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Investigation on novel modular sorption thermal cell with improved energy charging and discharging performance

Long Jiang^{a,b}, Ruzhu Wang^{a,*}, Yiji Lu^b, Anthony Paul Roskilly^b, Liwei Wang^a, Ke Tang^b

^a Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, Shanghai, 200240, China

^b Sir Joseph Swan Centre for Energy Research, Newcastle University, Newcastle NE1 7RU, UK

Abstract: Novel composite strontium chloride is developed with expanded natural graphite and carbon coated nickel as the additives. It is indicated that expanded natural graphite and carbon coated nickel are conducive to heat and mass transfer performance, which result in improved sorption characteristic. For composite sorbents with carbon coated nickel, thermal conductivity and permeability range from $0.57 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $1.93 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and from $2.98\times 10^{-10} \text{ m}^2$ to $2.71\times 10^{-13} \text{ m}^2$. Novel composite strontium chloride with carbon coated metal enjoys the faster desorption and sorption reaction rate than that without carbon coated metal. For different evaporation temperatures, sorption quantity of novel composite strontium chloride ranges from $0.28 \text{ kg}\cdot\text{kg}^{-1}$ to $0.7 \text{ kg}\cdot\text{kg}^{-1}$. Based on testing results of sorbents with carbon coated nickel, a promising sorption thermal cell is developed and analyzed for combined cold and heat storage, which greatly enhances the versatility and working reliability. Under different working conditions, cold and heat density range from $384 \text{ kJ}\cdot\text{kg}^{-1}$ to $811 \text{ kJ}\cdot\text{kg}^{-1}$ and $549 \text{ kJ}\cdot\text{kg}^{-1}$ to $1648 \text{ kJ}\cdot\text{kg}^{-1}$. Modular sorption thermal cell could be flexible connected to sorption battery for scaling applications, which reveals great potentials for renewable energy utilization and waste heat recovery.

Keywords: Composite strontium chloride, Heat and mass transfer, Sorption characteristic, Modular sorption thermal cell

* Corresponding author. Tel. +86-21-34206548

Email: rzwang@sjtu.edu.cn (R.Z. Wang)

24 Nomenclature

A	Area of ammonia vessel (m^2)
Al@C	Carbon coated aluminum
C	Specific heat ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)
CD	Cold density ($\text{kJ}\cdot\text{kg}^{-1}$)
ENG	Expanded natural graphite
g	Gravity acceleration ($9.80 \text{ m}\cdot\text{s}^{-2}$)
HD	Heat density ($\text{kJ}\cdot\text{kg}^{-1}$)
m	Mass of composite sorbent (kg)
NH_3	Ammonia
Ni@C	Carbon coated nickel
P	Pressure (Pa)
PCM	Phase change material
PD	Power density ($\text{W}\cdot\text{kg}^{-1}$)
SrCl_2	Strontium chloride
STES	Sorption thermal energy storage
T	Temperature ($^{\circ}\text{C}$)
TES	Thermal energy storage
t	Time (s)
x	Sorption quantity ($\text{kg}\cdot\text{kg}^{-1}$)

25 Greek letters

v'	Specific volume of saturated liquid ammonia ($\text{m}^3\cdot\text{kg}^{-1}$)
v''	Specific volume of saturated vapor ammonia ($\text{m}^3\cdot\text{kg}^{-1}$)

26 Subscripts

c	Cold
eva	Evaporation
eq	Equilibrium
h	Heat

in	Input
out	Output
R	Reaction
SrCl_2	Strontium chloride
Sorb	Sorbent

1. Introduction

It is widely recognized that thermal energy storage (TES) plays an essential role in achieving efficient utilization of renewable energy[1] and industrial waste heat[2]. Advanced TES technology can improve operating flexibility and reliability to overcome the drawbacks of time discrepancy, distance discrepancy and instability of different heat sources by adjusting mismatch between energy supply and demand[3].

As for present states, TES could be generally classified into three aspects, i.e. sensible heat energy storage, latent heat energy storage by using phase change material(PCM), and thermochemical energy storage[4]. Among them, an urgent challenge lies in low energy storage density for renewable energy utilization e.g. solar energy due to the fact that energy varies with time and place[5]. Consequently, it is desirable to realize efficient seasonal solar TES[6]. Present mature solar TES product is solar hot water tank, which suffers the disadvantages of unsteady working temperature and large system volume. PCM is also not suitable for seasonal energy storage because it could take the risk of releasing the heat in advance, which results in large heat losses during the storage duration[7]. Therefore, thermochemical energy storage is expected to have the better energy storage performance.

As a major thermochemical process, sorption process has been extensively investigated in term of refrigeration[8] and heat pump[9]. For sorption refrigeration cooling power is supplied by evaporation latent heat of the refrigerant. Nonetheless, specific sorption heat is usually higher than specific evaporation latent heat. Thus sorption process is more suitable for TES with larger energy output[10]. Heat could be stored in the form of chemical potential, which leads to higher energy density than that of sensible and latent heat storage[11]. Besides, sorption thermal energy storage (STES) has two other distinguished traits which are superior to that of other TES forms. One is that discharge temperature can be flexibly adjusted to satisfy demands of end users by changing working pressure due to its monovariant characteristics of sorption working pairs[12]. The other is that STES has different multiple working modes i.e. direct heat supply[13], cold and heat cogeneration to supply useful cold and

heat simultaneously[14] as well as energy upgrade to improve the quality of low grade heat[15]. Recently, a novel phrase of sorption thermal battery is proposed to discriminate the difference between STES and other energy storage technologies[16]. Concept of sorption thermal battery is analogous to electric battery. Temperature difference and heat provided by thermal battery is similar as voltage difference and current supplied by electric battery[17]. In fact, electrical battery is composed of several cells for easy connection. Similarly, sorption thermal battery should also be composed of sorption thermal cells. This modular unit is required to be designed and defined properly, which will be flexible to be combined for scaling applications. Also for electric cells, charging and discharging rate are considered as key parameters. With regard to sorption thermal cell, heat charging and discharging rate should be also taken into account, which are much relevant with heat and mass transfer performance and sorption kinetics. Granular salts usually have poor heat and mass transfer performance due to swelling and agglomeration phenomena, which will greatly reduce the sorption and desorption rate[18]. Composite sorbent with various matrix is a common solution to overcome the drawbacks of granular salts by improving thermal conductivity[19] and permeability[20]. Expanded natural graphite (ENG) have proved to be conducive to heat transfer performance with limited improvement for mass transfer. Recently nanoparticles such as carbon coated metal have attempted to be an additive for composite sorbent, which is expected to have a desirable heat and mass transfer performance[21].

This paper aims to present and evaluate modular sorption thermal cell with improved heat charging and discharging performance, which will be a potential solution to solar energy storage. The innovative contributions lie in three aspects as follows: First, modular sorption thermal cell is defined and designed properly. Different from STES and thermal battery, layout of modular sorption thermal cell is transformed into vertical arrangement, which will be more conducive to condensation and evaporation of the refrigerant. Also worth noting that novel composite sorbent is developed. ENG is selected for better heat transfer whereas carbon coated nickel (Ni@C) is used for enhanced mass transfer, which will be more conducive to sorption and desorption characteristics. Eventually, modular thermal cell with improved energy storage performance will be further investigated and analyzed for combined cold and heat storage based on the properties of novel composite sorbent. Different combinations of modular sorption thermal cell will be provided for different applications.

2. Development of novel composite sorbent

Compared with conventional sorbents, novelty of composite strontium chloride (SrCl_2) is to add the nanoparticle i.e. Ni@C into the sorbent with ENG. Thermochemical reaction process of SrCl_2 with ammonia can be according to equations 1-2. The development of novel composite SrCl_2 can be referred to the references[22]. ENG is firstly 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 aggregation in the mixing process. SrCl_2 , ENG and Ni@C are stirred and mixed by ultrasonic treatment for another 30 minutes. The mixture will be dried in an oven at 120°C for two days. Eventually, the mixture is pressed into a vessel by a pressing machine for testing. In order to observe elements distribution, novel composite SrCl_2 is investigated by Energy Dispersive X-ray spectroscopy (DEX) as shown in Fig.1. It indicates even distribution of element Ni and Cl, which illustrates the uniformity of Ni@C and SrCl_2 .

where reaction enthalpy between SrCl_2 and NH_3 is $41432 \text{ J} \cdot \text{mol}^{-1}$ [22].

Fig.1. EDX mapping of novel composite SrCl_2 with Ni@C .

It is acknowledged that density and mass ratio of salt are significant for the development of composite sorbent. The higher density and lower mass ratio are, the lower permeability and higher thermal conductivity will become. For testing thermal properties, density of novel composite SrCl_2 is selected in the range from $500 \text{ kg} \cdot \text{m}^{-3}$ to 600

kg·m⁻³. Mass ratio between SrCl₂ and ENG ranges 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[21]. Since anisotropic characteristics of consolidated ENG have already been investigated[23], only plate samples are developed for optimal performance, i.e. heat and mass transfer direction is perpendicular to compression direction.

2.1. Thermal conductivity and permeability of novel composite strontium chloride

For testing thermal conductivity of novel composite SrCl₂, laser flash measuring method is adopted, and testing details can be referred to the reference[24]. Thermal conductivity of novel composite SrCl₂ is investigated and compared for densities from 500 kg·m⁻³ to 600 kg·m⁻³ and mass ratios of salt from 50% to 83%, which is shown in Table 1. Difference matrix i.e. ENG, Ni@C and carbon coated aluminum (Al@C) are evaluated and compared in term of different composite sorbents. Heat and mass transfer performance of sorbents with Al@C is introduced which can be referred to our previous work[25]. It is worth noting that pure Ni@C and Al@C have relatively low thermal conductivity which are no more than 0.23 W·m⁻¹·K⁻¹. Comparably, ENG is able to reach 2.89 W·m⁻¹·K⁻¹ when the density is 600 kg·m⁻³. For novel composite SrCl₂ with Ni@C, thermal conductivity increases with the decrease of mass ratio of salt and the increase of density. The highest thermal conductivity could reach 1.93 W·m⁻¹·K⁻¹ for the density of 600 kg·m⁻³, which is about 10 times higher than that of ordinary granular SrCl₂. For different densities and mass ratios of salt, thermal conductivity ranges from 0.57 W·m⁻¹·K⁻¹ to 1.93 W·m⁻¹·K⁻¹. For different composite sorbents, composite SrCl₂ with ENG shows the best result, which indicates that carbon coated metal is not conducive to thermal conductivity. Since pure Al@C has the higher thermal conductivity and lower density than Ni@C, composite sorbents with Al@C show higher values than that with Ni@C. One remarkable fact is that ENG takes a leading role in heat transfer enhancement. Carbon coated metal is expected to improve mass transfer based on composite sorbent with ENG.

Table 1. Thermal conductivity of novel composite SrCl₂.

Matrix	Density /ratio	Thermal conductivity (W·m ⁻¹ ·K ⁻¹)	Composite sorbents	Thermal conductivity (W·m ⁻¹ ·K ⁻¹)				
				50%	67%	75%	80%	83%
Ni@C	500	0.08	SrCl ₂ -ENG-Ni@C	1.52	1.2	1.05	0.81	0.57
	600	0.1		1.93	1.64	1.4	1.06	0.74
Al@C	500	0.17	SrCl ₂ -ENG-Al@C	1.64	1.28	1.12	0.82	0.58
	600	0.23		2.02	1.71	1.46	1.07	0.75
ENG	500	2.56	SrCl ₂ -ENG	1.73	1.49	1.18	1.01	0.95
	600	2.89		2.06	1.75	1.48	1.23	1.03

Permeability of different composite sorbents is tested by the unit which is specially designed. Since there is no compressibility effects, Ergun model is applied for the measurement [26]. Permeability of sorbents with different matrix is also investigated and compared when densities and mass ratios of salt range from 400 kg·m⁻³ to 600 kg·m⁻³ and from 50% to 87%, respectively. As shown in Table 2, for different composite sorbents permeability ranges from 2.98×10⁻¹⁰ m² to 2×10⁻¹³ m². Permeability increases with the decrease of density and the increase of mass ratio of salt. It is indicated that sorbents with carbon coated metal enjoy the higher permeability than that without carbon coated metal. The nanoparticle proves to be conducive to mass transfer since it tends to be easier to occupy the porous structure of composite SrCl₂ than that of pure salts, which avoids serious swelling and agglomeration. It is worth noting that mass transfer should be further improved in the premise of desirable heat transfer performance. Novel composite sorbent demonstrates improved heat and mass transfer performance when mass ratio of carbon coated metal is lower than 10%, which will have the positive influence on sorption and desorption characteristic.

Table 2. Permeability of novel composite SrCl₂.

Type of sorbent	Ratio/Density	400	500	600
SrCl ₂ -ENG-Ni@C	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
SrCl ₂ -ENG- Al@C	67%	2.14×10 ⁻¹²	5.23×10 ⁻¹³	2.01×10 ⁻¹³
	75%	1.51×10 ⁻¹¹	5.1×10 ⁻¹²	7.12×10 ⁻¹³
	80%	2.98×10 ⁻¹⁰	3.16×10 ⁻¹¹	4.29×10 ⁻¹²
SrCl ₂ -ENG	67%	1.72×10 ⁻¹²	4.83×10 ⁻¹³	2×10 ⁻¹³
	75%	1.31×10 ⁻¹¹	4.41×10 ⁻¹²	6.86×10 ⁻¹³
	80%	2.46×10 ⁻¹⁰	2.26×10 ⁻¹¹	3.69×10 ⁻¹²

Thermal conductivity is investigated by LFA467 instrument. The random error of the testing equipment is less than 0.1%, and the largest relative error of thermal conductivity is 5%. With respect to permeability, the largest

relative error is 5.08%.

2.2. Sorption characteristic

Sorption characteristic of novel composite SrCl_2 is investigated by testing rig as shown in Fig.2. Testing rig is mainly composed of a sorption reactor, a refrigerant vessel, two thermostat baths i.e. high temperature and low temperature thermostat baths, a differential pressure transmitter, three platinum resistance thermometers, a pressure sensor and several valves, etc. Refrigerant vessel plays a role as condenser or evaporator, which is determined by operation conditions. Temperatures of sorption reactor and refrigerant vessel are controlled by two thermostat baths. Sorption performance i.e. sorption quantity and sorption rate are evaluated, and testing procedures are as follow:

Sorption process: open valves V1 and V3. Keep the refrigerant vessel at a constant pressure according to set evaporation temperature by low-temperature thermostat bath, and control the temperature of sorption reactor as environmental temperature. For each testing point with predetermined refrigerant temperature and sorption temperature, fluid level in the refrigerant vessel is recorded by the smart differential pressure transmitter.

Desorption process: sorption reactor is heated to the constant desorption temperature whereas the refrigerant vessel is controlled at a constant pressure. Then data of the liquid level in the refrigerant vessel is recorded. The sorption and desorption quantity of composite SrCl_2 are calculated by the liquid level in the vessel, which could be according to equation 3.

$$\Delta x = \frac{1}{m_{\text{salt}}} \cdot \Delta \left\{ \left(1 - \frac{v'(T_e)}{v''(T_e)} \right) \cdot \frac{A_c}{g} \cdot \Delta P \right\} \quad (3)$$

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

Mass of novel composite SrCl_2 is measured by the balance (BS2202S) with measuring error of 0.01 g.

Pressure difference between liquid end and vapor end of evaporator/condenser is measured by smart differential pressure transmitter with testing error of 0.2%. The largest relative error of sorption quantity of novel composite SrCl_2 is 0.37%, which can be calculated according to equation 4.

$$\left| \frac{d\Delta x}{\Delta x} \right| \leq \left| \frac{dm_{\text{salt}}}{m_{\text{salt}}} \right| + \left[\frac{d\left((1 - \nu'(T_e) / \nu''(T_e)) \cdot (A_c / g) \cdot \Delta(\Delta p) \right)}{\Delta\left((1 - \nu'(T_e) / \nu''(T_e)) \cdot (A_c / g) \cdot \Delta(\Delta p) + V / \nu''(T_e) \right)} \right] \quad (4)$$

Fig.2. Sorption performance testing rig.

Global conversion rate is defined as the percentage of composite sorbent that reacted with the refrigerant, which is significant to assess the working performance of working pairs[27]. In order to investigate the influence of carbon coated metal on sorption and desorption characteristics, global conversion rate X of composite SrCl_2 with different matrix is evaluated and compared, which is shown in Fig.3. 180°C desorption temperature is exemplified for desorption process in Fig.3a whereas 10°C evaporation temperature is chosen for sorption process in Fig.3b. It is demonstrated that novel composite SrCl_2 with Ni@C and Al@C generally enjoy the faster desorption and sorption rate than that with ENG, which reveal that desorption and sorption time will be reduced by adding carbon coated metal into composite SrCl_2 with ENG. Also composite sorbent with Ni@C and Al@C show the similar performance in the desorption process. Comparably, sorbent with Ni@C shows the better

performance than that with Al@C in the sorption process. This is mainly because sorption process with small pressure driven potential is more dependent on mass transfer performance whereas desorption process is more related with heat transfer. When the reaction proceeds 70% of desorption process i.e. global conversion rate is 0.3, it takes about 8.1 minutes for novel composite SrCl₂ with Ni@C and Al@C, which is about 1.7 minutes less than that without carbon coated metal. Similarly when global conversion rate is 0.7 in the sorption process, it takes 15.5 minutes and 17.9 minutes for novel composite SrCl₂ with Ni@C and Al@C, which are 5.5 minutes and 3.1 minutes less than that with ENG under the condition of 10°C evaporation temperature.

Fig.3. Desorption/sorption characteristic of composite SrCl₂ (a) desorption process; (b) sorption process.

Since composite sorbent with Ni@C shows the best sorption and desorption rate, the rest of paper will be focus on the improved performance between the sorbent with Ni@C and without Ni@C, which has the larger improvement between the sorbent with Al@C and without Al@C. Fig.4 indicates global conversion rate and sorption quantity of composite SrCl₂ under the condition of different evaporation temperatures ranging from -30°C to 20°C when sorption process undergoes for 30 minutes. When global conversion rate equals to 1, the corresponding maximum equilibrium sorption quantity of composite SrCl₂ is 0.752 kg·kg⁻¹. Theoretical global

conversion rate is eventually bound to be 1 with sufficient sorption duration when the constraining temperature/pressure keeps away from equilibrium condition. For real sorption process, it is difficult for global conversion rate to reach 1 with limited duration because sorption rate is remarkably influenced by limited heat or mass transfer performance. It is indicated that composite SrCl_2 could reach a maximum sorption quantity of $0.707 \text{ kg} \cdot \text{kg}^{-1}$ within 2 hours, which accounts for about 97% of the maximum theoretical value. This is attributed to the fact that ENG and Ni@C improves heat and mass transfer performance, thus preventing swelling and agglomeration of granular SrCl_2 . Also worth noting that sorption quantity difference between composite sorbent with and without Ni@C increases with the decrease of evaporation temperature. This is mainly because sorption quantity is more sensitive to mass transfer with the decrease of evaporation temperature. For different evaporation temperatures, sorption quantity of composite SrCl_2 with Ni@C ranges from $0.28 \text{ kg} \cdot \text{kg}^{-1}$ to $0.7 \text{ kg} \cdot \text{kg}^{-1}$, which is improved by 33.3% to 4.5% when compared with that without Ni@C .

Fig.4. Sorption characteristic of composite SrCl_2 with or without Ni@C vs. different evaporation temperatures

(a) global conversion rate; (b) sorption quantity.

3. Modular sorption thermal cell

Fig.5 indicates the concept of modular sorption thermal cell. Different from conventional STES, modular sorption thermal cell integrates sorption reactor, condenser and evaporator into one sorption tank, which is arranged as up and down structure. To avoid heat loss between sorption reactor and liquid tank, insulation layer is adopted between them, and two apparatus are connected with a mass channel and a valve. Under this scenario, liquid tank acts condenser and evaporator alternately, which is determined by working modes in the charging and discharging process. For the charging process, sorption reactor is heated by external low grade heat such as industrial waste heat or solar energy. Refrigerant is desorbed from sorption reactor to liquid tank, and then condensed by releasing its condensation heat to environmental heat sink. Since liquid tank lies in the up side, it will be conducive to condensation process. After the charging process, the valve between sorption reactor and liquid tank will be closed to separate the sorbent and refrigerant. Thermal energy will be stored and transformed to chemical potential. Once cold and heat demands are required, the valve between sorption reactor and liquid tank is opened again. For the discharging process, liquid tank will be cooled to evaporation temperature, and the refrigerant will be evaporated and flow into sorption reactor. Liquid tank lies in the down side, which will be conducive to evaporation process. Sorption heat released by the sorbent will provide useful heat for end user. Simultaneously, evaporation heat of the refrigerant will supply useful cold. It is quite flexible for modular sorption thermal cell to supply cold and heat separately or combined cold and heat for end user since evaporation heat and sorption heat could supply cold a relatively low temperature and heat at a high temperature.

Fig.5. Concept of modular sorption thermal cell (a) charging process; (b) discharging process.

3.1. Schematic diagram of modular sorption thermal cell

For modular sorption thermal cell, various working pairs could be selected i.e. physical working pairs such as silica gel-water, activated carbon-ammonia, and chemical working pairs such as chloride-ammonia. Chemical working pair of chloride-ammonia will be selected for further illustration. For chemical working pair, working pressure is determined by working temperature, which can be according to Clapeyron equation 5. Due to the monovariant characteristic, sorption thermal cell could be easily adapted to external conditions. The general P - T diagram of sorption thermal cell is shown in Fig.6. For the charging process, the sorbent will be heated from point D to point A. Ammonia will be desorbed and flow into liquid tank. Desorption process will proceed from point A to point B. In this process, thermal energy is converted into chemical potential by breaking the binding force between chloride and ammonia. The higher temperature difference is, the faster desorption rate will become. For the discharging process, evaporator is cooled to evaporation temperature at point C whereas sorption reactor is cooled to point D. In this case, heat output temperature is much lower than heat input temperature in the charging process. Ammonia will be evaporated and sorbed by sorption reactor. Sorption process will proceed from point C to point D. In this process, chemisorption potential is converted into thermal energy in the form of evaporation latent heat and sorption heat. The stable cold and heat output could be obtained by controlling the temperature of sorption reactor and liquid tank. Working mode of cold and heat cogeneration is very suitable for long-term cold and heat storage since it demonstrates a good match between energy supply and demand.

$$\ln(P_{eq}) = -\frac{\Delta H_R}{RT_{eq}} + \frac{\Delta S}{R} \quad (5)$$

Fig.6. P - T diagram of modular sorption thermal cell for cold and heat cogeneration.

In order to evaluate flexible modes of modular sorption thermal cell, $\text{SrCl}_2\text{-NH}_3$ working pair is analyzed as shown in Fig.7. As Fig.7a shows, different temperatures are investigated for elaborating different working modes, i.e. direct heat supply as well as cold and heat cogeneration. In the charging process, SrCl_2 is heated by low grade heat with input temperature of 96°C . Ammonia will be desorbed and condensed with condensation pressure of 1.15 MPa by releasing condensation heat to heat sink at 30°C . In the discharging process, liquid tank will be connected to sorption reactor again. Sorption heat released by SrCl_2 can supply heat for end user and evaporation heat of ammonia could supply cold. For direct heat supply mode, heat could be produced at output temperature of 87°C when evaporation temperature is 20°C . For cold and heat cogeneration, heat could be supplied at temperature of 78°C when evaporation temperature is obtained at 10°C for air conditioning condition. Cold could also be supplied in freezing condition or even deep freezing condition ranging from -10°C to -30°C whereas heat output temperature ranges from 42°C to 60°C . Thus, sorption thermal cell has the distinct capability of supplying cold and heat with different output temperatures in the discharging process. To have a comprehensive understanding of different working modes, Fig.7b indicates working range of cold and heat equilibrium temperatures which is according to P - T diagram as shown in Fig7a. Due to the monovariant characteristic of sorption process, a cold

output equilibrium temperature corresponds with a heat output equilibrium temperature. It is worth noting that theoretical heat output temperature varies from 42°C to 87°C when equilibrium cold output temperature ranges from -30°C to 20°C.

(a)

(b)

Fig.7. Schematic diagram of modular sorption thermal cell for cold and heat cogeneration by using $\text{SrCl}_2\text{-NH}_3$

(a) P - T diagram; (b) working range.

3.2. Evaluation of modular sorption thermal cell

Heat output of modular sorption thermal cell in the discharging process can be expressed as equation 6:

$$Q_{h,out} = Q_R \pm Q_{\text{reactor}} \quad (6)$$

where Q_R is reaction heat, Q_{reactor} is sensible heat consumed by sorption reactor which includes sensible heat of composite sorbent and metal part of sorption reactor.

Cold output of sorption thermal cell in the discharging process could be expressed as equation 7:

$$Q_{c,out} = Q_{\text{eva}} - Q_{\text{evaporator}} \quad (7)$$

where Q_{eva} is evaporation heat of ammonia, $Q_{\text{evaporator}}$ is sensible heat consumed by evaporator when it is cooled from environmental temperature to evaporation temperature, which includes sensible heat of ammonia and metal part of evaporator.

Energy storage density, which is defined as the amount of energy output based on the mass of sorbent, is used to assess the performance of sorption thermal cell for combined cold and heat storage. Cold and heat density are expressed as equations 8 and 9.

Cold density for cold output:

$$CD = \frac{Q_{c,out}}{M_{\text{sorb}}} \quad (8)$$

Heat density for heat output:

$$HD = \frac{Q_{h,out}}{M_{\text{sorb}}} \quad (9)$$

where M_{sorb} is the mass of novel composite SrCl_2 .

Power density, which is defined as the amount of power output based on the mass of sorbent, is also used to evaluate the performance of sorption thermal cell for combined cold and heat storage. Cold and heat power density are expressed as equations 10 and 11.

Cold power density for cold output:

$$PD_c = \frac{Q_{c,out}}{t_s \cdot M_{\text{sorb}}} \quad (10)$$

Heat power density for heat output:

$$PD_h = \frac{Q_{h,out}}{t_s \cdot M_{sorb}} \quad (11)$$

where t_s is sorption time.

3.3. Performance analysis

Based on properties of composite $SrCl_2$, performance of modular sorption thermal cell is analyzed and compared. For evaluating energy storage density and energy power density, sensible heat will not be considered due to the fact that sensible heat will play different roles for different working conditions. Sensible heat could be utilized for short term energy storage whereas it cannot be used for long term or seasonal energy storage. Comparably, sorption heat will be relatively stable for both short term and long term energy storage.

Since different evaporation temperatures demonstrate similar trends, 10°C evaporation temperature is selected to illustrate energy density of composite $SrCl_2$ with and without $Ni@C$, which is shown in Fig.8. It is worth noting that both cold and heat density increase with the increase of sorption time. The highest cold and heat density could reach 1079 $kJ \cdot kg^{-1}$ and 1611 $kJ \cdot kg^{-1}$, respectively when sorption time is 30 minutes. For different sorption times ranging from 5 minutes to 30 minutes, cold and heat density of novel composite $SrCl_2$ with $Ni@C$ range from 490 $kJ \cdot kg^{-1}$ to 1079 $kJ \cdot kg^{-1}$ and 732 $kJ \cdot kg^{-1}$ to 1611 $kJ \cdot kg^{-1}$, which are improved up to 51.3% when compared with that without $Ni@C$. It is demonstrated that heat density is relatively higher than cold density under the same working condition. This is mainly because that heat output is provided by sorption heat which is much higher than evaporation latent heat for cold output. Also worth noting that sorption process is more suitable for TES than refrigeration. When sorption time is selected as 30 minutes, cold and heat density are evaluated with different evaporation temperatures as shown in Fig.9. Considering different evaporation temperatures, working conditions could be classified into air conditioning condition and freezing condition. Cold and heat density increase more

obviously in freezing condition than in air conditioning condition. For different evaporation temperatures, cold and heat density range from 384 $\text{kJ}\cdot\text{kg}^{-1}$ to 811 $\text{kJ}\cdot\text{kg}^{-1}$ and 549 $\text{kJ}\cdot\text{kg}^{-1}$ to 1648 $\text{kJ}\cdot\text{kg}^{-1}$.

Fig.8. Energy storage density of modular sorption thermal cell vs. different sorption times (a) cold density; (b) heat density.

Fig.9. Energy storage density of modular sorption thermal cell vs. different evaporation temperatures (a) cold density; (b) heat density.

Fig.10 indicates cold and heat power density of modular sorption thermal cell at different evaporation

temperatures by using composite SrCl_2 with and without Ni@C . Results indicate that cold and heat power density increase with the increase of evaporation temperature which are similar with cold and heat density. For different evaporation temperatures, cold and heat power density of novel composite SrCl_2 range from $215 \text{ W}\cdot\text{kg}^{-1}$ to $450 \text{ W}\cdot\text{kg}^{-1}$ and $407 \text{ W}\cdot\text{kg}^{-1}$ to $966 \text{ W}\cdot\text{kg}^{-1}$, respectively, which are greatly improved when compared with that without Ni@C . Due to the better heat and mass transfer performance of novel composite sorbent, the faster sorption rate will be obtained, which leads to the higher cold and heat power density of modular sorption thermal cell.

Fig.10. Energy power density of modular sorption thermal cell vs. different evaporation temperatures (a) cold power density; (b) heat power density.

3.4. Integrated applications

As series and parallel connections of electric cell are able to be utilized for different electrical applications, similar scenarios are suitable for modular sorption thermal cell since it is compared to electric cell. As for series connections of electric cell, voltage will be accumulated. Likewise, temperature difference will be increased through series connections of modular sorption thermal cell. Fig.11 indicates the concept of serious connections for modular sorption thermal cell. Different sorbents with gradient equilibrium reaction temperature will be used

in different modular sorption thermal cell. The inlet and outlet of each sorption reactor and liquid tank will be connected in turn. For the charging process, heat source with the higher temperature will drive the sorbent from the highest equilibrium temperature to the lowest temperature, which indicates the better adjustment for heat source. For the discharging process, the larger cold and heat temperature slide could be obtained. For cold and heat output, heat will be promoted into a higher temperature utilization whereas cold could be supplied with deep freezing temperature. With respect to parallel connections of electric cell, current will be boosted. Likewise, input and output thermal energy will be increased with the certain temperature difference through parallel connections of modular sorption thermal cell. Fig.12 indicates the concept of parallel connections for modular sorption thermal cell. All the inlets of liquid tank and reactor are connected, and so are the outlets. The sorbent with the same equilibrium reaction temperature will be selected. The cold and heat output will be controlled with the increment of modular sorption thermal cell, which will also avoid the possibility of pressure vessel for ammonia systems.

Fig.11. Series connections of modular sorption thermal cell (a) charging process; (b) discharging process.

Fig.12. Parallel connections of modular sorption thermal cell (a) charging process; (b) discharging process.

4. Conclusions

Novel modular sorption thermal cell is presented and evaluated with improved energy storage performance by using novel composite SrCl_2 with carbon coated metal. Various matrix i.e. Ni@C , Al@C and ENG are adopted for investigating and comparing heat and mass transfer performance as well as sorption characteristic of novel composite sorbents. Conclusions are yielded as follows:

[1] ENG takes a leading role of heat transfer enhancement whereas carbon coated metal is selected for mass transfer improvement. Thermal conductivity increases with the decrease of mass ratio of salt and the increase of the density while permeability shows the reverse trend. The highest thermal conductivity of novel composite SrCl_2 with Ni@C could reach $1.93 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for the density of $600 \text{ kg} \cdot \text{m}^{-3}$, which is about 10 times higher than that of granular SrCl_2 . For different densities and mass ratios of salt, thermal conductivity and permeability of sorbents with Ni@C range from $0.57 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $1.93 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and from $2.98 \times 10^{-10} \text{ m}^2$ to $2.71 \times 10^{-13} \text{ m}^2$.

[2] Novel composite SrCl_2 with Ni@C and Al@C generally enjoy the faster desorption and sorption rate than that with ENG, which reveal that desorption and sorption time will be reduced by adding carbon coated metal. When the reaction proceeds 70% of desorption process, it takes about 8.1 minutes for

novel composite SrCl_2 with Ni@C and Al@C , which is about 1.7 minutes less than that without carbon coated metal. Similarly when global conversion rate is 0.7 in the sorption process, it takes 15.5 minutes and 17.9 minutes for novel composite SrCl_2 with Ni@C and Al@C , which are 5.5 minutes and 3.1 minutes less than that with ENG under the condition of 10°C evaporation temperature. For different evaporation temperatures, sorption quantity of novel composite SrCl_2 ranges from $0.28 \text{ kg}\cdot\text{kg}^{-1}$ to $0.7 \text{ kg}\cdot\text{kg}^{-1}$, which is improved by 33.3% to 4.5% when compared with that without Ni@C .

[3] Based on better sorption and desorption characteristics of novel sorbent with Ni@C , performance of sorption thermal cell is also improved. For different sorption times ranging from 5 minutes to 30 minutes, cold and heat density increase from $490 \text{ kJ}\cdot\text{kg}^{-1}$ to $1079 \text{ kJ}\cdot\text{kg}^{-1}$ and $732 \text{ kJ}\cdot\text{kg}^{-1}$ to $1611 \text{ kJ}\cdot\text{kg}^{-1}$, which are improved up to 51.3% when compared with that without Ni@C . For different evaporation temperatures, cold and heat density of novel composite SrCl_2 range from $384 \text{ kJ}\cdot\text{kg}^{-1}$ to $811 \text{ kJ}\cdot\text{kg}^{-1}$ and $549 \text{ kJ}\cdot\text{kg}^{-1}$ to $1648 \text{ kJ}\cdot\text{kg}^{-1}$. Cold and heat power density range from $215 \text{ W}\cdot\text{kg}^{-1}$ to $450 \text{ W}\cdot\text{kg}^{-1}$ and $407 \text{ W}\cdot\text{kg}^{-1}$ to $966 \text{ W}\cdot\text{kg}^{-1}$, respectively.

[4] Modular sorption thermal cell could be flexible connected to battery for different scaling applications. Series connections of modular sorption thermal cell will be conducive to the adjustment for heat source. The larger cold and heat temperature slide could be obtained. For parallel connections, quantity of cold and heat output will be increased with the increment of modular sorption thermal cell.

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