J/g) |
|-----------------------------|-----------------------------------|---------------------------------|-------------------|
| molten salt near the positive plate | 397.9                            | 414.1                           | 207.7             |
| normal molten salt          | 408.8                            | 420.5                           | 224.8             |

The two DSC curves in Figure 2 are carbonate near the negative plate and the normal molten salt respectively. It can be seen that the phase change interval of molten salt near the negative plate has an obvious left shift. Combined with the data of phase change temperature interval in Table 2, it can be seen that the starting point and ending point of molten salt near the negative plate are both reduced by about 10℃ compared with the normal molten salt, and the latent heat is also reduced by 10J/g. Obviously, the phenomena are similar to that of molten salt near the positive plate. By comparing the DSC curves of molten salt near the positive and negative plate (shown in Figure 3), it is found that the phase change temperature and latent heat of the two samples are close to each other.

Figure 2. DSC curves of molten salt near the negative plate and normal molten salt

Table 2. Phase change temperature and latent heat of molten salt near the negative plate and normal molten salt

| Sample                      | Starting point of phase change(℃) | Ending point of phase change (℃) | Latent heat (J/g) |
|-----------------------------|-----------------------------------|---------------------------------|-------------------|
| molten salt near the negative plate | 398.6                            | 410.7                           | 214.8             |
| normal molten salt          | 408.8                            | 420.5                           | 224.8             |
Figure 3. DSC curves comparison of molten salts at positive and negative plates

Through the above experimental phenomena, it can be found that the phase change temperature and latent heat of molten carbonate near the positive and negative poles are reduced by the electric field at the same time, and this phenomenon may be related to the structural deformation of molten salt ions under the action of the electric field. Liquid molten salt is an ionic liquid, and positive and negative ions can move freely. The effect of the electric field makes the ions with the same electric property accumulate, resulting in a large repulsion force between the ions. In this state, the solidified molten salt has poor stability, so it is easier to melt at high temperature, and the absorbed heat in the melting process is relatively low.

3.2 Heat stability
The molten salt near the positive and negative plates as well as the normal molten salt were heated to over 700℃, and the thermogravimetric curves were shown in Figure 4. At 700℃, the mass loss of the molten salt near the positive plate was 0.81%, the molten salt near the negative plate 1.44%, and the normal molten salt 3.96%. This phenomenon shows that the mass loss rate of molten salt solidified in the electric field is reduced at high temperature and the thermal stability is stronger. One possible reason is that ions of the liquid salt have shifted in the electric field, resulting in the composition of molten salt at the positive and negative plates different from that of normal molten salt.

Figure 4. Thermogravimetric curves of three molten salt samples

3.3 Microstructure of molten salt
The microscopic morphology of normal molten salt was observed through electron microscope. It is found that the surface is relatively flat, even at the granular surface (shown in Figure 5). In contrast, the structure of molten salt solidified in the electric field is quite different. The molten salt structure near the negative plate is shown in Figure 6(a). At the same magnification, many evenly distributed tiny white bumps are found on the sample surface. Figure 6 (b) shows the molten salt structure near the positive plate, and a large number of rod-like structures appear in the sample.
Figure 5. Micromorphology of normal ternary carbonate molten salt

Figure 6. Morphologies of molten salt solidified in the electric field: (a) molten salt near the negative plate; (b) molten salt near the positive plate

The appearance of these two special structures may be related to two aspects. The first one is the molten salt composition near the positive and negative plates. The second one is the regular arrangement of ions in the electric field. Cations tend to move towards the negative plate and anions tend to move towards the positive plate. The degree of this deviation is related to the strength of the applied electric field. At the same time, the irregular Brownian Motion of the positive and negative ions in the high temperature molten salt is restrained to a certain extent under the action of electric field force, tending to present a regular arrangement structure.

4. Conclusion
The effects of applied electric field on the phase change temperature, latent heat, thermal stability and microstructure of Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ ternary molten salt were studied. Results show that the applied electric field can reduce the starting and ending phase change temperature of the molten salt by about 10℃ and the latent heat by about 10J/g, which may be related to the structural deformation of molten salt ions under the action of the electric field. The mass loss rates of molten salt samples near the positive and negative plates at 700℃ were 1.44% and 0.81% respectively, which were lower than that of normal molten salt, indicating that the carbonate molten salt near these two plates have stronger high-temperature stability. New microscopic point-like and rod-like structures were found in molten salt samples near negative and positive plates, which may be related to the composition of molten salt and the regular arrangement of ions near electrode plates.

Acknowledgments
This research was financially supported by the Natural Science Foundation of Qinghai Province (2017-ZJ-945Q) and One Thousand Talents Plan for High-end Innovation of Qinghai Province.

References
[1] Y. L. He, W. Q. Wang, Y Qiu, et al. (2019) Convective heat transfer characteristics of molten salts flowing in complex flow structures: Experimental studies and progress (in chinese). Chin Sci
Bull, 64: 3007-3019.

[2] X. Y. Dong, Q. C. Bi, F. Yao. (2019) Experimental investigation on the heat transfer performance of molten salt flowing in an annular tube. Experimental Thermal and Fluid Science, 102: 113-122.

[3] H. Y. Shi, M. J. Li, W. Q. Wang, et al. (2020) Heat transfer and friction of molten salt and supercritical CO₂ flowing in an airfoil channel of a printed circuit heat exchanger. International Journal of Heat and Mass Transfer, 150: 1-13.

[4] X. L. Wei, P. Xie, X. C. Zhang, et al. (2019) Research on preparation and thermodynamic properties of chloride molten salt materials. http://kns.cnki.net/kcms/detail/11.1946.TQ.20200318.1432.007.html.

[5] Y. Han, Y. T. Wu, C. F. Ma. (2019) Comparative analysis of thermophysical properties of mixed nitrates. Energy Storage Science and Technology, 8(06): 1224-1229.

[6] L. X. Sang, M. C. Cai, N. Ren, et al. (2015) Modified Preparation and Analysis of Thermal Physical Properties of Mixed Carbonates. Journal of Engineering Thermophysics, 36(03): 615-618.

[7] B. Liu, X. L. Wei, Q. Peng, et al. (2018) Research on preparation and properties of quinaty chloride molten salt. Acta Energiae Solaris Sinica, 39(07): 1815-1821.

[8] D. Y. Shin, D. Banerjee. (2014) Specific heat of nanofluids synthesized by dispersing alumina nanoparticles in alkali salt eutectic. International Journal of Heat and Mass Transfer, 74: 210-214.

[9] H. Tiznobaik, D. Shin. (2013) Experimental validation of enhanced heat capacity of ionic liquid-based nanomaterial. Applied Physics Letters, 102: 173906.1-173906.3.

[10] Y. X. Xiong, Z. Y. Wang, P. Xu, et al. (2018) Effect of MgO and SiO₂ nanoparticles on specific heat capacity of binary carbonate eutectic. Journal of Chemical Industry and Engineering(China), 69(12): 4959-4965.

[11] S. Frangini, A. Masi. (2016) Molten carbonates for advanced and sustainable energy applications: Part I. Revisiting molten carbonate properties from a sustainable viewpoint. International Journal of Hydrogen Energy, 41: 18739-18746.