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Development of novel thermal conductive composite strontium chloride for sorption refrigeration

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Abstract: A novel type composite strontium chloride (SrCl_2) is developed with porous material of expanded natural graphite (ENG) and nanoparticle of Carbon coated Nickel (Ni@C) as the additives. Samples with different densities and mass ratios of salt are produced, and thermo-physical properties such as thermal diffusivity, thermal conductivity and permeability are investigated and analyzed. It is indicated that the highest thermal diffusivity could reach $6.2 \text{ mm}^2 \cdot \text{s}^{-1}$. Correspondingly the highest thermal conductivity is $4.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is about 20 times higher than that of ordinary granular SrCl_2 . The permeability of the novel composite SrCl_2 range from $1.31 \times 10^{-9} \text{ m}^2$ to $1.07 \times 10^{-13} \text{ m}^2$ with the densities from $400 \text{ kg} \cdot \text{m}^{-3}$ to $600 \text{ kg} \cdot \text{m}^{-3}$. Moreover, sorption characteristic for the novel composite SrCl_2 is also evaluated, and it is worth noting that samples with Ni@C have the better sorption performance than that without Ni@C due to the improved heat and mass transfer performance. Sorption quantities of novel composite SrCl_2 range from $0.39 \text{ kg} \cdot \text{kg}^{-1}$ to $0.67 \text{ kg} \cdot \text{kg}^{-1}$ when the evaporating temperature varies from -15°C to 15°C . One remarkable fact is that the addition of ENG and Ni@C shows the great potential for sorption refrigeration by adjusting the concentration swing.

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22 **Keywords:** Composite SrCl_2 , Carbon coated Nickel (Ni@C), Heat and mass transfer,

23 Sorption characteristics

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27 **Nomenclature**

A	Area of ammonia vessel (m^2)
B	Shape factor
C	Specific heat ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)
d	Thickness of sample (mm)
ENG	Expanded natural graphite
GWP	Global Warming Potentials
g	Gravity acceleration ($9.80 \text{ m}\cdot\text{s}^{-2}$)
K	Permeability (m^2)
m	Gas mass flow rate ($\text{kg}\cdot\text{s}^{-1}$)
Ni@C	Carbon coated Nickel
ODP	Ozone Depletion Potential
P	Pressure (Pa)
q	Gas volume flow rate ($\text{L}\cdot\text{min}^{-1}$)
R	Gas constant ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)
SrCl_2	Strontium chloride
SCP	Specific cooling power ($\text{W}\cdot\text{kg}^{-1}$)
T	Temperature ($^{\circ}\text{C}$)
t	Time (s)
x	Sorption quantity ($\text{kg}\cdot\text{kg}^{-1}$)

28 Greek letters

α	Thermal diffusivity ($\text{mm}^2 \cdot \text{s}^{-1}$)
λ	Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
μ	Gas viscosity ($\text{Pa} \cdot \text{s}$)
ρ	Density ($\text{kg} \cdot \text{m}^{-3}$)
v'	Specific volume of saturated liquid ammonia ($\text{m}^3 \cdot \text{kg}^{-1}$)
v''	Specific volume of saturated vapor ammonia ($\text{m}^3 \cdot \text{kg}^{-1}$)
v	Velocity ($\text{m} \cdot \text{s}^{-1}$)

29 Subscripts

a	Axial
c	Condensation
e	Evaporation
eq	Equilibrium
in	Inlet
out	Outlet
ref	Refrigeration
SrCl_2	Strontium chloride

30

31 1. Introduction

32 Utilization of low grade heat is one of the main options to overcome the developing

constraints with ever rising energy demands[1]. As one effective energy conversion technology driven by the low grade heat, sorption refrigeration has drawn burgeoning attentions since it is characterized as easy to control and utilizing green refrigerants without Ozone Depletion Potential (ODP) and Global Warming Potentials (GWP)[2]. One of the key parameters for sorption refrigeration is specific cooling power (SCP), which is mainly relevant with the sorption/desorption rate. The larger sorption /desorption rate is, the higher SCP will become, which will result in the better refrigeration performance and system compactness. There are two main methods to improve the sorption/desorption rate. One is the heat and mass transfer enhancement[3]. The other is the modification of sorption kinetic [4]. These two aspects are often interdependent.

For heat and mass transfer intensification, composite sorbent has been developed with various forms. As one major matrix, expanded natural graphite (ENG) has been extensively investigated for both physical and chemical sorbents[5], which was invented by the Carburet Company in US firstly[6]. Mauran et al.[7] introduced the ENG as a matrix to the consolidated composite sorbent, which demonstrated the better thermal conductivity for the metal chlorides. Later, Based on Darcy's law, Han and Lee [8] tested the permeability of different chlorides with ENG, and found that the permeability was in range of 10^{-16} - 10^{-12} m². Jiang et al [3, 9] comprehensively investigated thermal conductivity and permeability of eight different chlorides with ENG, and compared the properties among different composite sorbents in the sorption process. Recently, expanded natural graphite treated by sulfuric acid (ENG-TSA) was introduced to further improve the heat and mass transfer performance of the metal chlorides [10, 11]. The highest thermal conductivity of the composite sorbent was able to reach $88.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ while the permeability decreased to 10^{-14} m²[12]. Nonetheless, one

drawback is that the price of ENG-TSA is 60 times higher than that of ENG, and the limited improvement could be achieved for the real application of sorption refrigeration system[13, 14]. It is worth noting that thermal conductivity of the composite sorbent has improved significantly through various matrix when compared with the value of granular chlorides. Comparably, mass transfer performance is stagnated or even slightly backwards. Also one remarkable fact is that in some freezing cases of sorption processes, mass transfer will be the key parameter for the improvement of the system performance since the temperature potential is sufficient to reach the sorbent.

For better sorption kinetics, nanoparticles have been regarded as one possible way to improve the working performance of the organic sorbent which is similar as its application for the absorption process. Franco et al. [15] investigated the sorption kinetic of asphaltene by means of nickel oxide nanoparticles. Results demonstrated that isothermal sorption reaction rate increased with the increase of the nanoparticles. Later, it was indicated that other nanoparticles such as aluminum oxide can also effectively shorten the sorption time [16, 17]. However, with regard to sorption reactions for refrigeration, there is less report of composite metal chlorides to improve sorption kinetic with the nanoparticles. The sorption performance on the packed multi-walled carbon nanotube (CNT) and ammonia was analyzed by Yan et al. Results indicated that pure multi-walled CNT could be selected as the additive for chemical sorbents to improve thermal characteristics though it was not suitable for the sorption refrigeration owing to its relatively low sorption quantity[18]. Later, Yan et al.[19]investigated the sorption characteristic of composite CaCl_2 with multi-walled CNT as the additive, and

found that multi-walled CNT had no influence on the sorption kinetics of the composite sorbent. This is mainly because CNT is characterized as curved and entangled together, it is not easy to be arranged homogeneously for optimal direction. Compared with CNT, nanoparticles such as Carbon coated Nickel (Ni@C) with core-shell structure manifests the potentials for the improvement of the sorption kinetics. One remarkable fact is that carbon coating is able to protect the external conditions for the metal core, and the metal core may take promoting effects on the composites while maintaining its desirable thermal properties[20-22]. The granular shape in nanometer size tends to be easier to occupy the porous structure of the composite sorbent with ENG. Meanwhile it could also avoid causing greater swelling and agglomeration in the sorption process.

Compared with Calcium chloride (CaCl_2), less concerning researches are reported for strontium chloride (SrCl_2), especially when both ENG and nanoparticles are selected as the additives for the composite sorbent. In this paper, SrCl_2 impregnated with both ENG and Ni@C is investigated for thermal properties, permeability as well as the sorption characteristics. Based on the testing results, the sorption refrigeration performance is also be evaluated and analyzed. In some cases, performance of the novel composite sorbent will be compared with SrCl_2 -ENG i.e. without Ni@C for further elaboration.

2. Development of novel composite SrCl_2

The thermochemical sorption reaction process of SrCl_2 with ammonia can be expressed as the equations 1-2. The development of the novel composite SrCl_2 can be referred to the reference[22]. ENG is expanded by the optimal expanding process, i.e. heating untreated

natural graphite in an oven at the temperature of 600°C for 8 minutes [21]. First, ENG is dried in the oven with controlled temperature of 120°C. Meanwhile, Ni@C is dispersed in ethanol with ultrasonic bath for 30 minutes to prevent the aggregation of Ni@C in the mixing process. SrCl₂, ENG and Ni@C are stirred and mixed together by the ultrasonic treatment for another 30 minutes. The mixture will be dried in an oven at 120°C for 48 h. Finally, the mixture is put into a vessel and pressed by a pressing machine.

In order to observe the elements distribution, the novel composite SrCl₂ is investigated by a Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (DEX), which are shown in Fig.1. Fig.1a indicates the SEM image of the sample, which illustrates the surface morphology. Fig.1b and Fig.1c show the distributions of element Cl and Ni, corresponding to the area shown in Fig.1a. It demonstrates the good uniformity of Ni@C and the salt.

Fig.1. SEM image and EDX mapping of novel composite SrCl₂ (a) SEM; (b) EDX Mapping of the element Cl ; (c) EDX Mapping of the element Ni.

where the enthalpy for the reaction between SrCl₂ and NH₃ are 41432 J·mol⁻¹[23].

Mass ratio of salt and density are usually considered to be two major factors in the development of composite sorbent. The higher density and lower mass ratio of salt are, the lower permeability and the higher thermal conductivity will become. For testing the thermal properties, density of the novel composite SrCl_2 is selected in the range of $500 \text{ kg}\cdot\text{m}^{-3}$ - $1000 \text{ kg}\cdot\text{m}^{-3}$. The mass ratio between SrCl_2 and ENG range from 50% to 83% i.e. from 1:1 to 5:1 whereas the ratio between ENG and Ni@C is adopted as 20:1[22]. Since the anisotropic characteristic of consolidated ENG matrix have already been studied[24], both plate samples and disk samples are developed for comparison as shown in Fig.2. For disk samples shown in Fig.2a, heat and mass transfer directions are parallel to the compression direction. For plate samples shown in Fig.2b, heat and mass transfer directions are perpendicular to the compression direction.

Fig.2. The rig and novel composite SrCl_2 (a) disk samples; (b) plate samples.

3. Testing method of novel composite SrCl_2

3.1. Thermal conductivity

Thermal conductivity is investigated by the Laser flash method. Fig.3 demonstrates the diagram of the testing equipment, i.e. LFA467 instrument. The testing unit is mainly composed of heater, optical filter, infrared detector, sample changer, reflector and flash lamp.

As testing temperature T is controlled by a furnace heated condition, a beam of light pulse is emitted by the laser instantaneously, which is uniformly illuminating in the sample surface. The temperature transient increases from the hot end of one-dimensional heat conduction to the cold end propagation. The temperature could be monitored by means of an infrared detector, which is calibrated by liquid nitrogen. The thermal diffusivity could be determined through the curve of temperature vs. time.

Fig.3. Schematic of thermal conductivity testing unit.

Since the width of the optical pulse is infinitely small, heat conduction of the testing sample is regarded as one-dimensional heat transfer. The semi-heating time t_{50} is evaluated by the equation 3:

$$\alpha = \frac{0.1388 \cdot d^2}{t_{50}} \quad (3)$$

where α is the thermal diffusivity ($\text{mm}^2 \cdot \text{s}^{-1}$), d is the thickness of the testing samples (mm), t_{50} is the semi-heating time (s).

$$\lambda(T) = \alpha(T) \cdot C_p(T) \cdot \rho(T) \quad (4)$$

where $\lambda(T)$ is the thermal conductivity at a testing temperature ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), $\alpha(T)$ is the thermal diffusivity ($\text{mm}^2 \cdot \text{s}^{-1}$), C_p is the specific heat ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$), $\rho(T)$ is the density of the

sample ($\text{kg}\cdot\text{m}^{-3}$). The random error of the testing equipment is less than 0.1%, and the largest relative error is 5%.

3.2. Permeability

The permeability of the samples is tested by the unit which is specially designed as shown in Fig.4. The testing unit is mainly composed of the sample chamber, pressure difference transmitter and the rotermeter. When the gas nitrogen is flowing through the sample with flow rate q_v , pressure drop Δp will be measured. To obtain the permeability K , parameters Y and X are evaluated by means of the testing data of flow rate, the outlet gas pressure and pressure drop, etc. $1/K$ is the intercept of the linear fitting line of Y and X .

Since the samples are porous materials with very low velocities, Ergun model is suitable to be applied in the measurement since there is no compressibility effects [25]. The intrinsic characteristic of the material can be expressed by the equations 5 and 6:

$$Y = BX + \frac{1}{K} \quad (5)$$

in which

$$Y = \frac{(P_{\text{in}}^2 - P_{\text{out}}^2)S}{2RT\mu m_a \Delta z}; \quad X = \frac{m_a}{\mu S}; \quad m_a = \rho A v_a \quad (6)$$

where K is the permeability of the samples (m^2), B is the shape factor, P_{in} and P_{out} are the inlet and outlet pressure of the gas nitrogen, A is the area of sample cross section (m^2), R is the gas constant ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$), T is the sample temperature (K) which doesn't various greatly, Δz is the thickness of the sample, μ and ρ are the gas viscosity ($\text{Pa}\cdot\text{s}$) and density ($\text{kg}\cdot\text{m}^{-3}$), respectively; m_a is the mass flow rate of the gas ($\text{kg}\cdot\text{s}^{-1}$), v_a is the axial velocity ($\text{m}\cdot\text{s}^{-1}$).

Fig.4. The test unit of permeability.

The error of permeability can be expressed as equation 7:

$$\left| \frac{dK}{K} \right| = \left| \frac{dY - BdX}{Y - BX} \right| \leq \left| \frac{dY}{Y - BX} \right| + \left| \frac{BdX}{Y - BX} \right| \quad (7)$$

The pressure is investigated by the environmental temperature. The differential pressure that is tested by the differential pressure meter with the error of 0.5%, and the gas mass flowrate is tested by the flow meter with the error of 4%. The average relative error of K is calculated, and the error of permeability is 5.08%.

3.3. Sorption characteristic

The sorption characteristic of the novel composite SrCl_2 is tested by the unit as shown in Fig.5. The test unit is mainly composed of a sorption reactor, a refrigerant vessel, two thermostat baths i.e. high-temperature and low-temperature thermostat baths, a pressure transmitter, three platinum resistance thermometers, a pressure sensor and several valves, etc.

The refrigerant vessel plays the role as condenser or evaporator, which is determined by the operation conditions. Temperature of sorption reactor and the refrigerant vessel are controlled by two thermostat baths. The sorption performance is investigated by testing sorption quantity and sorption rate, and the procedures are as follow:

Sorption process: Open the valves V1 and V3 in Fig.5. Keep the refrigerant vessel at a constant pressure according to the set evaporation temperature by low-temperature thermostat bath, and control the temperature of sorption reactor as environmental temperature. For each test point with predetermined refrigerant temperature and sorption temperature the fluid level in the refrigerant vessel is recorded by the smart pressure transmitter when the data doesn't change for at least 6 minutes.

Desorption process: By the similar way the reactor is heated to the constant desorption temperature whereas the refrigerant vessel is controlled at a constant pressure. Then the data of the refrigerant level in the refrigerant vessel is recorded.

The sorption quantity of composite sorbent is calculated by the refrigerant level in the vessel, which could be evaluated according to equation 8.

$$\Delta x = \frac{1}{m_{salt}} \cdot \Delta \left\{ \left(1 - \frac{v'(T_e)}{v''(T_e)} \right) \cdot \frac{A_c}{g} \cdot \Delta P \right\} \quad (8)$$

where m_{salt} is the mass of the composite $SrCl_2$ (kg), $v'(T_e)$ and $v''(T_e)$ are the specific volume of saturated liquid ammonia and saturated vapor ammonia respectively ($m^3 \cdot kg^{-1}$), A_c is the effective area of cross section of ammonia in the evaporator/condenser (m^2), g is the gravity acceleration ($9.80 m \cdot s^{-2}$), ΔP is the pressure difference for the condensation and evaporation process (Pa).

Fig.5. Test unit for the sorption performance.

The mass of the novel composite SrCl_2 is measured by the balance (BS2202S), and its measuring error is 0.01 g. The pressure difference between the liquid end and vapor end of the evaporator/condenser is measured by the smart differential pressure transmitter with the testing error of 0.2%. The relative error of sorption/desorption quantity of the novel sorbent is 0.37%, which can be calculated by equation 9.

$$\left| \frac{d\Delta x}{\Delta x} \right| \leq \left| \frac{dm_{\text{salt}}}{m_{\text{salt}}} \right| + \left[\frac{d \left((1 - \nu'(T_e)) / \nu''(T_e) \right) \cdot (A_c / g) \cdot \Delta(\Delta p)}{\Delta \left((1 - \nu'(T_e)) / \nu''(T_e) \right) \cdot (A_c / g) \cdot \Delta(\Delta p) + V / \nu''(T_e)} \right] \quad (9)$$

4. Experimental results and discussions

4.1. Thermal diffusivity

Since the samples with different densities and ratios show the similar trends with regard to thermal diffusivity, mass ratios of 50% between SrCl_2 and ENG and densities from 500 $\text{kg} \cdot \text{m}^{-3}$ to 800 $\text{kg} \cdot \text{m}^{-3}$ are selected for further elaboration, which is shown as Fig.6. Fig.6a and Fig.6b indicate the thermal diffusivity of both disk and plate samples with different testing temperature from 20°C to 100°C. It is demonstrated that the thermal diffusivity increases with the decrease of testing temperature. This is mainly because the higher temperature usually

results in the friable structure of the novel composite SrCl_2 , which leads to the larger thermal contact resistance inside. Also noting that thermal diffusivity of plate samples are almost triple higher than that of disk samples. The highest thermal diffusivity for plate and disk samples are able to reach $5.9 \text{ mm}^2\cdot\text{s}^{-1}$ and $2 \text{ mm}^2\cdot\text{s}^{-1}$, respectively when the testing temperature is 20°C . For different testing temperature, the thermal diffusivities are in the range from $1.43 \text{ mm}^2\cdot\text{s}^{-1}$ to $2 \text{ mm}^2\cdot\text{s}^{-1}$ and $4.29 \text{ mm}^2\cdot\text{s}^{-1}$ to $5.9 \text{ mm}^2\cdot\text{s}^{-1}$. Since the plate samples are consistent with the heat and mass transfer direction of the real sorption reactor[24], the rest of the paper will further investigate and analyze the plate samples.

Fig.6. Thermal diffusivity of novel composite SrCl_2 vs. different testing temperature (a) disk; (b) plate.

In order to overall analyze the thermal diffusivity, plate samples with different densities and mass ratios of salt are evaluated and compared when the temperature is selected as 20°C . Fig.7 indicates the thermal diffusivity of novel composite SrCl_2 , which range from $500 \text{ kg}\cdot\text{m}^{-3}$

to $1000 \text{ kg}\cdot\text{m}^{-3}$ and from 50% to 83%, respectively. For the mass ratios higher than 75%, the densities are developed from $600 \text{ kg}\cdot\text{m}^{-3}$ to $1000 \text{ kg}\cdot\text{m}^{-3}$. The reason is that the samples with higher ratios tend to crack for the density of $500 \text{ kg}\cdot\text{m}^{-3}$. It is demonstrated that the thermal diffusivity increases with the decrease of mass ratio of salt and the increase of the density. The highest thermal diffusivity of the novel composite SrCl_2 could reach $6.2 \text{ mm}^2\cdot\text{s}^{-1}$ with density of $1000 \text{ kg}\cdot\text{m}^{-3}$ and mass ratio of 50%. For different densities and mass ratios of salt, thermal diffusivity range from $2.2 \text{ mm}^2\cdot\text{s}^{-1}$ to $6.8 \text{ mm}^2\cdot\text{s}^{-1}$.

Fig.7. Thermal diffusivity of novel composite SrCl_2 vs. different densities and mass ratios of salt.

4.2. Thermal conductivity

According to the Laser flash measuring method, thermal conductivity of the novel composite SrCl_2 can be assessed by the equation 4, in which the specific heat can be evaluated by the equation 10. Since the ratio of the Ni@C accounts for quite a small part of the novel composite sorbent, SrCl_2 and ENG will have the major influence on the specific heat of the composite sorbent. Similar as the thermal diffusivity with 20°C testing temperature, thermal

conductivity of the novel composite SrCl_2 is investigated and compared for the densities from $500 \text{ kg}\cdot\text{m}^{-3}$ to $1000 \text{ kg}\cdot\text{m}^{-3}$ and mass ratios of salt from 50% to 83% which is shown in Fig.8. Results show that the thermal conductivity increases with the decrease of mass ratio of salt and the increase of the density. The highest thermal diffusivity of novel composite SrCl_2 could reach $4.03 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the density of $1000 \text{ kg}\cdot\text{m}^{-3}$ and mass ratio of 50%, which is about 20 times higher than that of ordinary granular SrCl_2 . For different densities and mass ratios of salt, thermal conductivity ranges from $1.06 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $4.03 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

$$C_p = \beta \cdot C_{p,\text{salt}} + \gamma \cdot C_{p,\text{ENG}} + (1 - \beta - \gamma) \cdot C_{p,\text{Ni@C}} \quad (10)$$

where β is the mass ratio of SrCl_2 with respect to the total mass of the novel composite sorbent, γ is the mass ratio of ENG with respect to the total mass.

Fig.8. Thermal conductivity of novel composite SrCl_2 vs. different densities.

4.3. Permeability

Table 1 shows the permeability of novel composite SrCl_2 with different densities and mass ratios of salt, which range from $400 \text{ kg}\cdot\text{m}^{-3}$ to $600 \text{ kg}\cdot\text{m}^{-3}$ and from 50% to 87%, respectively. It is indicated that for different samples permeability ranges from 1.31×10^{-9} to

1.07×10⁻¹³ m². Permeability increases with the decrease of density and the increase of mass ratio of salt. In order to get a comprehensive understanding of the novel composite SrCl₂, permeability of plate samples with Ni@C is compared with that SrCl₂-ENG without Ni@C, which is shown in Fig.9. It is worth noting that when the mass ratio of SrCl₂ is lower than 67%, permeability increases slightly when the mass ratio increases. For the composite SrCl₂ with ratio larger than 67%, permeability of composite sorbent increases significantly with increment of the mass ratio. In addition, for different densities and mass ratios of salt, composite SrCl₂ with Ni@C enjoys the relatively higher permeability than that without Ni@C. One remarkable fact is that the nanoparticle is conducive to the improvement of the mass transfer performance of the composite SrCl₂. The nanoparticle tends to be easier to occupy the porous structure of the composite SrCl₂ than that of pure salts, which avoid the serious swelling and agglomeration. The difference of permeability between the composite SrCl₂ with and without Ni@C increases with the decrease of the density. This is mainly because the ENG will play the leading role for the higher density of the composite sorbent since the ratio of the Ni@C is relatively small. Actually the thermal conductivity of pure Ni@C is relatively low. If the ratio of the Ni@C is increased, the thermal conductivity will be affected. The mass transfer should be further improved in the premise of heat transfer performance is desirable.

Table 1 Permeability of novel composite SrCl₂.

Ratio/Density	400	500	600
50%	1.73×10 ⁻¹²	3.85×10 ⁻¹³	1.07×10 ⁻¹³
67%	2.44×10 ⁻¹²	5.49×10 ⁻¹³	2.71×10 ⁻¹³
75%	1.81×10 ⁻¹¹	5.78×10 ⁻¹²	7.62×10 ⁻¹³
80%	2.98×10 ⁻¹⁰	3.35×10 ⁻¹¹	4.79×10 ⁻¹²
83%	1.31×10 ⁻⁹	2.62×10 ⁻¹⁰	1.14×10 ⁻¹¹

Fig.9. Permeability of the composite SrCl_2 with and without Ni@C.

4.4. Sorption characteristic

As it is discussed above, ENG and Ni@C are conducive to both heat transfer and mass transfer, which will have a promoting influence on the sorption characteristic. One of the key parameters for assessing the performance of sorption characteristic is the global conversion rate X , which represents the percentage of the composite sorbent reacting with the refrigerant[26]. In order to investigate the influence of nanoparticle on sorption kinetics, the global conversion rate of the composite SrCl_2 with and without Ni@C is compared, which is shown in Fig.10. 10°C and -10°C evaporation temperature are selected as the examples while the temperature of composite SrCl_2 is controlled by the environmental medium. It is indicated that the novel composite SrCl_2 with Ni@C has the faster sorption reaction rate than that without Ni@C. It means that by adding the Ni@C into the composite SrCl_2 -ENG, the sorption time will be reduced under the same working conditions. When the global conversion rate is

0.7, it takes 14.5 minutes for the novel composite SrCl_2 with Ni@C for the sorption process, which is 6 minutes less than that without Ni@C under the condition of 10°C evaporation temperature. For freezing condition of -10°C evaporation temperature, the improvement will be more obvious, which is up to 7.5 minutes.

Fig.10. Sorption characteristic of composite SrCl_2 with and without Ni@C .

When the global conversion rate equals to 1, it demonstrates that 1 mol of SrCl_2 reacts with 7 mol of ammonia according to equation 1. The corresponding maximum equilibrium sorption quantity is 0.752 kg of ammonia per kilogram SrCl_2 . Theoretically, the global conversion rate is bound to reach 1 in the end with sufficient reaction duration when the constraining pressure is away from the equilibrium conditions. Nonetheless, it is always difficult for global conversion rate to reach 1 with finite sorption duration for a real sorption process because the reaction rate is greatly influenced by the heat or mass transfer of the sorbent. Fig.11 indicates the global conversion rate of the novel composite SrCl_2 under the condition of the different evaporation temperature ranging from -5°C to 15°C . The

corresponding sorption reaction takes place from $\text{SrCl}_2 \cdot \text{NH}_3$ to $\text{SrCl}_2 \cdot 7\text{NH}_3$. It is noted that the global conversion rate varies significantly with the increment of the evaporation temperature, which becomes more prominent from the freezing condition to the air conditioning condition. This is mainly because the sorption quantity is mainly determined by the driving pressure difference ($P_e - P_{eq}$) between the constraining evaporation pressure (P_e) and the equilibrium pressure (P_{eq}). The higher evaporation temperature is, the larger driving pressure difference becomes, thus leading to the faster sorption reaction rate. For the sorption time of 30 minutes, the highest global conversion rate is about the 0.93 for the evaporation temperature of 15°C . The lowest global conversion rate could reach 0.7 when the evaporation temperature is -5°C .

Fig.11. Sorption characteristic of novel composite SrCl_2 vs. different evaporation temperature.

When 30 minutes is selected as the sorption time, the sorption quantity of novel composite SrCl_2 is investigated with different evaporation temperatures ranging from -15°C to 15°C . The sorption quantities of the composite SrCl_2 with Ni@C and without Ni@C are

shown in Fig.12. It is observed that with the sufficient duration or larger pressure difference, the composite sorbent is able to reach a maximum sorption quantity of $0.707 \text{ kg} \cdot \text{kg}^{-1}$, which accounts for about 97% of the maximum theoretical equilibrium value. This would be attributed to the fact that the addition of porous ENG and Ni@C can prevent the serious swelling and agglomeration of the granular SrCl_2 . Also noting that the difference of sorption quantity between composite sorbent with and without Ni@C decreases with the increase of the evaporation temperature. This is because mass transfer performance takes the leading role for the sorption quantity with the decrease of the evaporation temperature especially for the freezing condition. Compared with composite SrCl_2 without Ni@C, the novel composite SrCl_2 with Ni@C takes the advantages for the mass transfer, which improves the sorption characteristic. For different evaporation temperature, the sorption quantity of composite SrCl_2 with Ni@C range from $0.39 \text{ kg} \cdot \text{kg}^{-1}$ to $0.67 \text{ kg} \cdot \text{kg}^{-1}$, which improved by 22.2% to 5.6% when compared with that without Ni@C.

Fig.12. Sorption quantity of composite SrCl_2 with or without Ni@C vs. different evaporation temperature.

Based on the sorption characteristic of composite sorbent with and without Ni@C, the performance of sorption refrigeration will be further evaluated and compared for illustrating the improvement of the novel composite SrCl₂.

The refrigeration power is calculated according to equation 11:

$$Q_{\text{ref}} = \frac{m_{\text{salt}} \cdot \Delta x \cdot L(T_c) - m_{\text{salt}} \cdot \Delta x \cdot C_p \cdot (T_c - T_e)}{t_{\text{cycle}}} \quad (11)$$

where Q_{ref} is refrigerating power (kW), m_{salt} is the mass of composite SrCl₂ (kg), Δx is the sorption quantity of sorbent (kg·kg⁻¹), $L(T_c)$ is the latent heat of vaporization of liquid ammonia (kJ·kg⁻¹), C_p is specific heat of saturated liquid ammonia (4.7218 kJ·kg⁻¹·K⁻¹), T_c and T_e are the cooling temperature and evaporation temperature, respectively (°C), t_{cycle} is the cycle time (s).

The specific cooling power (SCP) is defined according to the equation 12:

$$SCP = \frac{Q_{\text{ref}}}{m_{\text{salt}}} \quad (12)$$

Fig.13 reveals the relation between SCP and evaporation temperature for the composite SrCl₂ with Ni@C and without Ni@C. Results indicate that SCP increases with the increment of the evaporation temperature. The highest SCP of the novel composite SrCl₂ is able to reach 254.4 W·kg⁻¹ for 15°C evaporation temperature. For different evaporation temperature, the performance of SCP range from 101.4 W·kg⁻¹ to 254.4 W·kg⁻¹. It is also demonstrated that the novel composite SrCl₂ has the better refrigeration performance than that of sorbent without Ni@C, which is mainly due to the improvement of the sorption characteristic. The largest improvement of SCP between the sorbents with and without Ni@C could reach 34.5% when the evaporation temperature is -15°C. Even the lowest improvement is still able to reach 16.1%

for 15°C evaporation temperature. It is worth noting that the novel composite SrCl_2 takes the advantage for the lower evaporation temperature. It is general admitted that sorption characteristics is influence by the heat and mass transfer performance. Heat transfer plays the leading role for air conditioning condition i.e. evaporation temperature is above 5°C. For the freezing condition, the mass transfer will take the priority. The novel composite SrCl_2 will be more suitable for the freezing conditions when compared with air conditioning condition.

Fig.13. SCP vs. evaporating temperature (cooling temperature is 30°C).

5. Conclusions

In order to analyze the overall thermo-physical properties of the novel composite SrCl_2 , heat and mass transfer properties as well as sorption characteristic with different densities and mass ratios of salt are studied. Thermal diffusivity, thermal conductivity and permeability are tested by Laser flash measured method and the principle of Ergun model, respectively. Sorption characteristic is also investigated by the unit which is specially designed. Conclusions are yielded as follows:

- [1] The thermal diffusivity increases with the decrease of testing temperature. Thermal

diffusivity of plate samples are almost triple higher than that of disk type. The highest thermal diffusivity for plate and disk samples are able to reach $5.9 \text{ mm}^2 \cdot \text{s}^{-1}$ and $2 \text{ mm}^2 \cdot \text{s}^{-1}$ respectively when the testing temperature is 20°C . For different testing temperature and densities, the thermal diffusivity range from $1.43 \text{ mm}^2 \cdot \text{s}^{-1}$ to $2 \text{ mm}^2 \cdot \text{s}^{-1}$ and $4.29 \text{ mm}^2 \cdot \text{s}^{-1}$ to $5.9 \text{ mm}^2 \cdot \text{s}^{-1}$, respectively.

[2] The thermal diffusivity and thermal conductivity increases with the decrease of mass ratio of salt and the increase of the density. The highest thermal diffusivity and thermal conductivity of composite SrCl_2 could reach $6.2 \text{ mm}^2 \cdot \text{s}^{-1}$ and $4.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is about 15 times higher than that of ordinary granular SrCl_2 . For different densities and mass ratios of salt, thermal diffusivity and thermal diffusivity range from $2.2 \text{ mm}^2 \cdot \text{s}^{-1}$ to $6.8 \text{ mm}^2 \cdot \text{s}^{-1}$ and $1.06 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $4.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively.

[3] For different samples of novel composite SrCl_2 permeability range from $1.31 \times 10^{-9} \text{ m}^2$ to $1.07 \times 10^{-13} \text{ m}^2$. Permeability increases when the density decreases and mass ratio of salt increases. For different densities and mass ratios of salt, samples with Ni@C enjoys the higher permeability than that without Ni@C.

[4] The novel composite SrCl_2 with Ni@C enjoy the faster sorption reaction rate than that without Ni@C. If the sorption time is selected as 30 minutes, the global conversion rate range from 0.7 to 0.93 when the evaporation temperature various from -15°C to 15°C . For different evaporation temperature, the sorption quantity of the novel composite SrCl_2 with Ni@C range from $0.39 \text{ kg} \cdot \text{kg}^{-1}$ to $0.67 \text{ kg} \cdot \text{kg}^{-1}$, which improved by 22.2% to 5.6% when compared with that without Ni@C.

[5] For the performance of sorption refrigeration SCP increases with the increment of the evaporation temperature. For different evaporation temperature, the performance of SCP range from 101.4 W·kg⁻¹ to 254.4 W·kg⁻¹. The novel composite SrCl₂ has the better refrigeration performance than that of sorbent without Ni@C. The largest improvement between the sorbents with and without Ni@C could reach 34.5% when the evaporation temperature is -15°C.

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