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Sr(NH₃)₈Cl₂-Expanded Natural Graphite composite for thermochemical heat storage applications studied by in-situ neutron imaging

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ABSTRACT

This work presents an in-situ neutron imaging study of the ammonia sorption reaction in a SrCl₂-Expanded Natural Graphite (ENG) composite loaded into a honeycomb-shaped stainless-steel scaffold and enclosed in a thermochemical heat storage (THS) reactor prototype. The performance of SrCl₂/Sr(NH₃)₈Cl₂-ENG under different pressures and temperatures was investigated and the spatio-temporal content of ammonia was calculated from neutron radiograms. Quantitative image analysis revealed the formation of Sr(NH₃)₈Cl₂ upon ammonia uptake, while the desorption studies revealed a partial ammonia desorption resulting in the formation of the monoamine phase Sr(NH₃)₂Cl₂ via a stepwise release of ammonia. Neutron imaging also allowed the indirect evaluation of the stainless-steel honeycomb heat conductivity and showed that heat is transferred prevalently via the ENG matrix. Finally, neutron tomography of the reactor prototype was performed to ensure the stability of the THS system and composite material throughout the ammonia cycling experiments.

1. Introduction

Thermal energy storage and reutilization of the waste heat can give a significant contribution to reduce our carbon footprint. Different types of thermally driven materials and systems for both large and small scale applications have been developed in the past decade [1–4]. Among the various types of the thermal energy storage technologies, thermochemical heat storage (THS) systems have gained high interest and are considered as promising systems [5–7]. They can be operated using hydrates or ammines forming carbonates or metal halides for high, low or medium temperature storage, respectively. The salt-ammonia working pairs have shown high efficiency and cyclability compared to other solutions [8]. Besides, metal halide ammines have also been studied as potential hydrogen and ammonia storage materials [9–13].

The low temperature SrCl₂-NH₃ working pair has been extensively investigated by various techniques to characterize its kinetics, reaction pathways and cyclability [14–17]. The chemical reaction between SrCl₂ and NH₃ proceeds with the formation of Sr(NH₃)₈Cl₂ octammine at room temperature (RT) with a volume expansion of the material by up to 300%. In the desorption process, NH₃ release generally results in the formation of Sr(NH₃)₂Cl₂ monoammine [14] at 40-50 °C under 1 bar of NH₃. Alternatively, the formation of Sr(NH₃)₂Cl₂ diammine can precede the formation of monoammine under selected NH₃ pressures [15]. The full NH₃ desorption occurs above 150 °C against 1 bar of NH₃. The desorption reaction results in a contraction of the material volume and formation of macro and microporous structures within the grains [18]. The extreme volume increase is the main drawback of most salt-ammonia based working pairs. If no precautions are applied, this behavior can limit their applications on account of system safety and drastically reduce the heat transfer because of the formed porous structure. Several studies have shown the possibility to circumvent the volume expansion problem in various salt-ammonia working pairs by mixing the salts with expanded natural graphite (ENG) and thus forming composites [19–23]. In addition, thermal studies showed up to 182% increase in the thermal conductivity for SrCl₂-ENG composites when compared to the pure salt [19,24,25]. While the ENG shows no affinity to NH₃ [26], it can help to control the volume expansion in Sr(NH₃)₂Cl₂ by acting as a buffer.

The work presented here shows an in-situ neutron imaging study on a SrCl₂-ENG composite placed in a stainless-steel honeycomb heat exchanger mounted inside a model THS reactor. The honeycomb heat exchanger represents the basic unit of a THS reactor prototype. The full-
size THS reactor will comprise eleven of these honeycomb discs with a total volume of 0.5 L. Neutron imaging offers the unique possibility to analyze the spatio-temporal ammonia content in the composite material due to the high penetration power and the strong interaction of neutrons with hydrogen [27]. Neutron imaging, as a complimentary technique to X-ray imaging [28], provides a valuable information about inner structures of bulk materials. The sensitivity of neutrons to hydrogen and other light elements (e.g. lithium) makes neutron imaging a powerful characterization method widely used for energy storage materials studies such as batteries, hydrogen storage systems and fuel cells [29–36].

Recently, similar neutron imaging experiments were conducted on the SrCl$_2$/Sr(NH$_3$)$_2$Cl$_2$ system within the same THS reactor prototype, and the fragility of the powder bed subjected to a large volume expansion was reported [37]. Furthermore, the deformation of the stainless-steel honeycomb due to the thermal expansion and mechanical stresses caused by the volume expansion during Sr(NH$_3$)$_2$Cl$_2$ formation was presented. On the contrary, our study reports a remarkable mechanical stability of SrCl$_2$-ENG during NH$_3$ uptake and release with only slight expansion and contraction of the composite material, providing a homogeneous NH$_3$ uptake and showing excellent thermal conductivity. The hydrogen present in the ammonia molecule allows to detect the areas within the honeycomb, where Sr(NH$_3$)$_2$Cl$_2$ is formed, and here it is demonstrated for the first time how the NH$_3$ content in composite materials within a THS reactor can be calculated from neutron radiography images. Additionally, the heat released during NH$_3$ absorption reaction was monitored and the efficiency of the stainless-steel honeycomb serving as a heat exchanger and sample holder within the THS reactor is discussed. Complementary neutron tomography study revealed in-depth information about the honeycomb and the THS reactor, and the obtained results are compared to the previous neutron imaging study [37]. The neutron radiography data presented here will be compared to numerical simulations using COMSOL Multiphysics modeling software. It is integrated with calculation of thermal and mass flow within the reactor including thermochemistry of the materials with a high degree of accuracy. The ammonia cycling and the subsequent heat transfer studies provided by numerical modeling will help to optimize the THS reactor design and obtain high heat power [38].

2. Experimental

2.1. Sample preparation

The SrCl$_2$-ENG composite was prepared by impregnation of expanded natural graphite (ENG) sheets (from SGL Carbon, 95 % purity) with SrCl$_2$ (from AMMINEX, 99.9 % purity) by submerging the ENG into SrCl$_2$.H$_2$O for 72 hours. Prior to the impregnation process, ENG was dried at 180 °C for 8 hours and then soaked into ethanol for 2 hours for reducing the surface tension between non-polar ENG and polar SrCl$_2$.H$_2$O [39]. The impregnated ENG was then dried in an oven at 90 °C for 12 hours and further dehydrated in vacuum at 300 °C for 12 hours. Using this impregnation method, a SrCl$_2$-ENG composite with 76 wt% of SrCl$_2$ and 24 wt% of ENG was obtained. The composite sheets were obtained by compressing the SrCl$_2$-ENG composites, resulting in a packed density of 543 kg·m$^{-3}$. Hexagonal pellets with height of 10 mm were cut out from the SrCl$_2$-ENG composite sheets and loaded into the stainless-steel honeycomb half disc (See Fig. S1).

2.2. THS set-up

The SrCl$_2$-ENG composite pellets (total mass of 8.4 g) were loaded into a stainless-steel honeycomb half-disc containing a heating element with thermocouple (T$_h$) and a second thermocouple (T$_c$) to monitor the sample temperature during ammonia cycling. T$_h$ was inserted to the top of the honeycomb and surrounded by stainless-steel walls with thickness of ~2.5 mm. The honeycomb half-disc was then inserted into the THS reactor, which was connected to an absorption/desorption rig (see Fig. 1). The detailed parameters of the THS reactor are described elsewhere [37]. Prior to the neutron imaging experiment the sample was dried at 200 °C under dynamic vacuum for 3 hours, to remove any possible water impurities. A reservoir with 100 g of Sr(NH$_3$)$_2$Cl$_2$ powder, denoted as the ‘ammonia reservoir’, served as the ammonia source and was connected to the THS reactor with stainless steel tubes. A flowmeter with a readout range of 0–200 ml·min$^{-1}$ was implemented between the THS reactor and the reservoir in order to monitor the NH$_3$ gas flow during cycling. A magnetic valve (M) connected to the THS reactor ensured a remote control of the NH$_3$ gas flow between SrCl$_2$-ENG in the honeycomb and the reservoir. A pressure transducer (P) mounted between the flowmeter and the reservoir allowed a continuous monitoring of the pressure.

The ammonia absorption in SrCl$_2$-ENG was achieved by heating up Sr(NH$_3$)$_2$Cl$_2$ in the ammonia reservoir, to release NH$_3$ into the setup, while the ammonia desorption was studied by heating ammoniated Sr (NH$_3$)$_2$Cl$_2$-ENG in the THS reactor at various temperatures. Such closed system ensured safe handling of NH$_3$ gas during the experiment.

2.3. Neutron imaging set-up

The neutron imaging experiments were performed at the NeXT beamline (D50) [40] at the Institute Laue-Langevin (ILL) research reactor in Grenoble, France. A cold neutron beam with a flux of 1.5·10$^8$ n·cm$^{-2}$·s$^{-1}$ was collimated by a 23 mm pinhole (L/D ~ 435) and transmitted through the sample. The sample was mounted in front of a Gadox scintillator screen with a field of view 10 cm x 10 cm and a thickness of 50 μm. The scintillated light was captured by a CMOS camera (Hamamatsu Orca 4V2) providing images with a time resolution of 1 s. For three sequential radiography images, one average image was produced.

The radiography images were normalized and analyzed using ImageJ [41] and the transmission of the SrCl$_2$/Sr(NH$_3$)$_2$Cl$_2$-ENG composite material was calculated according to:

$$ I = I_0 e^{-\mu x} \tag{1} $$

where $I$ is the intensity transmitted through the sample, $I_0$ is the incident intensity, $\mu$ is the linear attenuation coefficient and $x$ is the sample thickness.

The neutron transmission values of NH$_3$ absorbed in the composite material were obtained by dividing the overall stack of images by the first image (for absorption) or by the last image (for desorption) in order to remove the SrCl$_2$-ENG contribution from the images and to observe only absorbed or desorbed NH$_3$ in the radiogram. The mean transmission values for the NH$_3$ were obtained from selected hexagon-shaped areas within each cell of the honeycomb. The density of NH$_3$ was calculated according to:

$$ \rho_{NH_3} = \left( \frac{\rho_{Sr(NH_3)2Cl2} - \rho_{SrCl2} \cdot M}{N_A \cdot \sigma_{NH_3}} \right) \tag{2} $$

where $\rho_{Sr(NH3)2Cl2}$ is the attenuation coefficient of the ammoniated composite, $\rho_{SrCl2}$ is the attenuation coefficient of the composite without ammonia, $M$ is the molar mass of ammonia, $N_A$ is Avogadro constant and $\sigma_{NH_3}$ is the total neutron cross section of ammonia. The mass of ammonia $m_{NH3}$ is calculated from the density given by Equation-2 multiplied with the volume of NH$_3$ obtained from each radiogram. Then the gravimetric NH$_3$ content (wt%) in Sr(NH$_3$)$_2$Cl$_2$ during absorption and desorption was calculated from:

$$ x_{NH_3} = \frac{m_{NH_3}}{m_{SrCl2} + m_{SrCl2}} \times 100\% \tag{3} $$

where $m_{SrCl2}$ is the mass of the SrCl$_2$ in the composite material in the initial state.
Neutron tomography of the composite material was carried out by rotating the THS reactor over a 360° range at 0.225° per step and resulting in 1600 projections (one image per step). The initial state, the absorbed and desorbed states of the composite material were scanned and reconstructed using XAct software [42] and visualized with VG Studio Max© software [43].

3. Results and discussions

3.1. Ammonia sorption and heat storage properties of the SrCl₂-ENG composite in the THS system

In total four NH₃ absorption desorption cycles in the SrCl₂-ENG composite were studied. Each absorption was followed by desorption with a dwell time to allow the THS reactor or the ammonia reservoir to cool down.

Absorption reactions were conducted at RT and at different NH₃ gas pressures. Fig. 2a depicts the evolution of the NH₃ gas pressures during the four absorption processes. The first (Absorption-1, blue curve) and second (Absorption-2, red curve) absorption were performed at similar NH₃ pressures of ~2.5 bar which increased up to 2.7 bar due to the saturation of Sr(NH₃)₂Cl₂-ENG while the NH₃ gas was still provided by the ammonia reservoir. The third absorption (Absorption-3, green curve) was achieved under 1.5 bar of NH₃ and remained almost constant during the whole absorption process. This is due to the slower NH₃ absorption in the SrCl₂ salt under lower NH₃ gas pressures, allowing for less variations in the total pressure of the system. The fourth absorption (Absorption-4, yellow curve) started at 3 bar of NH₃ and the pressure was immediately increased up to 3.5 bar over 30 min by increasing the temperature of the ammonia reservoir. The higher NH₃ gas pressure in this case resulted in fast absorption reaction with the subsequent drop in the pressure down to ~3.3 bar.

The NH₃ gas flow during Absorption-1 and -2 showed similar behavior with the flow increase up to 200 ml·min⁻¹ at the very beginning of the experiment and then reduced to 0 ml·min⁻¹. The flowmeter detected the NH₃ gas flow end close to 2 hours, indicating that the

Absorption-1 and -2 were complete at that time. The NH₃ flow during Absorption-3 increased to 140 ml·min⁻¹ and slowly reduced by the end of the absorption reaction of 3.2 hours. Absorption-4, conducted at higher NH₃ pressure (3.5 bar), was complete in over 1 hour as the flowmeter recorded NH₃ gas flow termination. Due to the saturation of the flowmeter at its highest possible readout of 200 ml·min⁻¹ during some absorption and desorption cycles (Fig. 2b), the amount of ab-/desorbed NH₃ is underestimated, and therefore the total amount of NH₃ was not calculated from flowmeter data.

Heat is released during the Sr(NH₃)₂Cl₂ formation due to the exothermic absorption reaction. The temperature at the top of the honeycomb (Tₜ) was therefore recorded in order to evaluate the temperature increase during absorption. Fig. 2c shows the temperatures measured as Sr(NH₃)₂Cl₂-ENG is formed during the absorption processes 1 to 4. At Absorption-1 and -2 (~2.5 bar of NH₃) the temperature increased up to ~46 °C, while at 3 bar and 1.5 bar of NH₃ the temperature reached up to 53.5 °C and 33.1 °C, respectively. These results show that the heat released during absorption processes can be controlled by the NH₃ gas pressure applied to the system.

The four NH₃ desorption processes were carried out under 0.8 bar of NH₃ and temperatures between 100 °C and 200 °C. Fig. 3a shows the NH₃ pressure increase at the start of each desorption due to the released NH₃ which was then absorbed in the ammonia reservoir resulting in a subsequent pressure drop. The first (Desorption-1, blue curve) and the last (Desorption-4, yellow curve) desorption were conducted at the same temperature (200 °C). In both cases, the pressure raised to 1.2 bar in 30 min, remained constant for a short time and then decreased and the desorption process was complete in less than 1 hour.

During the second desorption (Desorption-2, red curve) at 150 °C, the pressure increases up to 1.1 bar and reduces to 0.9 bar as the NH₃ desorption is complete in ~1.3 hours. For Desorption-3 (green curve), conducted at the lowest temperature of 100 °C, the pressure increased only up to 0.95 bar. This shows that the pressure change during the desorption processes depend on the heating temperature of the Sr(NH₃)₂Cl₂-ENG composite material.

The temperature of the sample, Tₛ, was also measured during the
desorption cycles at the top of the honeycomb to evaluate the heat distribution over the honeycomb area (Fig. 3c). The highest $T_s$ is 83.5 °C when the sample was heated at 200 °C (Desorption-1 and -4). The slight increase up to 90 °C in Desorption-4 was due to increasing the set temperature of the heating element to 230 °C at the end of the Desorption-4. At the lower desorption temperatures of 150 °C (Desorption-2) and 100 °C (Desorption-3), $T_s$ reached only 63.5 °C and 46 °C, respectively. The difference in recorded temperature between the heating element and the thermocouple is mainly due to the distance between the heating element and the thermocouple. In addition, the heat distribution over the honeycomb area might be affected by the endothermic nature of the desorption reactions. It should be also noted that the thermocouple was positioned in between the ~2.5 mm stainless steel walls which might prevent reading the actual temperature of the sample during the sorption processes.

3.2. Neutron radiography

The four cycles of NH$_3$ absorption and desorption in the SrCl$_2$-ENG composite under different temperatures and NH$_3$ pressures were investigated by in-situ neutron radiography. After the last desorption the sample was heated up to 230 °C under vacuum to remove all possible NH$_3$ left in the composite material. Due to the attenuation of neutron beam by hydrogen present in ammonia, the NH$_3$ uptake by SrCl$_2$-ENG composite results in formation of dark areas in the radiograms, and during the desorption the dark areas in the radiogram become brighter as a result of the ammonia release. The NH$_3$ absorption reaction was homogeneous over the honeycomb area (See Fig. S2), but the desorption showed dependence of the heat transfer properties on the stainless-steel honeycomb.

Fig. 4 shows the normalized radiography images after 30 min of the four desorption performed on Sr(NH$_3$)$_8$Cl$_2$-ENG at different temperatures. The lower heating temperatures result in slower NH$_3$ release. The desorption of NH$_3$ starts from the areas of the honeycomb close to the heating element placed at its bottom, and thus showing the relatively poor heat conductivity of the stainless-steel honeycomb. In all four desorption cases, the NH$_3$ desorbed from each cell in the honeycomb is a result of the heat transferred through the composite material rather than the heated walls of the honeycomb cells.

For calculating the NH$_3$ content, several areas of the honeycomb were selected and numbered (see Fig. S3). Fig. 5a depicts a schematic view of the honeycomb with four cells marked as cell-3, -5, -7 and -12. The NH$_3$ contents of Sr(NH$_3$)$_8$Cl$_2$ formed in these selected cells calculated according to Eq. (3) are plotted as function of time in Fig. 5b-i. For Absorption-1 (~2.5 bar of NH$_3$) the total NH$_3$ uptake reaches up to 45.7 wt% in cell-5 (Fig. 5b) which is very close to the theoretical 46.2 wt% for a complete absorption. The NH$_3$ content in the cell-3, -7 and -12 reached 44.9 wt%, 45.1 and 43.5 wt%, respectively. Cell-12 shows the lowest NH$_3$ content throughout the cycling. This might be due to a slight inhomogeneity of the SrCl$_2$ content in the ENG matrix, which might differ.
from cell to cell and deviate from the overall value of 76 wt%. Finally, the ammoniated salt Sr(NH$_3$)$_8$Cl$_2$ represented 85 wt% of the composite, 15 wt% being the ENG and the gravimetric NH$_3$ capacity of the Sr(NH$_3$)$_8$Cl$_2$-ENG composite evaluated to be of 38.8 wt%. The results for Desorption-1 at 200 °C (Fig. 5c) show how the relative distance of the different cells from the heating element affects the desorption time. Sr(NH$_3$)$_8$Cl$_2$ in cell-5 and -12 desorbed NH$_3$ in ~0.3-0.5 hours and for cell-7 and -3 in about 0.7 hours. Only 7 out of the 8 NH$_3$ moles were released and the monoamine was obtained with the NH$_3$ content kept as 5.4-5.7 wt%. The NH$_3$ wt% for monoammine was calculated relative to octammine. The change between Sr(NH$_3$)$_8$Cl$_2$ monoammine and Sr(NH$_3$)$_8$Cl$_2$ octammine occurred in all the following cycles.

Therefore, Absorption-2 starts from 5.4-5.7 wt% and then 38.4 wt% of NH$_3$ was absorbed resulting in 44.6 wt% of ammonia in the salt at 2.5 bar (Fig. 5d). After 2 hours, the absorption curves flatten out indicating saturation of the powder particles. The desorption at 150 °C (Desorption-2, Fig. 5e) shows that 7 moles of NH$_3$ are released within 1.5 hours and the desorption trend in each cell is the same as for the previous desorption. Absorption-3 at 1.5 bar of NH$_3$ resulted in a slow absorption process taking more than 3 hours due to the low NH$_3$ pressure (Fig. 5f). The obtained NH$_3$ content reached up to 44.3 wt% in the cells. The following Desorption-3 at 100 °C resulted in the desorption of 7 moles of NH$_3$ in 2.5 hours (Fig. 5g). The last cycle of the NH$_3$ sorption was performed at 3.0 bar for absorption of NH$_3$ reaching up to 45.6 wt% (Fig. 5h) and desorption at 200 °C (Fig. 5i).

The effect of the low heating temperature on the performance of the honeycomb during Desorption-2, -3 and -4 can be seen from plots in Fig. 5e, g and i. At 0.8 hours of Desorption-2 (T = 150 °C), temporary slowdowns of the desorption for cells-3 and -7 were observed as “bumps” in the curves (Fig. 5e). The desorption curves for cell-3, -5 and -7 (Fig. 5g) contain two distinct “bumps”, and during Desorption-4 (T = 200 °C) the single “bump” in cell-3 and -7 appear at 0.55 hours. This is probably due to the endothermic nature of the desorption reaction and the heat dissipation within the honeycomb. It results in delayed heat transfer to the next cells and therefore slows down the ammonia release in the cells that are away from the heat source. However, the bumps in the desorption curves between 12 wt% and 20 wt% might also be the result of a multi-step desorption of NH$_3$. The Sr(NH$_3$)$_8$Cl$_2$ octammine releases 7 moles of NH$_3$ followed by Sr(NH$_3$)$_8$Cl$_2$ monoammine formation at 40-50 °C under 1 bar of NH$_3$ [14]. However, this reaction has been
reported to occur in two steps under selected NH$_3$ pressures and slow heating rates with the Sr(NH$_3$)$_2$Cl$_2$ diammine forming first and followed by the Sr(NH$_3$)$_2$Cl$_2$ monoammine [15]. The bumps observed at ~12 wt% might therefore correspond to the formation of the diammine.

A similar NH$_3$ uptake and release behavior was observed for the other honeycomb cells not plotted here. These data are included in the Supplementary material (See Figs. S4 and S5). The slight mismatches of the NH$_3$ wt% values at the end of absorption and beginning of desorption curves are likely due to at least 30 minutes waiting time for cooling down the ammonia reservoir or the THS reactor in order to proceed with the next cycling step. During that cooling time no neutron radiography measurements were performed, and some NH$_3$ was likely reabsorbed or further desorbed before the start of the next sorption process.

Assuming the Sr(NH$_3$)$_2$Cl$_2$ octammine formation from SrCl$_2$ during Absorption-1, only 7 moles of NH$_3$ were ab/desorbed during the following ab-/desorption reactions, following the reaction Sr(NH$_3$)$_2$Cl$_2$ $\rightarrow$ Sr(NH$_3$)$_2$Cl$_2$+7NH$_3$. During the desorption processes at temperature above or equal to 150 °C and against 0.8 bar of NH$_3$ (Fig. 5 c, e and i) the full NH$_3$ desorption did not occur which is likely due to the poor heat conductivity of the stainless-steel honeycomb and loss of heat to the ambient via the THS reactor walls. Even with a heating temperature of 200 °C, the maximum temperature recorded at the honeycomb thermocouple ($T_c$) was 83.5 °C.

This was confirmed during our final neutron radiography experiment performed after Desorption-4 where the temperature was kept at 230 °C under dynamic vacuum for 15 min. Radiography during this final step showed a change in image intensity (See Fig. S6), indicating an additional release of NH$_3$ and suggesting further desorption from the remaining monoammine Sr(NH$_3$)$_2$Cl$_2$.

The different pressures ($P$) of the applied NH$_3$ gas during absorption processes showed that the formation of Sr(NH$_3$)$_2$Cl$_2$-ENG is faster at higher NH$_3$ pressures and slower at lower NH$_3$ pressures. Additionally, the temperature of the sample (Sr(NH$_3$)$_2$Cl$_2$-ENG) increases when the applied NH$_3$ gas pressure was increased (see Section 3.1) due to the exothermic absorption reaction. Therefore, the NH$_3$ absorption time and the heat released during absorption can be controlled by the applied NH$_3$ gas pressure. Meanwhile, the NH$_3$ desorption is governed by the heating temperature ($T$) of Sr(NH$_3$)$_2$Cl$_2$-ENG. At the higher temperatures the NH$_3$ desorption is faster whilst at the lower temperatures the NH$_3$ release is slower. Additionally, the lower heating temperatures during the NH$_3$ desorption allowed to observe the step-desorption of the NH$_3$ and therefore formation of Sr(NH$_3$)$_2$Cl$_2$.

3.3. Neutron tomography

Three-dimensional images of the investigated sample were reconstructed from the neutron radiograms obtained during its rotation over 360° around its axis (See Fig. S7). The information about the inner structure of the THS reactor prototype is acquired from the orthogonal planes of the 3D images, showing the arrangement of the hexagonal pellets of SrCl$_2$-ENG composite within the cells of the honeycomb. Fig. 6a shows the orthogonal view of the samples in the XY and XZ-planes before NH$_3$ cycling. A space between the pellets and the honeycomb walls can be seen in both planes, and thus allowing the pellets to expand and occupy the whole volume of the cells during the NH$_3$ absorption.

The ENG matrix in the composite acts as a buffer during NH$_3$ cycling limiting the expansion and contraction of SrCl$_2$-ENG during NH$_3$ uptake and release, respectively. Fig. 6b presents the XY and XZ-planes of the Sr(NH$_3$)$_2$Cl$_2$-ENG after partial NH$_3$ desorption. Due to the NH$_3$ present in the salt, the pellets still occupy a large fraction of the available volume. It can also be noticed that the expansion of the composite in the axial directions (perpendicular to the honeycomb) is not limited by the walls of the honeycomb cells. This feature of the ENG is beneficial for the heat transfer between the active material and the honeycomb, and thus allowing to increase the efficiency of the THS reactor and the system.

3.4. Comparison with the previous work

In the previous neutron imaging study of the SrCl$_2$/Sr(NH$_3$)$_2$Cl$_2$ system within the same THS reactor prototype only qualitative analysis of the neutron radiography data was performed [37]. Some of the SrCl$_2$ powder had fallen out of the honeycomb during the sample mounting and volume expansion resulting in continuous changes of the SrCl$_2$ powder bed thickness, which could not be determined accurately and prevented any quantitative analysis [37]. A known thickness of the investigated area is needed for quantitative analysis of neutron radiography images (see Eq. (1)). This was achieved in the present work by the confinement of SrCl$_2$ in the porous ENG matrix ensuring the stability of the SrCl$_2$-ENG composite against external forces while allowing free expansion of the powder within the porous media. The composite material provided fast absorption and desorption processes compared to the previous study proving the improvement for the reaction kinetics when the salt is confined in porous ENG matrix. The desorption of 7 moles of NH$_3$ form Sr(NH$_3$)$_2$Cl$_2$ powder was complete within 4 hours at 100 °C in previous results [37], while it was completed within 2.5 hours in Sr(NH$_3$)$_2$Cl$_2$-ENG composite at the similar conditions. The enhanced thermal conductivity and permeability of the SrCl$_2$-ENG composite material due to the increased porosity and thermal conductivity of ENG allowed for better heat and mass transfer during NH$_3$ cycling [24]. A thermal equilibrium of the system depends on the heat transfer, therefore high heating rates are required for the material with poor heat transfer (e.g. Sr(NH$_3$)$_2$Cl$_2$ powder). The high heating rate also causes the chemical non-equilibrium and the possible absence of the intermediate reaction process [26]. Meanwhile, the higher heat transfer provided by ENG allows for the thermal equilibrium at slower heating rates. This in turn helped to observe the formation of Sr(NH$_3$)$_2$Cl$_2$ diammine during NH$_3$ desorption at lower $T=100-150$ °C, which was not observed when pure SrCl$_2$ powder was used in previous studies [37]. Ultimately, an enhanced thermal conductivity is expected to improve the thermal energy storage performance of the system.

Additionally, investigation of the heat transfer efficiency of the honeycomb and the spatio-temporal NH$_3$ concentration in the composite material during cycling in this study provides a valuable information about the efficient performance of the THS reactor. The presented
neutron radiography results in this work were compared with the numerical simulations from COMSOL Multiphysics modeling software. This modeling includes the NH$_2$ flow and heat transfer function of the honeycomb heat reactor which will provide high accuracy and close equivalence to the sorption reaction observed with neutron radiography.

Neutron tomography of the THS reactor prototype with SrCl$_2$/Sr(NH$_3$)$_2$Cl$_3$ system revealed the distortion of the honeycomb after NH$_3$ cycling, where the honeycomb back plate was bended due to the volume expansion of the sample [37]. In this work we note that the mechanical stresses on the honeycomb were minimized by confining the SrCl$_2$ in ENG matrix. Therefore, the mechanical stability of the stainless-steel honeycomb together with the limited expansion/contraction of the SrCl$_2$-ENG composite make the investigated THS reactor a safe system for the future applications.

4. Conclusion

It is demonstrated that neutron imaging is a useful technique for determination of spatio-temporal NH$_2$ content in Sr(NH$_3$)$_2$Cl$_3$-ENG composite pellets produced for thermochemical heat storage applications. ENG mixed with SrCl$_2$ showed excellent kinetics during the NH$_3$ absorption and desorption. The results from neutron radiography and tomography confirmed the mechanical stability of the SrCl$_2$-ENG composite upon cycling. The stainless-steel honeycomb in which the pellets were embedded, showed a poor heat transfer efficiency during the desorption processes resulting in an inhomogeneous NH$_3$ desorption process. The heat release during exothermic Sr(NH$_3$)$_2$Cl$_3$-ENG formation with the temperatures of up to $T = 53.5$ °C has been detected. The exothermic and endothermic NH$_3$ cycling monitored during in-situ neutron radiography revealed a high potential of the SrCl$_2$-ENG composite materials for the low temperature thermochemical heat storage applications.

CRediT authorship contribution statement

Perizat Berdiyeva: Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. Anastasia Karabanova: Methodology, Formal analysis, Investigation, Writing - review & editing. Didier Blanchard: Conceptualization, Methodology, Investigation, Resources, Project administration, Writing - review & editing, Funding acquisition. Björn C. Hauback: Writing - review & editing, Supervision. Stefano Deledda: Conceptualization, Methodology, Investigation, Resources, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in
