ENHANCEMENT OF THE CHEMISORPTION REFRIGERATION BY NOVEL SORBENTS USING CARBON COATED NI AND FE

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ABSTRACT

This paper experimentally investigates the chemisorption refrigeration technology, mixing carbon-coated Nickel and Iron (Ni@C and Fe@C) with the conventional composite of $MnCl_2$-EG as the sorbents. A modified manufacture methodology is developed and reported. The thermal conductivity is improved by the nanomaterials with a maximum increase of 3.0 %, and adsorption and desorption are accelerated as well. SCP of the sorbents is enhanced up to 11.02 %, indicating the enhancement of the low-grade heat conversing into the cooling power, by the application of MnCl2-EG-Ni/Al@C chemisorption.

Keywords: $MnCl_2$-EG-Ni@C, $MnCl_2$-EG-Fe@C, ammonia, chemisorption refrigeration

1. INTRODUCTION

Low-grade thermal energies, such as solar energy and industrial waste heat, attract growing research interests as the substitutions for the conventional fuels. Using low-grade heat, chemisorption technologies are promising to produce the cooling, store the energy, or pump the heat grade.

Therefore, many studies were done to improve the sorption performance from various perspectives. Y. Lu et al. applied the mass and heat recovery process on a novel resorption cogeneration with the improvement of coefficient of performance (COP) up to 38 % [1]. Later, he proposed a dual-source chemisorption system to recovery dual heat sources [2]. The bottom part of the system using $SrCl_2$ achieved the highest thermal efficiency of 11 %. C. Corgnale et al. examined a heat exchanger with innovative honeycomb fins to accelerate the desorption rate [3]. Y. Wang et al. adopted a micro vacuum pump into a solar adsorption refrigeration system to enhance the mass transfer and showed an improved average COP of 35.9 % [4]. K. Ndiaye et al. compared two prototypes of low temperature energy storage and found an increase of the heat storage from 44 % to 71 % by substituting the metal tube with PVC tube [5]. Organic Rankine cycle (ORC) was once combined with solid sorption technology to be used to recovery the waste heat of a medium-duty diesel engine, and the overall energy efficiency was enhanced from 40 % to 47 % [6]. Different from the mentioned improvements of the reactor or the system structure, enhancement was made to modify the sorbent as well. J. Jing et al. proposed a self-activation method via thermally preheating CaO/Ca_3Al_2O to achieve the higher sorption capacity [7]. P. Jimenez used natural minerals to disperse nanoparticles coating the sorbent grains and enabled the resistance to pore-plugging and sintering [8]. In previous study, expanded graphite (EG), with a stable structure and high bulk heat conductivity, formed the composite sorbent with improved heat transfer [9]. Low-temperature salt (LTS) composite Strontium Chloride ($SrCl_2$) - EG added Ni@C and found a reduction of the sorption time [10].

In this paper, the sorption performance is experimentally investigated and analysed with the detected thermal properties of high-temperature salt (HTS) composite Manganese Chloride-Expanded Graphite ($MnCl_2$-EG) with Ni@C and Fe@C. Specific cooling power (COP) of the sorbent is calculated to compare the refrigeration characteristics.

2. METHEDOLOGIES

2.1 Manufacturing of MnCl₂-EG-0/Ni/Fe@C

For the improvement of the homogenous property, some modifications are made by the authors to the routine procedures, as shown in Fig 1. An extra ultrasonic bath is added to vibrate and smash the tiny conglomerate of the nanoparticles in the ethanol. Another ultrasonic treatment after adding EG is for the more evenly distributed Ni/Fe@C between the EG layers or on its surface, as this process is more superior for micro-mixing compared with mixing by hand or stirrer. One reason using the ethanol as the media is that the density of this organic fluid is smaller than water, enabling a lower resistance effect on the physical movements. Moreover, it is very easy to volatile without any residue at the room temperature. Nevertheless, water is still needed for the salt to be solved.
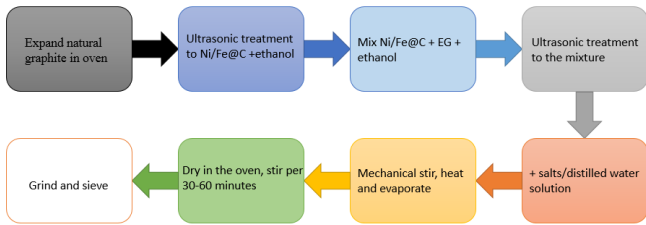

Fig 1 Upgraded manufacturing method

2.2 Tests of the thermal properties

Heat transfer is one of the essential factors affecting sorbent performance. The sorbent samples with or without carbon-coated metals are sent for Laser Flash Analysis (LFA). By this accurate and reliable solution, the thermal diffusivity and conductivity are tested.

During the test, a laser sends energy pulse to heat one side of a plane-parallel sample, which results in a temperature rise on the other side. The temperature change is measured by a detector and transformed into thermal diffusivity via the integrated software. Equation (1) calculates the thermal conductivity k based on the obtained thermal diffusivity α. ρ is the bulk density of the specimen, and C_p is the specific heat capacity.

$$k = \alpha \rho c_p \tag{1}$$

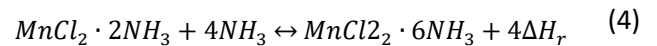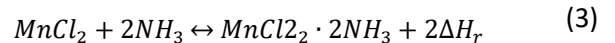The equipment applied in this project is LFA 467 Hyper Flash, declaring the accuracy of ±8%.

2.3 Experiments of the sorption performance

The sorption system is established in the laboratory, which mainly consists of an adsorbent bed and an ammonia container with other accessories. During the desorption process, the adsorption reactor is heated by the oil bath shown on the left of the photo and thus the ammonia is released to the condenser. A condensation heat is therefore obtained based on the amount of the reacted refrigerant. In the period of adsorption, the adsorbent bed is cooled by tap water to reject the adsorption heat, while the ammonia vessel is controlled to a testing temperature. The ammonia evaporates and then flows through the pipe to be adsorbed by the sorbent, which leads to a refrigeration production from the evaporator.

The mass of the ammonia m_{am} in this system is expressed in Equation (3). The subscription of g and l refers to the gas phase and liquid phase, respectively. V is the volume of the adsorbent tube while A_c is the cross- sectional area of that. The term g stands for the gravitational acceleration and Δp is the differential pressure tested by the sensor.

$$m_{am} = \rho_{am,g} \cdot V - (1 - \frac{\rho_{am,g}}{\rho_{am,l}}) \cdot \frac{A_c}{g} \cdot \Delta p \tag{2}$$

The reaction equations between the sorbent and ammonia are stated in Equation (3) and (4). From the left side to the right side of the equations are the adsorption processes, while the desorption starts in the opposite direction. Because the temperature requirement of Equation (3) is over the oil bath working range, only process (4) is considered in this paper. ΔH_r is the reaction heat per mole ammonia.

$$MnCl_2 + 2NH_3 \leftrightarrow MnCl2_2 \cdot 2NH_3 + 2\Delta H_r \tag{3}$$

$$MnCl_2 \cdot 2NH_3 + 4NH_3 \leftrightarrow MnCl2_2 \cdot 6NH_3 + 4\Delta H_r \tag{4}$$

The global ammonia conversion ratio x is assessed by Equation (5). The symbol of m_{4NH_3} refers to the mass of ammonia in the condenser when the sorbent adsorbs only two portions of ammonia. M_{4NH_3} represents the mass of the term 4NH₃ in Equation (4).

$$x_{MnCl_2} = \frac{m_{4NH_3} - m_{am}}{M_{4NH_3}} \tag{5}$$

Equation (6) is the calculation of the cooling power produced during adsorption. $n_{r,am}$ is the molecular number of the reacted NH$_3$. Equation (7) expresses the calculation of specific cooling power (SCP) of the sorbent, where m$_a$ is the mass of the adsorbent and t is the cycle time.

$$Q_{ref} = n_{r,am} \cdot \Delta H_r \qquad (6)$$
$$SCP = Q_{ref}/(m_a \cdot t) \qquad (7)$$

3. RESULTS AND DISCUSSION

3.1 Thermal conductivity

Fig 2 shows the thermal conductivities of the manufactured sorbent samples with a density of 600 kg/m^3 at various experimental temperatures. It is demonstrated that with the testing temperature increasing, the thermal conductivity of the sorbent positively develops, as the orange bars are higher than the green bars. Among the three tested candidates, the highest thermal conductivity is 1.166 W/(m·K) found in 180 ℃ test of MnCl$_2$-EG-Ni@C. The result shows 2.6 % or 1.8 % improvement of the thermal conductivity at 180 ℃ by adding Ni@C or Fe@C, respectively. For a working temperature of 160 ℃, the enhancement is 2.8 % by Ni@C or 3.0 % by Fe@C. The LFA result presents the potential of these additives to positively influence on the sorption performance as the combination of Ni@C and Fe@C slightly improves the heat transfer process.
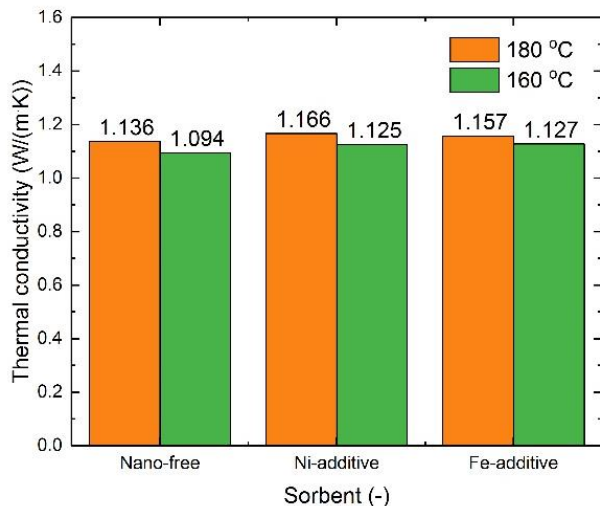

Fig 2 Thermal conductivity of the sorbents

3.2 Ammonia conversion ratio during the sorption

Fig 3 is the desorption performance in the time scale of 65 min when the heat source is at 180 ℃. In this condition, the condenser temperature is set at -20 ℃ to accelerate the condensation of the released ammonia from the reactor side. A rapid reaction is found in each curve of the ammonia conversion ratio at first, and then the dropping speed of the curves is reduced, tending to be stable until the end. It reflects the nature of developing regulations during the chemical reaction, which means rapid reaction rate at the first and slowed rate with time elapsing because of the reduced amount of the active reactants.
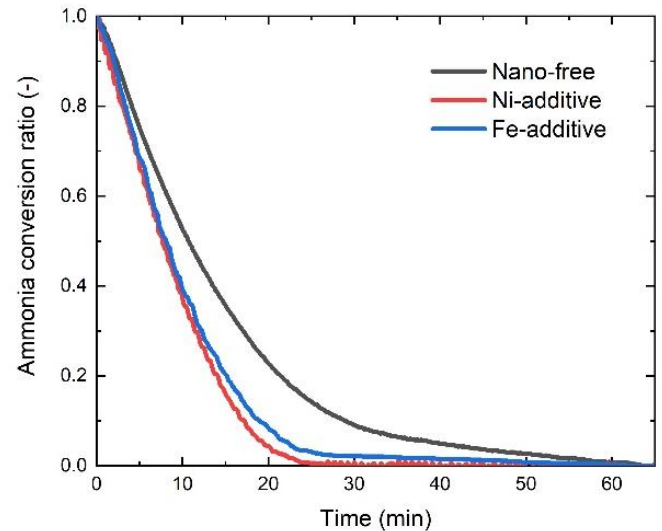

Fig 3 Desorption performance at 180 ℃

In Fig 3, the red line is the evolution of the global conversion ratio recorded the sorption performance of the sorbent with Ni@C. It lies at the bottom presenting the fastest reaction rate, compared to other two candidates. The red line reaches the ammonia conversion ratio of zero, costing reaction time of 25.83 min, while the desorption time for MnCl$_2$-EG-Fe@C is 62.92 min to meet the ratio of zero. Time for the conventional MnCl$_2$-EG to achieve the condition in above statement is 64.17 min. Therefore, the additional Ni@C and Fe@C can reduce the reaction time to 40.25 % and 98.05 % of the original one, corresponding to the discussed condition. The result is due to the improvement of the thermal conductivity, which also matches the discovery in the LFA tests and meets the expectations from the authors.
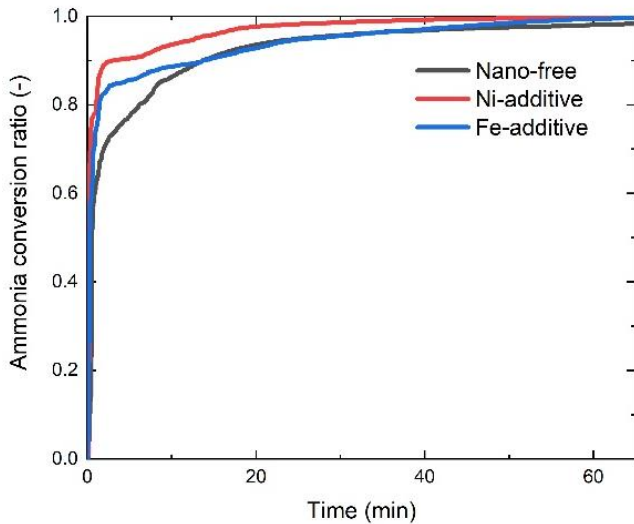
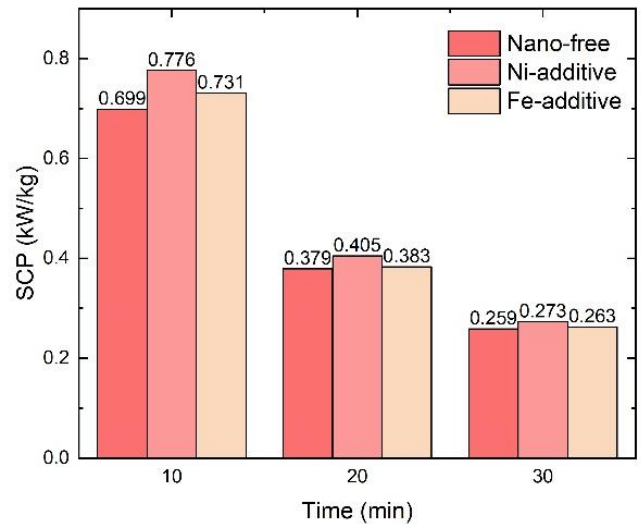**Fig 4** Adsorption performance at 20 ℃

Fig 5 SCP

Fig 4 displays the adsorption process cooling the sorbent bed by tap water and using the thermostat connected with the ammonia vessel to simulate the environmental temperature of 20 ℃. The ammonia conversion ratio sharply jumps to over 0.7 during the first minute, and then the curves slow the increasing speed and tend to be stable. The reaction rate follows the increasing order from $MnCl_2$-EG-Ni@C, $MnCl_2$-EG-Fe@C and $MnCl_2$-EG, indicating the improved heat and mass transfer process. The consumption of the reaction time is 13.58 min, 8.42 min and 2.25 min for the conventional, Fe@C-added and Ni@C-added $MnCl_2$ to reach a conversion ratio of 0.8, respectively. So, the adsorption time is saved to 16.57 % and 62.00 % of that required by the traditional HTS, by Fe@C and Ni@C, separately.

Fig 5 presents the calculation results of SCP, based on the experimental data displayed in last two illustrations. When the evaporator is controlled at 20 ℃, SCP of conventional HTS of $MnCl_2$-EG in 10 min, 20 min and 30 min is 0.699 kW/kg, 0.379 kW/kg and 0.259 kW/kg. The maximum SCP made by Ni@C and Fe@C is 11.02% and 4.58% higher than that of the original sorbent, obtained when the reaction time is 10 min. With the time increasing, the difference between the sorbents is decreased. At the reaction time of 30 min, the enhancement is 5.41 % and 1.54 % made by Ni@C and Fe@C, respectively.

4. CONCLUSIONS

This paper manufactured novel HTS with additional Ni@C and Fe@C with the upgraded preparation procedures. The thermal conductivities are analyzed by LFA, showing an improvement of up to 3.0 %. Moreover, the authors also conduct the adsorption and desorption performance tests on the prepared sorbents, discovering the accelerated reaction rate in the sorption reaction. A maximum reduction, 40.25 % of the desorption time or 16.57 % of the adsorption time, is found corresponding to the experimental conditions, due to the improvement of the heat transfer. Moreover, the SCP calculation demonstrates that the enhancements made by $MnCl_2$-EG-Ni@C range from 5.41 % to 11.02 %, while the growth achieved by adding Fe@C is from 1.54 % to 4.58 %. It reveals these novel sorbents can reduce the cycle time and the energy consumption, which demonstrates the feasibility to enhance the conversion of the low-grade heat into refrigeration.

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