Integrated chemisorption cycles for ultra-low grade heat recovery and thermo-electric energy storage and exploitation

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HIGHLIGHTS

- Integrated chemisorption cycle for simultaneous electric and thermal energy storage.
- Recover ultra-low grade heat (30–100 °C) with the aid of the compression process.
- Thermal efficiency and exergy efficiency is 47–100% and 62–93%, respectively.
- Upgrade the low-grade heat by between 10 and 80 °C depending on adsorbent pairs used.
- The round-trip efficiency of electric energy storage could achieve 100% or higher.

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ABSTRACT

The integrated chemisorption technology driven by ultra-low grade heat for simultaneous electrical power and thermal energy storage has been investigated in this work. A resorption cycle employing low and high temperature salts, with the coupling between manganese chloride (MnCl₂), calcium chloride (CaCl₂) and sodium bromide (NaBr), was evaluated and compared in the proposed integrated system for a heat source temperature of between 30 °C and 100 °C. During the energy charging process, working fluid compression was introduced to convert mechanical power or electricity into chemical energy so that it could be stored during the adsorption process at the same time as utilising low temperature heat energy. During the energy discharging process, mechanical power could be generated via the expansion of the desorbed high pressure working vapour from the low temperature salt reactor, there is also a by-product potential of the cooling energy which can be extracted from the cold expansion exhaust. In addition to the power generation and the potential cold energy, upgraded heat could also be provided by the exothermic adsorption process in the high temperature salt reactor. The performance of this integrated cycle in terms of energy and exergy efficiency and energy density have been discussed. With the help of ultra-low grade heat, a 100% round-trip electricity storage efficiency of the proposed system has been found to be achievable using CaCl₂–NaBr and MnCl₂–CaCl₂ pairs when the heat source temperature was higher than 50 °C and 60 °C, respectively. Also a temperature lift of the heat by 15–33 °C and 22–68 °C respectively was possible using these two adsorbent pairs.

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1. Introduction

Low-grade heat sources are ubiquitous, with industrial waste heat in the UK estimated to be as high as 40 TW h annually and is enough to heat over 2 million homes a year [1]. Investigations have indicated that low grade waste heat accounts for 50% or more of the total heat produced by industry and the total waste heat available above 30 °C from US power plants is estimated to be 60% of the input energy, with a weighted average temperature of 88 °C [2,3]. Therefore, the recovery of waste low grade heat, commonly taken as below 150 °C, is of great significance and importance if improvements in efficiency and reductions in energy demand are to be achieved. Renewable low grade heat, such as from solar thermal and geothermal sources, is also extremely valuable and is of increasing interest to support the energy mix. Various thermodynamic cycles, such as the organic Rankine, supercritical Rankine, Kalina, Goswami, trilateral flash, and adsorption cycles have been proposed for the conversion of low-grade heat to electrical power [4–10]. However, technologies available...
to recover ultra-low grade heat below 100 °C, which constitutes
the majority of existing wasted thermal energy, are currently
extremely limited.

Chemisorption heat pump and thermal storage based on revers-
ible chemical reactions, such as ammonia-salt systems, has
attracted increasing attentions over the last decades as a result of
its low grade heat utilisation, long-term storage ability, and the
higher energy densities in comparison with physisorption systems,
e.g. water- or methanol-based systems. To increase the flexibil-
ity and extend the application of chemisorption technology, me-
chanical components have been proposed to integrate with pure heat-
driven cycles. Wang et al. [9] proposed and theoretically analysed
a resorption cogeneration cycle of power and cooling production,
which integrated an expander with four solid-sorbent reactors so
that the system could overcome the inherent intermittence of
chemisorption system and realise continuous and simultaneous
a lab-scale prototype based on adsorption-expander combination,
and demonstrated the chemisorption cogeneration potential and
the significance of the capacity match between adsorption reactor
and the mechanical component. Al Mousawi et al. [12] explored
the cogeneration potential of the integrated system of metal
organic framework (MOF)-water adsorption. Physisorption sys-
tems including water- and methanol-based systems normally
work at relatively low pressure, close to atmospheric level. Conse-
quently, the refrigerants in those physisorption systems have
lower vapour density. That implies a higher volume flow rate that
would require a bigger size of expander for a given power genera-
tion capacity [13]. van der Pal et al. [14] evaluated a hybrid heat
pump system that combined compressor with sorbent reactors.
The comparative analysis between the hybrid system and the
purely heat-driven system suggested the former system could
effectively reduce the minimum temperature of the recoverable
waste heat and also increase the upgraded heat temperature. In
the subsequent work, van der Pal et al. [15] carried out experimen-
tal tests on a hybrid adsorption-compression heat pump based on a
roots-type compressor and silica gel-water adsorption to find out
the optimal integrating configuration. This tentative work studied
physisorption system, but the ultimate goal emphasised is still to
develop hybrid ammonia-salt heat pump system because the latter
one is more suitable for the targeted high heat-upgrading purpose.

This present study proposes a new integrated system that com-
bines chemisorption reactors, compressor and expander and it is
aimed to recover ultra-low grade heat for thermo-electric energy
storage and exploitation. For chemisorption cycles, the integration
with both vapour expansion and compression technology further
provides greater versatility and the potential to provide cooling,
heating and power generation, and the technology of the reversible
gas compressor–expander allows the compact integrating configu-
ration. The combination of these energy vectors offers flexibility
and adaptability to various operational conditions. Consequently,
the presented conceptual Sorption Thermo-Electric Energy Storage
(STEES) system potentially realises thermal energy and electrical
power storage simultaneously and for example could store off-
peak electricity while recovering ultra-low grade heat from indus-
trial processes, or could be deployed with solar photovoltaic ther-
mal (PVT) panels to store the renewable electricity while collecting
the solar thermal energy. The objective of this work is to explore
the maximum potential and provide a greater understanding of
the theoretical viability of the proposed system and to assess the
energy and exergy efficiencies, round-trip efficiency and energy
density for different heat source temperatures. Using ammonia as
the working fluid, three reactive metallic salts, manganese chloride
(MnCl₂), calcium chloride (CaCl₂) and sodium bromide (NaBr)
which have different thermodynamic equilibrium properties of
the chemical reaction with ammonia, were investigated and dis-
cussed in detail.

2. Working principle

2.1. Chemisorption cycle

The basic single-effect resorption cycle uses two adsorbent
reactors, each containing a different metallic salt, which can rever-
sibly react with the same working fluid. When one of the reactors
is heated using low-grade thermal energy the decomposition of the
working fluid from the salt takes place, whilst the other salt expe-
riences synthesis with the working fluid and this reaction process
is reversible. At the same working pressure, one salt has a higher
equilibrium reaction temperature than the other salt and therefore
they are distinguished as the high temperature salt (HTS) and low

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>c_p</td>
<td>specific heat capacity (J/(kg K))</td>
</tr>
<tr>
<td>E</td>
<td>exergy (J)</td>
</tr>
<tr>
<td>h</td>
<td>enthalpy (J/kg)</td>
</tr>
<tr>
<td>ΔH_r</td>
<td>reaction enthalpy (J/mol)</td>
</tr>
<tr>
<td>m</td>
<td>mass (kg)</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight (kg/mol)</td>
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<tr>
<td>P</td>
<td>pressure (Pa)</td>
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<td>Q</td>
<td>heat (J)</td>
</tr>
<tr>
<td>R.Store</td>
<td>round-trip efficiency (–)</td>
</tr>
<tr>
<td>ΔS_r</td>
<td>reaction entropy (J/(mol K))</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>U</td>
<td>energy (J)</td>
</tr>
<tr>
<td>W_e</td>
<td>work (J)</td>
</tr>
<tr>
<td>x</td>
<td>ammonia uptakes (mol/mol)</td>
</tr>
<tr>
<td>η</td>
<td>efficiency (–)</td>
</tr>
<tr>
<td>ρ_bulk</td>
<td>density (kg/m³)</td>
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Subscripts

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<tr>
<th>Subscript</th>
<th>Description</th>
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<tr>
<td>ad</td>
<td>adsorption or adsorbent</td>
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amb | ambient
com | compression
de1 | desorption in the first phase of cycle
de2 | desorption in the second phase of cycle
den | density
en | energy
ex | exergy
exp | expansion
f | final
h | high
in | inlet
out | outlet
rec | recovery
ref | refrigeration
sen | sensible heat
spe | specific
w | work
temperature salt (LTS) respectively. The resorption cycle can use a variety of reactive salt candidates covering a wide range of working temperatures and three representative salts, MnCl₂, CaCl₂ and NaBr, taken in this work to assess the performance of the STEES system using ammonia as the working fluid. MnCl₂ was used as the HTS in combination with the LTS of either CaCl₂ or NaBr, or alternatively CaCl₂ was used as the HTS with NaBr acting as the LTS. The following equations give the reversible chemical reaction processes of the selected salts with ammonia.

\[
\begin{align*}
\text{MnCl}_2 \cdot 2\text{NH}_3 + 4\text{NH}_3 & = \text{MnCl}_2 \cdot 6\text{NH}_3 + 4\Delta H_i \\
\text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 & = \text{CaCl}_2 \cdot 8\text{NH}_3 + 4\Delta H_i \\
\text{NaBr} + 5.25\text{NH}_3 & = \text{NaBr} \cdot 5.25\text{NH}_3 + 5.25\Delta H_i
\end{align*}
\]

2.2. Integrated storage cycle

When the temperature of the heat supplied to the HTS reactor is too low, as shown in Fig. 1(a), the equilibrium pressure of the HTS reactor is not high enough to force the HTS reactor to adsorb the ammonia vapour; a compressor can be used to pressurise the desorbed vapour and assist both the decomposition and synthesis within two reactors, respectively. Thereafter, both the low grade heat and electrical power can be converted to chemical energy and stored in the adsorbent reactors.

In the discharging process, as shown in Fig. 1(b), low grade heat or ambient heat can be utilised for LTS decomposition and the desorbed ammonia vapour will have a relatively high pressure so that it can be expanded to produce mechanical work or generate electric power. At the same time the HTS reactor will release heat because of adsorbing the exhausted ammonia from the expander, and the equilibrium temperature of this adsorption process could be higher than the temperature of the input low grade heat so that the system can also behave as a heat transformer.

The STEES cycle using the adsorbent pairs of MnCl₂ (HTS)-CaCl₂ (LTS) and CaCl₂ (HTS)-NaBr (LTS) were taken as examples to depict the ideal thermodynamic states in the Clapeyron diagram, as shown in Fig. 2, and the T–S diagram as shown in Fig. 3. The closed loop A–B–C–D–E–F denotes the cycle states using the MnCl₂–CaCl₂ pair and the dashed-line loop A’–B’–C’–D’ denotes the cycle using CaCl₂–NaBr. The cycle operation using these pairs is described as follows.

1. MnCl₂-ammoniate undergoes decomposition at the heat source temperature (A, \(T_{source}\), the desorbed ammonia vapour afterwards is pressurized in an isentropic compression process (A to B) to achieve the equilibrium pressure of CaCl₂-ammoniate synthesis (B, \(P_{eq}(\text{CaCl}_2\cdot30^\circ\text{C})\)) so that CaCl₂-ammoniate can adsorb ammonia at point C. If using the same heat source in the discharging process, after the consumption of sensible heat to rise the temperature of the solid CaCl₂-ammoniate from ambient level to desorption temperature (C to D), CaCl₂-ammoniate extracts more heat for decomposition (D) and the desorbed ammonia vapour goes through an isentropic expansion (D to E). To maintain healthy operation of the expander, particularly if using turbo-machinery, liquid should be avoided so that the expansion is designed to stop before ammonia saturation (E, which is the intersection of the ammonia saturation curve and the expansion curve). The exhausted ammonia (E) is observably at low temperature (around –24 °C), which indicates certain capacity of useful cold production depending on refrigeration temperature required. By adding one
Table 1

<table>
<thead>
<tr>
<th>Salt</th>
<th>( \Delta H ) J/mol</th>
<th>( \Delta S ) J/(mol K)</th>
<th>Max. Uptakes g(NH(_3))/g(salt)</th>
<th>( c_p ) J/(kg K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl(_2) (2–6NH(_3))</td>
<td>47.416</td>
<td>228.07</td>
<td>0.540</td>
<td>( \frac{4.184}{M_{\text{salt}}} \times (16.2 + 0.0052 \times T(K)) )</td>
</tr>
<tr>
<td>NaBr (0–5.25NH(_3))</td>
<td>30.491</td>
<td>208.8</td>
<td>0.067</td>
<td>( \frac{4.145}{M_{\text{salt}}} \times (11.74 + 0.00233 \times T(K)) )</td>
</tr>
<tr>
<td>CaCl(_2) (4–8NH(_3))</td>
<td>41.013</td>
<td>230.3</td>
<td>0.013</td>
<td>( \frac{4.145}{M_{\text{salt}}} \times (16.9 + 0.00386 \times T(K)) )</td>
</tr>
</tbody>
</table>

In Fig. 3, the saturation temperature curve of ammonia vapour and the equilibrium temperature curves of the desorbed ammonia from metallic salt ammoniates are plotted against the entropy value. The A–B and D–E curves represent the isentropic compression and expansion, respectively, and B–C and E–F curves correspond with the isobaric adsorption of CaCl\(_2\) and MnCl\(_2\) ammoniates, respectively. For a Rankine cycle, the ammonia requires superheating to prevent the presence of liquid and potential expander damage and this makes it unfavourable as a working fluid. In the STEES cycle, it is evident in Fig. 3 that because of the thermodynamic equilibrium of the chemisorption the desorbed ammonia is already in the superheated vapour domain, which favours the vapour expansion. In other words, the STEE cycle alleviates the drawback of ammonia being wet and allows lower temperature heat source usage for electrical power generation. On the other hand, the vapour expansion in the STEES cycle is not just limited by the saturation condition of the working fluid but also the backpressure which is equivalent to the salt-ammoniate adsorption pressure, e.g. the process D–E is also theoretically constrained by the adsorption equilibrium pressure of MnCl\(_2\)-ammoniate at the heat sink temperature (30°C), however fortunately this pressure is usually very low.

(2) By the same principle, in Figs. 2 and 3, the processes A’–B’ and C’–D’ represent the isentropic compression and expansion of the ammonia vapour respectively in a STEES cycle with the CaCl\(_2\)–NaBr combination. The STEES cycle could use a low temperature for CaCl\(_2\)-ammoniate decomposition (A’) if simultaneously assisted by the compression process (A’–B’) when using NaBr as the LTS. The relatively high equilibrium pressure of NaBr-ammoniate makes ultra-low grade heat recoverable, i.e. ambient temperature as shown in the figure, for ammonia vapour expansion (C’–D’), resulting in power and cold generation as the exhausted ammonia is at around −16°C in this example. After the expansion process and cold collection the ammonia vapour can be absorbed by CaCl\(_2\)-ammoniate (A’). The isobaric line, \( \rho_{eq} \) (CaCl\(_2\), 30°C) which is the adsorption pressure of CaCl\(_2\)-ammoniate at the heat sink temperature, demarcates the expansion boundary though it does not affect the expansion since it is lower than the saturation pressure of ammonia at the heat sink temperature (D’).

As illustrated in above Figures, there is great potential to achieve heat upgrading and cold generation using the STEES cycle as well as mechanical power output. The heat output includes the compression heat from the charging process and the adsorption heat of HTS-ammoniates in the discharging process. The former is a relatively small amount of sensible heat and is better to be removed from the compressed fluid in any case. The latter, potentially containing a considerable amount of reaction heat, strongly depends on the adsorbent pairs in terms of the temperature level and quantity. The cold output is the by-product of the ammonia vapour expansion, the limited amount of sensible heat of the expansion exhaust, which is about one order of magnitude smaller than the reaction heat.

3. Analysis methodology

In order to explore the maximum potential benefits of the STEES system for power generation, heat upgrade and cold production, a theoretical investigation of the energy/energy efficiency, energy density, specific capacity and round-trip efficiency of energy storage was carried out using Eqs. (4)–(24). The real gas properties of the ammonia provided by NIST (National Institute of Standard and Technology) have been used in the calculation, other variables and parameters involved are tabulated in Table 1. The heat capacity of the salt ammoniates was estimated by using the method described by Hirata and Fujioka [16], which is expressed as the sum of the heat capacity of the salt and that of ammonia in a condensed phase that is confined within the solid ammoniates. A low temperature range below 100°C and a heat sink temperature of 30°C was used as the studying conditions. The analysed compound adsorbent of salt and expanded graphite has a mass ratio of 3:1 with a bulk density of 450 kg/m\(^3\), as Jin et al. [17] reported with the enhanced thermal conductivity and permeability by the addition of expanded graphite as porous inert matrix, which was 1.7–3.1 W/(m K) and in the magnitude of 10–12–10–11 m\(^2\), respectively, depending on different ammonia uptakes. The metallic reactor is not taken into consideration in the present calculation since various reactor designs reported so far have different sensible heat contribution to the whole system performance, however the present work is aimed to explore the maximum potential of the proposed concept and to provide more generic information.

The sensible heat, total heat input for desorption process, total recoverable heat of adsorption process and the corresponding exergy were calculated based on Eqs. (4)–(8) for both the HTS and LTS.

\[
\begin{align*}
Q_{\text{sen}} &= \int_{T_1}^{T_2} \sum_{i=1}^{3} (m \cdot c_p(T))_i dT \\
&= \int_{T_1}^{T_2} [(m \cdot c_p(T))_{\text{EG}} + (m \cdot c_p(T))_{\text{salt}} + (m \cdot c_p(T))_{\text{NH}_3}] dT \\
Q_{\text{heat,de}} &= Q_{\text{sen}} + \int_{\rho_{\text{eq}}}^{\frac{\Delta H}{\rho_{\text{source}}}} d\rho \\
E_{\text{heat,de}} &= (1 - \frac{T_{\text{amb}}}{T_{\text{source}}}) Q_{\text{heat,de}}
\end{align*}
\]
Q_{\text{upgrade}} = -Q_{\text{en}} + \int_{x_{1}}^{x_{2}} \Delta H_{\text{ab}} \, dx \tag{7}

E_{\text{upgrade}} = \left(1 - \frac{T_{\text{amb}}}{T_{b}}\right) Q_{\text{upgrade}} \tag{8}

\Delta T_{\text{upgrade}} = T_{b} - T_{\text{source}} = T_{\text{eq}}(P_{\text{ad,TRS}}) - T_{\text{source}} \tag{9}

The $Q_{\text{en}}$ used in Eq. (5) as the sensible heat load in the heat input process has $T_{1}$ and $T_{2}$ respectively referred to point C and D in Figs. 2 and 3, while the $Q_{\text{en}}$ used in Eq. (7) as the sensible heat load to be deducted from the total heat output has $T_{1}$ and $T_{2}$ respectively referred to point A and F. Eq. (9) shows the calculation of the temperature lifting, i.e. the upgrading degree. When compression or expansion takes place, the mechanical power input/output, the exergy of mechanical power, the cold energy and exergy possessed by the expansion exhaust, the recovery of compression heat and the corresponding exergy can be expressed as Eqs. (10)–(15), respectively. The cold extracted from the expansion exhaust was assumed to meet the refrigeration requirement at 0°C, i.e. the $\Delta H_{\text{ref}}$ in Eq. (12) was calculated as the difference between the enthalpy of the exhaust at the outlet of the expander and the enthalpy of the ammonia at 0°C and at the same pressure as the exhaust. The recoverable level of compression heat was defined to be higher than 100°C, therefore the $\Delta H_{\text{ref}}$ in Eq. (14) was the enthalpy change of the compressed ammonia during the isobaric recovery process, i.e. the difference between the enthalpy of superheated ammonia at the outlet of compressor and the enthalpy at 100°C and at the same pressure as this exhaust.

\[ W_{i} = m \cdot (h_{\text{out}} - h_{\text{in},r}) \tag{10} \]

\[ E_{w} = W_{i} \tag{11} \]

\[ Q_{\text{ref}} = m \cdot \Delta H_{\text{ref}} \tag{12} \]

\[ E_{\text{ref}} = \left(1 - \frac{T_{\text{amb}}}{T_{\text{ref}}}\right) Q_{\text{ref}} \tag{13} \]

\[ Q_{\text{rec,com}} = m \cdot \Delta H_{\text{rec}} \tag{14} \]

\[ E_{\text{rec,com}} = \left(1 - \frac{T_{\text{amb}}}{T_{\text{rec}}}\right) Q_{\text{rec,com}} \tag{15} \]

Energy and exergy efficiencies of the whole system were evaluated using Eqs. (16), (17):

\[ \eta_{\text{en}} = \frac{U_{\text{output}}}{U_{\text{input}}} = \frac{W_{\text{exp}} + Q_{\text{ref}} + Q_{\text{rec,com}} + Q_{\text{rec,ad}}}{Q_{\text{heat,de1}} + W_{\text{f,com}} + Q_{\text{heat,de2}}} \tag{16} \]

\[ \eta_{\text{ex}} = \frac{E_{\text{output}}}{E_{\text{input}}} = \frac{E_{\text{w,exp}} + E_{\text{ref}} + E_{\text{rec,com}} + E_{\text{rec,ad}}}{E_{\text{heat,de1}} + E_{\text{w,com}} + E_{\text{heat,de2}}} \tag{17} \]

Energy and exergy efficiency of work output was obtained using Eqs. (18) and (19):

\[ \eta_{\text{en,w}} = \frac{W_{\text{f,exp}}}{U_{\text{input}}} = \frac{W_{\text{f,exp}}}{Q_{\text{heat,de1}} + W_{\text{f,com}} + Q_{\text{heat,de2}}} \tag{18} \]

\[ \eta_{\text{ex,w}} = \frac{E_{\text{w,exp}}}{E_{\text{input}}} = \frac{E_{\text{w,exp}}}{E_{\text{heat,de1}} + E_{\text{w,com}} + E_{\text{heat,de2}}} \tag{19} \]

Thermal energy storage density and electrical power storage density of the STEES system can be expressed as Eqs. (20) and (21), respectively. The specific thermal energy storage and the specific electrical energy stored, defined as the amount of energy stored per mass unit of solid sorbent, were calculated by Eqs. (22) and (23), respectively.

\[ Q_{\text{den}} = \frac{Q_{\text{upgrade}} \cdot \rho_{\text{bulk}}}{m_{\text{ad}}} \tag{20} \]

\[ W_{\text{den}} = \frac{W_{\text{f,exp}} \cdot \rho_{\text{bulk}}}{m_{\text{ad}}} \tag{21} \]

\[ Q_{\text{spe,store}} = \frac{Q_{\text{upgrade}}}{m_{\text{ad}}} \tag{22} \]

\[ W_{\text{spe,store}} = \frac{W_{\text{f,exp}}}{m_{\text{ad}}} \tag{23} \]

The round-trip efficiency, $R_{\text{store}}$, defined as the ratio of regenerated work to the input work, is an important parameter to evaluate the performance of electrical power storage, as is the ratio of the electrical power generated at peak-demand to the stored or peak electrical power, which can be assessed by Eq. (24).

\[ R_{\text{store}} = \frac{W_{\text{f,exp}}}{W_{\text{f,com}}} \tag{24} \]
the dramatically surging pressure ratio between LTS desorption and HTS adsorption.

Taking the discharging process of the MnCl$_2$–NaBr pair as an example, the backpressure for the expansion is fixed at the equilibrium pressure of MnCl$_2$–ammoniate for the given heat sink temperature (30 °C in this case). As desorption temperature increasing, the pressure ratio increases as the result of the increasing desorption pressure of the NaBr ammoniate. Despite that, the expansion line which is the vertical distance between the NaBr-ammoniate equilibrium curve and ammonia vapour saturation curve is gradually shortened due to the converging trend of these two curves as the temperature increasing. Therefore the drawback of the wet fluid is only alleviated but still heavily hinders the full expansion. In contrast, although being faced with the same barrier, the CaCl$_2$–ammoniate equilibrium presents superiority over the NaBr–ammoniate equilibrium for ammonia expansion under the same conditions, as visualised in Fig. 3 that the former ammoniate allows the expansion starting state to further steer clear of the saturation curve. In this instance, at least one issue is clear to select the preferable LTS from large numbers of candidates. If NaBr is chosen as the LTS, then the expansion ratio or the expansion degree theoretically would not change much regardless of MnCl$_2$ or CaCl$_2$ being selected as the HTS, because the backpressure of both cases, i.e. the adsorption pressure of HTS ammoniates at heat sink temperature, would be sufficiently low enough to make almost no impact, then the ammonia saturation dominantly restricts the degree of evolution of the vapour expansion. Therefore in Fig. 4, the MnCl$_2$–NaBr cycle and the CaCl$_2$–NaBr cycle have almost the same expansion ratio, the curves overlapping with each other, even though the pressure ratio of the former pair is two orders of magnitude larger than that of the latter pair.

Fig. 5(a) shows the energy input for compression in the charging process and the energy output of expansion in the discharging process. The higher temperature heat source that is used, the less mechanical energy is required to pressurise the desorbed ammonia, due to the mono-variant equilibrium of the chemisorption. The MnCl$_2$–NaBr cycle has the highest energy demand for the compression process under the same conditions because the two salts involved have the biggest equilibrium difference. The work output decreases slightly as the increasing heat source temperature from 30 °C to 100 °C when NaBr was used as LTS, while it varies marginally with the heat source temperature when CaCl$_2$ was the LTS. The reason is prominent in Fig. 3 as the vertical distance, which reflects the expansion capacity, between NaBr equilibrium curve and ammonia saturation curve is gradually shortened as temperature increasing while the CaCl$_2$ equilibrium curve and ammonia saturation curve are nearly-parallel between 30 °C and 100 °C. The MnCl$_2$–CaCl$_2$ cycle out-performs the other two cycles as it almost doubles the work output due to the larger expansion ratio explained in Fig. 4. The CaCl$_2$–NaBr cycle only needs the aid of pressurisation when the heat source temperature is lower than 60 °C, and it could turn to solely-heat-driven power generation cycle once the heat source temperature is higher than 60 °C. The compression curve and expansion curve cross each other at approximately 50 °C. This suggests the cycle could potentially release full mechanical energy from the charging from the heat source at 50 °C, i.e. 100% electricity discharging/charging ratio. The MnCl$_2$–CaCl$_2$ cycle has this critical point at 60 °C, whereas, for the MnCl$_2$–NaBr cycle it exceeds the temperature range studied in this work.

Since the ammonia expansion only utilises a small part of the pressure difference that existing between the HTS and LTS reactors, the remainder can be utilised for the thermal energy discharging process, which is provided by the synthetic enthalpy of the HTS adsorbing the exhausted ammonia from the expander. Fig. 5(b) shows the exhausted vapour pressure from the expansion, especially the cycles those use NaBr as the LTS have the exhaust at relatively high pressure, from 2 bar to 27 bar varying upwards as the $T_{\text{source}}$ raises, while the exhausted pressure of the MnCl$_2$–CaCl$_2$ cycle is from 0.2 bar to 5.5 bar. The STEES cycles can take advantage of the mono-variant nature and convert the unexploited potential of the pressure difference for the heat transformer capability. Fig. 5(b) also shows the temperature lifting of the output upgraded heat comparing to the heat source. The MnCl$_2$–NaBr cycle could upgrade the heat by 70–80 °C and the MnCl$_2$–CaCl$_2$ cycle is capable of a 20–30 °C upgrade. The CaCl$_2$–NaBr cycle is inferior to the other two cycles in term of heat transformation even though it has relatively high adsorption pressure (i.e. exhausted pressure), mainly because the CaCl$_2$ ammoniate has a lower equilibrium temperature than MnCl$_2$ ammoniate at the same pressure.

The overall performance efficiencies of the STEES cycles based on the first and second laws of thermodynamics are presented in Fig. 6(a). Energy efficiency values of these three cycles generally reduce with the increasing heat source temperature. This is mainly attributed to the increasing sensible heat load and the reducing cold energy as the $T_{\text{source}}$ increases and the decreasing compression heat recovery due to a reduced compression requirement for a higher temperature heat source. The MnCl$_2$–NaBr cycle has the advantage of recovering considerable compression heat and achieves slightly higher thermal efficiency among the studied cycles. The MnCl$_2$–CaCl$_2$ cycle has the second highest energy efficiency when the $T_{\text{source}}$ is lower than 60 °C and becomes the lowest one when the $T_{\text{source}}$ exceeds 60 °C. That is mainly because of the
Energy storage density of STEES cycles with different adsorbent pairs. Also raises the threshold of the T source up to 95 °C, whereas the MnCl₂–CaCl₂ cycle appears to have the optimum $\eta_{\text{en},\text{w}}$ value when the $T_{\text{source}}$ is around 60 °C, nevertheless all the $\eta_{\text{en},\text{w}}$ curves are varying marginally against the $T_{\text{source}}$. The Eq. (18) has been used to evaluate the efficiency $\eta_{\text{en},\text{w}}$ and the Fig. 5(a) indicates that the numerator $W_{\text{exp}}$ changes little against the $T_{\text{source}}$ in the studied range. The denominator of Eq. (18), i.e. the total input energy, can be considered as three divided parts: the reaction heat, the sensible heat and the compression work. Since the reaction heat is basically a constant with a given conversion ratio, the increase of the $T_{\text{source}}$ only introduces variation of the sensible heat and the compression work as the former one increases with rising $T_{\text{source}}$ while the latter one adversely changes at the same time. Because these two elements are one order of magnitude smaller than the reaction heat, meanwhile they also offset each other to some extent, the final collective effect on the total input energy against the $T_{\text{source}}$ is relatively modest. All above explains the nearly flat $\eta_{\text{en},\text{w}}$ curves, and the peaked value on the MnCl₂–CaCl₂ curve is speculated as the balanced result of the opposite variation of the sensible heat and the compression work as the increasing $T_{\text{source}}$.

Unlike conventional sensible or latent heat thermal storage, the STEES system stores ultra-low grade heat and releases upgraded thermal energy and can restore the mechanical energy also. Low grade heat conversion relies on an energy source which would otherwise be wasted and therefore energy efficiency is only of secondary importance; the exergy efficiency is more significant. Observing the exergy efficiency curves in Fig. 6(a), as the heat source temperature increases, the exergy efficiency of all three STEES cycles rise to a peak optimal value and then drops down again. Each cycle using different adsorbent pairs performs better for a different heat source temperature range, i.e. the CaCl₂–NaBr, MnCl₂–CaCl₂ and MnCl₂–NaBr cycles are more effective when heat source temperature is lower than 60 °C, between 60 °C to 90 °C, and above 90 °C respectively, with the CaCl₂–NaBr cycle giving the highest efficiency value.

The energy storage density and specific storage capacity for different adsorbent pairs are given in Table 2. The three pairs studied have similar total specific energy storage capacity, including the work output and the upgraded heat output, from around 390 kJ/kg to 466 kJ/kg. In line with the superior work output performance for a different heat source temperature range, i.e. the CaCl₂–NaBr, MnCl₂–CaCl₂ and MnCl₂–NaBr cycles are more effective when heat source temperature is lower than 60 °C, between 60 °C to 90 °C, and above 90 °C respectively, with the CaCl₂–NaBr cycle giving the highest efficiency value.

Both the MnCl₂–NaBr and CaCl₂–NaBr cycles have the slightly declining $\eta_{\text{en},\text{w}}$ profiles against the $T_{\text{source}}$ in Fig. 6(b), whereas the MnCl₂–CaCl₂ cycle appears to have the optimum $\eta_{\text{en},\text{w}}$ value when the $T_{\text{source}}$ is around 60 °C, nevertheless all the $\eta_{\text{en},\text{w}}$ curves are varying marginally against the $T_{\text{source}}$. The Eq. (18) has been used to evaluate the efficiency $\eta_{\text{en},\text{w}}$ and the Fig. 5(a) indicates that the numerator $W_{\text{exp}}$ changes little against the $T_{\text{source}}$ in the studied range. The denominator of Eq. (18), i.e. the total input energy, can be considered as three divided parts: the reaction heat, the sensible heat and the compression work. Since the reaction heat is basically a constant with a given conversion ratio, the increase of the $T_{\text{source}}$ only introduces variation of the sensible heat and the compression work as the former one increases with rising $T_{\text{source}}$ while the latter one adversely changes at the same time. Because these two elements are one order of magnitude smaller than the reaction heat, meanwhile they also offset each other to some extent, the final collective effect on the total input energy against the $T_{\text{source}}$ is relatively modest. All above explains the nearly flat $\eta_{\text{en},\text{w}}$ curves, and the peaked value on the MnCl₂–CaCl₂ curve is speculated as the balanced result of the opposite variation of the sensible heat and the compression work as the increasing $T_{\text{source}}$.

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Fig. 7 shows the round-trip efficiency of electric energy storage, which is defined as the ratio of the discharging to the charging electricity. The CaCl₂–NaBr cycle and MnCl₂–CaCl₂ cycle potentially could fully restore the charging energy when heat is supplied at 50 °C and 60 °C respectively. If the heat is supplied at higher temperature, these two cycles are able to generate additional
power and the round-trip efficiency values dramatically increase up to 500% at 60 °C and 800% at 80 °C, respectively. The maximum value of round-trip efficiency with MnCl₂–NaBr STEES cycle is obtained as 38% when heat source temperature at 100 °C. However, this low round-trip efficiency indicates a larger potential for upgrading heat, e.g. the upgraded heat could be simultaneously delivered at 178 °C.

If the upgraded heat is preferred rather than the additional power, the cycle can be flexibly balanced so that the larger temperature lift could be achieved. The expansion process could be stopped at a certain place before the ammonia reaches its saturation state, then higher HTS adsorption pressure could be achieved for larger temperature lift. Fig. 8 shows the larger temperature lift when maintaining the round-trip efficiency at a maximum value of 100%. Using such a strategy, the temperature lift could be around 16 °C and 38 °C higher than those in the Fig. 5(b) for the CaCl₂–NaBr cycle and MnCl₂–CaCl₂ cycle respectively.

As discussed in Fig. 5(a), the work output capacity of the STEES cycles changes little or decreases slightly with a heat source temperature between 30 °C and 100 °C. Therefore, it is reasonable to drive LTS desorption in the discharging process by using an ambient heat source at 30 °C, which is the same temperature as the heat sink, and therefore the sensible and desorption heat input for LTS in the effective efficiency calculation could be reasonably considered to be zero. With such a considerable reduction in energy input in Eq. (16), the overall thermal efficiency could be expected to be at least 96%, which elevates the values by 50–100% compared to the data shown in Fig. 6(a). The overall exergy efficiency would slightly drop because of the inadequate heat-upgrading as a result of relatively low adsorption pressure of the HTS ammoniate. Fig. 9 shows the exergy efficiencies of work output for both cases, one using the same heat source for the discharging process as used for the charging process and the other using an ambient temperature heat source in the discharging process. If the same heat source was used for both charging and discharging processes, the work output exergy efficiency reduces with increased heat source temperature as the work output was hardly changed but the input desorption heats for both HTS and LTS ammoniates are at higher temperature even though the input compression work reduced. If an ambient heat source is used for LTS desorption in the discharging process whilst a 30–100 °C heat source is used for the charging process, the work output exergy efficiency would be higher, and the counterbalance between the increasing heat input exergy for HTS desorption and the decreasing compression work results in the non-monotone variation of work output exergy efficiency as can be seen from Fig. 9.

5. Conclusion

The potential of the integrated chemisorption cycle for simultaneous electric and thermal energy storage (STEEs cycle) has been explored using an ultra-low grade heat source from 30 °C to 100 °C. In contrast with conventional chemisorption systems, the STEES cycle embraces broader application with higher penetration of renewable energy; not just utilising thermal energy (waste heat, solar energy or geothermal energy) but also potentially storing intermittent electric power, e.g. from solar PV and wind power or off-peak cheap electricity.

The proposed chemisorption cycle stores mechanical or electrical power through compression and effectively recovers the ultra-low grade thermal energy. In the energy discharging process, besides the restored electric power the integrated system would also generate a considerable amount of upgraded thermal energy, plus small amount of cold energy depending on heat source temperature and the refrigeration requirement. The STEES system using three different adsorbent pairs has been studied and compared. The overall thermal efficiency and exergy efficiency of the cycles could achieve from 47% to 100%, and from 62% to 93%, respectively. The efficiency of heat transformation in the STEES cycles has been demonstrated and could increase the temperature of the low-grade heat by between 10 and 80 °C depending on
adsorbent pairs used. Each adsorbent pair has an individual advantage over the others in terms of thermal energy recovery for different heat source temperatures. The systems with the CaCl$_2$–NaBr pair and the MnCl$_2$–CaCl$_2$ pair could achieve 100% and even higher round-trip efficiency for electric energy storage when the heat source temperature is higher than 50 °C and 60 °C respectively. It is worth noting that the three pairs examined are not necessarily the only choices for the application and a great deal of reactant candidates are currently being explored.

Chemisorption is endowed with intrinsic feature of dramatically varying reaction rate, leading to unstable flow rate for compressor and expander. That would obviously affect the efficiency of the mechanical components which are expected to operate in a relatively narrow nominal range. Effective solutions are urged to optimally integrate the batched adsorption cycle with the continuous compressor/expander operation. From the perspectives of steady flow rate and continuous operation, chemisorption is not as ideal as absorption-based cycle for power generation. However, the advantages of chemisorption lies on other aspects, such as higher upgrading level, multiply type energy outputs and high density energy storage. It is certain that more efforts should be made in the future research, many uncertainties and challenges need to be addressed with further evaluation with more realistic parameters and factors and laboratory demonstration.

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References