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Wu, Wei

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Low-temperature compression-assisted absorption thermal energy storage using ionic liquids

Wei Wu
School of Energy and Environment, City University of Hong Kong, Hong Kong, China

ABSTRACT

Thermal energy storage technologies play a significant role in building energy efficiency by balancing the mismatch between renewable energy supply and building energy demand. The absorption thermal energy storage (ATES) stands out due to its high energy storage density (ESD), high coefficient of performance (COP), low charging temperature and wider application flexibility. A hybrid compression-assisted ATES (CATES) using ionic liquid (IL)-based working fluids is investigated to address the problems of the existing ATES cycle. Models for mixture property and cycle performance are established with verified accuracies. Four ILs ([DMIM][DMP], [EMIM][Ac], [EMIM][DEP], and [EMIM][EtSO₄]) are compared with H₂O/LiBr. Results show that the CATES effectively avoid the crystallization, decreases the circulation ratio, lowers the charging temperature, and improves the COP/ESD. H₂O/[DMIM][DMP] has the highest COP and performs better than H₂O/LiBr with generation temperatures above 86 °C, while H₂O/[EMIM][EtSO₄] shows the highest COP with generation temperatures below 75 °C. Among the H₂O/IL mixtures, H₂O/[EMIM][Ac] shows the highest ESD with generation temperatures above 86 °C, otherwise H₂O/[EMIM][EtSO₄] shows the highest. The optimal compression ratio is 1.6–2.8 for H₂O/[DMIM][DMP] under the generation temperatures of 90–70 °C with the maximum COP of 0.758–0.727. The ESD increases significantly with the compression ratio.

1. Introduction

Building energy efficiency plays an important role in mitigating the global warming problems due to the huge energy consumption in building sector, which accounts for 20–40% of the total energy use [1]. Among the building energy use, heating, ventilating and air-conditioning (HVAC) is typically the largest contributor. Renewable energy and waste heat have attracted increasing interests for improving the HVAC energy efficiency. However, most of the existing renewable/waste energy systems suffer from the mismatch (in terms of timing and intensity) between these intermittent energy sources and time-variable building loads. This mismatch will discount the energy saving potentials of renewable/waste energy systems. To address this issue, different thermal energy storage (TES) technologies have been proposed to balance the energy supply from renewable/waste energy sources and the energy demand of buildings [2].

Depending on the principles of energy storage, the TES systems are classified into sensible TES (e.g., heat storage in water, soil, and aquifer), latent TES (e.g., cold storage in ice and cold/heat storage in phase change materials, PCMs), and thermochemical TES (e.g., cold/heat storage via chemical reaction, solid adsorption, and liquid absorption processes) [3]. Different TES systems differ a lot in the energy storage density (ESD), the coefficient of performance (COP) and the applicable charging temperature. Comparing the existing TES technologies, the sensible TES suffers from low ESDs (small capacity of temperature change), while the latent TES has low COPs (low chilled water temperatures for ice storage) or slow charging/discharging processes (low thermal conductivities of PCMs). Among the thermochemical TES systems, the solid adsorption TES typically yields low COPs, while the chemical reaction TES usually requires a high charging temperature (minimum of 200 °C) [4]. Therefore, the liquid absorption thermal energy storage (ATES) stands out owing to its better comprehensive performance, i.e., relatively high ESDs, relatively high COPs, and relatively low charging temperatures. An additional advantage of the ATES systems is that the charged energy can be discharged in various forms including cooling, heating, and dehumidification, offering a wider flexibility in applications than most TES systems.

Working fluids greatly affect the performance of the ATES systems. The H₂O-based [5,6] and NH₃-based [7] solutions have been commonly studied, with the former featuring high COPs and ESDs, and the latter suitable for sub-zero cold storage. Comparisons of the mass-based ESDs of different working fluids under a heat source of 180 °C revealed that NH₃/H₂O showed the highest ESD (95 Wh/kg) for low-temperature cold storage (an evaporating temperature of –20 °C) while NaOH/H₂O yielded the highest ESD (260 Wh/kg) for normal-temperature cold storage (an evaporating temperature of 5 °C) [8]. Comparisons of the ESDs,
The literature review indicated that the current ATES suffers from crystallization of the conventional working fluids, limiting the ESD and system reliability. In addition, the charging temperature of the conventional cycle (minimum of 80 °C) cannot be further decreased while maintaining a satisfactory efficiency. To maximize the ATES’s contribution to energy saving, a hybrid compression-assisted ATES (ATES) cycle using liquid ionic liquids (ILs) as novel working fluids is proposed in this work. Although the current prices of ILs are still high, they are expected to decrease as the market and industry develop.

The ILs have been intensively investigated due to their negligible vapor pressure, good stability and high solubility with various refrigerants [12]. The introduction of ILs greatly enriches the family of absorption working fluids, including H₂O/IL, NH₃/IL, alcohol/IL, HFC/IL, HFO/IL and CO₂/IL [13–16]. However, the current studies on IL-based working fluids are all conducted for absorption chillers or heat pumps, with little research on ATES systems. The only study on ATES using IL-based working fluid is from our previous work [17], which compares the dynamic charging and discharging behaviors of a basic ATES cycle. As for the compression-assisted absorption cycle, it has been widely used to improve the cycle performance by integrating an auxiliary compressor after the evaporator to increase the absorption pressure or before the condenser to decrease the generation pressure [18,19]. This technique has been applied to different cycles (single-effect, multi-effect and GAX (generator absorber heat exchange)) [20–22] for different applications (cooling and heating) [23,24]. However, there is little research on ATES integrated with auxiliary compression, i.e., the proposed ATES cycle. Although the initial cost will be increased, it is still economic due to the significant performance improvement contributed by the auxiliary compression.

The proposed hybrid ATES can be charged at much lower temperatures with high COPs and to more concentrated solutions with high ESDs. The hybrid ATES will be compared with the basic ATES to evaluate the performance improvement. Different IL-based working fluids will be investigated to identify the best-performing alternative.

2. Methodology

The H₂O/IL mixture property model is first introduced, then the ATES thermodynamic model is briefed, and finally the models are validated or verified by the results for relevant references.

2.1. Property method of the H₂O/IL mixtures

We have compared 14 H₂O/IL mixtures with adequate experiment data, using the circulation ratio as an indicator. Among the 14 ILs, [EMIM][Ac], [EMIM][DEP] and [EMIM][EtSO₄] show the lowest circulation ratios in most conditions (Fig. 1). In addition, [DMIM][DMP] has also been widely investigated in absorption cooling systems. Therefore, based on our preliminary screening, four ILs are chosen for further detailed analysis, as listed in Table 1.

The non-random two liquid (NRTL) activity coefficient model is used to describe the vapor-liquid equilibrium (VLE) behavior, which are used to calculate the pressure, temperature or concentration from two of the

<table>
<thead>
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<th>Table 1</th>
<th>Basic information of different ILs.</th>
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<td><strong>Abbreviation</strong></td>
<td><strong>Full name</strong></td>
</tr>
<tr>
<td>[DMIM][DMP]</td>
<td>1,3-dimethylimidazolium dimethylphosphate</td>
</tr>
<tr>
<td>[EMIM][Ac]</td>
<td>1-ethyl-3-methylimidazolium acetate</td>
</tr>
<tr>
<td>[EMIM][DEP]</td>
<td>1-ethyl-3-methylimidazolium diethylphosphate</td>
</tr>
<tr>
<td>[EMIM][EtSO₄]</td>
<td>1-ethyl-3-methylimidazolium ethylsulfate</td>
</tr>
</tbody>
</table>

**Abbreviations**

ATES absorption thermal energy storage

CATES compression-assisted ATES

COP coefficient of performance

ESD energy storage density

HVAC heating, ventilating and air-conditioning

IL ionic liquid

NRTL non-random two liquid

PCM phase change material

TES thermal energy storage

VLE vapor-liquid equilibrium

**Subscripts and Superscripts**

a absorber

c condenser, compressor
e evaporator, electricity
g generator
i species index, isentropic, ideal
L liquid
mix mixing
p pump
r refrigerant
s saturation, strong, solution
w weak

COPs, charging temperatures, economics, and corrosion of different working fluids for long-term solar heat storage indicated that H₂O/IL had high ESD and COP but was too expensive; H₂O/KOH had low cost and high ESD but was too corrosive; H₂O/GaCl₂ was inexpensive but suffered from low ESD, with H₂O/LiBr being the best choice considering different factors comprehensively [9]. However, most of the aqueous salts have a risk of crystallization when the concentration is too high or the temperature is too low in the storage tank. Although some researchers studied the feasibility of three-phase ATES with crystallization [10,11], the accumulated solid crystal might be difficult to dissolve (especially for long-term storage), affecting the composition of the working fluid and the sustainability of the ATES cycle.
three parameters [25]:

\[ Y_i \rho \Phi_i = X_i \rho_i \rho_i^0 (i = 1, 2), \]

where \( X_i \) and \( Y_i \) are the liquid and vapor mole fractions; index 1 and 2 represent H2O and IL, respectively; \( Y_1 \) is 1 due to the neglected IL concentration in the vapor phase; \( p \) is the mixture pressure, kPa; \( \rho_i \) is the saturated vapor pressure, kPa; \( \gamma_i \) is the activity coefficient; \( \Phi_i \) is the correction factor; \( B_i \) is the second virial coefficient, cm\(^3\)/mol; \( V_i^0 \) is the saturated molar liquid volume, cm\(^3\)/mol.

The activity coefficients of the H\(_2\)O/IL mixtures are calculated by Eq. (3)–(6) [25]:

\[ \ln \gamma_1 = X_2^2 \left[ \frac{r_{12} G_{21}}{(X_1 + X_2 G_{21})^2} + \frac{r_{12} G_{12}}{(X_2 + X_1 G_{12})^2} \right] \] (3)

\[ \ln \gamma_2 = X_2^2 \left[ \frac{r_{12} G_{12}}{(X_1 + X_2 G_{12})^2} + \frac{r_{12} G_{21}}{(X_1 + X_2 G_{21})^2} \right] \] (4)

\[ G_{12} = \exp (-\alpha_T r_{12}), \quad G_{21} = \exp (-\alpha_T r_{21}) \] (5)

\[ r_{12} = \frac{\rho_1 + r_{12}^0}{T}, \quad r_{21} = \frac{\rho_2 + r_{21}^0}{T} \] (6)

where \( \alpha, r_{12}^0, r_{12}^1, r_{21}^0, r_{21}^1 \) are adjustable parameters which are regressed from experimental data [26–29]. The regressed adjustable parameters of the four selected mixtures are presented in Table 2.

The enthalpies of the H\(_2\)O/IL mixtures are calculated by Eq. (7)–(9) [29]:

\[ H = X_1 H_1 + X_2 H_2 + \Delta H_{\text{mix}} \] (7)

\[ H_2 = \int_{T_0}^T \frac{C_p \cdot dT}{T} + H_0 \] (8)

\[ H_{\text{mix}} = -R T^2 \left[ X_1 \left( \frac{\partial \ln \gamma_2}{\partial T} \right)_{p, \gamma} + X_2 \left( \frac{\partial \ln \gamma_1}{\partial T} \right)_{p, \gamma} \right] \] (9)

where \( H_1 \) and \( H_2 \) are, respectively the enthalpies of liquid H\(_2\)O and IL, J/mol; \( \Delta H_{\text{mix}} \) is the mixing enthalpy, J/mol; \( T_0 \) is the reference temperature (273.15 K); \( H_0 \) is the reference enthalpy at the reference temperature, J/mol; \( R \) is the universal gas constant (8.314472 J/(mol K)); \( C_{p, \text{IL}} \) is the heat capacity of the IL (J/(mol K)) regressed from experimental data:

\[ C_{p, \text{IL}} = C_0 + C_T T \] (10)

The densities of the H\(_2\)O/IL mixtures are estimated by Eq. (11) and (12) [25]:

\[ \rho = x_1 \rho_1 + x_2 \rho_2 \] (11)

\[ \rho_2 = D_0 + D_1 T \] (12)

where \( x_1 \) and \( x_2 \) are the mass fractions of H\(_2\)O and IL, respectively; \( \rho_1 \) and \( \rho_2 \) are the densities of the liquid H\(_2\)O and IL, kg/m\(^3\). The coefficients of heat capacities (Eq. (10)) and densities (Eq. (11)) of the four selected ILs are listed in Table 3.

2.2. Thermodynamic models of the CATES

Fig. 2 shows the schematic diagram of the CATES, in which a compressor is located between the solution tank and the refrigerant tank. A valve is installed in parallel with the compressor to realize mode switch between the process with compression and the process without compression. In the charging process, the solution tank (acting as the generator) is heated by the external heat source (e.g., renewable energy or waste energy) to generate vapor H\(_2\)O, which is then condensed in the refrigerant tank (acting as the condenser) with the condensation heat removed by the external cooling water. As the vapor H\(_2\)O being generated from
the solution tank, the H₂O/IL solution gets more and more concentrated, thus the thermal energy is stored in the tank. In the discharging process, the liquid H₂O evaporates from the refrigerant tank (acting as the evaporator) while producing cooling effect. The vapor H₂O is then absorbed by the solution tank (acting as the absorber) with the absorption heat removed by the external cooling water. These processes are similar to the normal ATES without compression.

If the available charging temperature is relatively low, the solution IL fraction at the end of the charging process is low. Therefore, the solution IL fraction at the beginning of the discharging process is also low and the absorption process is weak. As a consequence, the performance of the ATES system is worsened. With the assistance of the compression in the discharging process of the CATES system, the absorption pressure is boosted by a factor of compression ratio (CR) [30]. In this manner, the absorption process is strengthened, and the system performance is improved even under relatively low charging temperatures. It is worth noticing that the compressor can also be bypassed by the valve when the available charging temperature is high enough and the CATES is not necessarily better than the normal ATES system. This bypass function can maximize the energy storage performance under different conditions.

It is assumed that the refrigerants leaving the evaporator/condenser are saturated; the solutions exiting the generator/absorber are in equilibrium; the flow resistance, the pressure losses, and the heat losses are ignored; the throttling processes are isenthalpic. This work aims to compare the cycle performance of the CATES to screen novel working fluids (instead of the charging/discharging behavior), so the steady-state equations are used [11]. The dynamic behaviors will be detailed in the future work. The CATES is modeled based on the mass and energy balances [25–29]:

\[
\sum m_{\text{out}} = \sum m_{\text{in}} \tag{13}
\]

\[
\sum m_{\text{out}}x_{\text{out}} = \sum m_{\text{in}}x_{\text{in}} \tag{14}
\]

\[
W + Q + \sum m_{\text{out}}h_{\text{out}} = \sum m_{\text{in}}h_{\text{in}} \tag{15}
\]

where \(m_{\text{in}}\) and \(m_{\text{out}}\) are the inlet and outlet mass flow rates of each component, kg/s; \(x_{\text{in}}\) and \(x_{\text{out}}\) are the inlet and outlet concentrations (refrigerant mass fractions); \(h_{\text{in}}\) and \(h_{\text{out}}\) are the inlet and outlet enthalpies, kJ/kg; \(Q\) is the heat load and \(W\) is the electrical power input, kW.

For absorption cycles, the circulation ratio \(f\), defined as the ratio of the solution pump flow rate to the refrigerant flow rate, is an important performance indicator. The circulation ratio is calculated from the mass conservation of refrigerant:

\[
m_{f}f x_{w} = m_{i} + m_{f} (f - 1) x_{s} \tag{16}
\]

The power of the compressor is calculated by Wu et al. [31]:

\[
W_{c} = m_{i} (h_{\text{dis}} - h_{\text{vac}}) \frac{m_{i} (h_{\text{dis}} - h_{\text{vac}})}{\eta_{i}} \tag{17}
\]

where \(h_{\text{dis}}, h_{\text{dis}}\) and \(h_{\text{dis}}\) are respectively suction enthalpy, discharge enthalpy and ideal discharge enthalpy, kJ/kg; \(\eta_{i}\) is the isentropic efficiency, an index representing the difference of an actual compression in relative to an isentropic compression, and is set to 0.7 in this study [31].

For the absorption cycles with auxiliary compression, the compression ratio (CR) indicating the increment of absorption pressure is defined as:

\[
CR = \frac{p_{a}}{p_{e}} \tag{18}
\]

where \(p_{a}\) and \(p_{e}\) are the absorption pressure and evaporation pressure, respectively, kPa.

The two most important performance indices of the CATES system, COP and ESD, for cold storage are defined as:

\[
COP = \frac{Q_{c}}{(Q_{c} + (W_{c} + W_{p})/\eta_{c})} \tag{19}
\]

\[
ESD = \frac{Q_{c}}{V_{T} + V_{f}} \tag{20}
\]

where \(Q_{c}\) and \(Q_{p}\) are the cumulative cooling capacity during the discharging process and heat input during the charging process, kW; \(W_{c}\) and \(W_{p}\) are the electrical powers of the compressor and pump, kW; \(\eta_{c}\) is the power generation efficiency (45%); \(V_{T}\) and \(V_{f}\) are volumes of the solution tank and refrigerant tank, m³. The volumes of the auxiliary compressor and accessories are not considered following the convention of the studies on ATES systems [32]. This is reasonable considering that the solution and refrigerant tanks typically have much larger volumes.

This work investigates the effect of operating parameters on the cycle performance, while the influence of different types of heat exchangers will be considered in future studies. The software MATLAB [33] is used for the programming.
Due to a lack of studies on the ATES system with IL-based working fluids, the performance data of a normal absorption cooling is used to verify the CATES model. The calculated COPs using the model are compared to those from the reference [29], which adopted a single-effect absorption cooling cycle using H2O/[DMIM][DMP] as working fluid. The condensation, absorption, and evaporation temperature are respectively 40 °C, 30 °C and 10 °C for the comparison. Fig. 4 shows that the two sets of data agree well with each other, in terms of the cooling COP as well as the operating temperature range. The relative deviations are within ±2% in most conditions, indicating high accuracy of the CATES model in predicting the performance of absorption cycles.

3. Performance of the CATES under various temperatures

The circulation ratios, COPs and ESDs of the CATES system using different ILs are compared in this section. The conventional ATES system without compression is included as the baseline cycle while the conventional H2O/LiBr is included as the baseline working fluid. The compression ratio CR is fixed at 1.5 for the CATES system in this section.

3.1. Comparison of circulation ratio

Under a typical cooling condition with a chilled water temperature of 7 °C and a cooling water temperature of 35 °C, the evaporation temperature (T_e) is set to 5 °C and the condensation temperature (T_c) is set to 40 °C. The absorption temperature (T_a) is regarded as the same as T_e with a parallel configuration of cooling water. The generation temperature (T_g), which corresponds to the charging temperature, varies from 70 °C to 100 °C. The circulation ratios of the ATES and CATES using different working fluids are compared in Fig. 5. For both cycles, the circulation ratio decreases fast first and slowly later as the generation temperature increases. When the generation temperature increases to a certain value, the circulation ratio keeps relatively stable, so the charging temperature does not need to be too high. When the generation temperature decreases to a certain value, the circulation ratio is too high or even negative, so the cycle yields very low efficiency or even refuses to work.

Comparing the ATES and CATES cycles, it is found that the CATES can be charged by lower temperatures and the circulation ratio is much lower under the same generation temperature. This is because the absorption pressure is boosted by the compression (from p_0 to CR p_0) and thus the absorption process is strengthened, contributing to larger concentration differences and lower circulation ratios. Comparing different working fluids, it is found that the conventional H2O/LiBr is constrained by crystallization, i.e., there is a risk of crystallization (with a 3% safety margin) when the generation temperature is above 90 °C. Among the H2O/IL mixtures, H2O/[EMIM][EtSO₄] shows the lowest circulation ratio under lower generation temperatures while H2O/[EMIM][Ac] shows the lowest under higher generation temperatures.
3.2. Performance under various generation temperatures

Figs. 6 and 7 compare the COPs and ESDs of the ATES and CATES cycles under various generation temperatures. Compared with the ATES, the CATES can operate under lower charging temperatures. This is because a high enough concentration difference can be obtained under reduced charging temperature with the help of compression. For the CATES, H$_2$O/[DMIM][DMP] has the highest COP and performs better than H$_2$O/LiBr with $T_g$ above 86 °C. When $T_g$ is below 75 °C, H$_2$O/[EMIM][EtSO$_4$] shows the highest COP among all the working fluids. The COP keeps relatively stable for H$_2$O/[DMIM][DMP] with $T_g$ above 90 °C and for other H$_2$O/IL mixtures with $T_g$ above 85 °C. H$_2$O/[EMIM][EtSO$_4$] can operate under 70 °C, so that the CATES can be charged with lower-temperature thermal energy. This can be well explained by the circulation ratio (Fig. 4), i.e., [EMIM][EtSO$_4$] has the lowest circulation ratio under lower generation temperatures.

Compared with the ATES, the CATES yields much higher ESDs. The conventional H$_2$O/LiBr has a risk of crystallization with $T_g$ above 90 °C and has lower ESDs than H$_2$O/[EMIM][EtSO$_4$] with $T_g$ below 76 °C. Given $T_g$ of 100 °C, the ESD is 65.9, 67.6, 55.8 and 55.6 kWh/m$^3$ for H$_2$O/[DMIM][DMP], H$_2$O/[EMIM][Ac], H$_2$O/[EMIM][DEP] and H$_2$O/[EMIM][EtSO$_4$], respectively. Given $T_g$ of 80 °C, the ESD is 22.2, 30.0, 26.9 and 35.5 kWh/m$^3$, respectively. Among the H$_2$O/IL mixtures, H$_2$O/[EMIM][Ac] shows the highest ESD with $T_g$ above 86 °C, while H$_2$O/[EMIM][EtSO$_4$] shows the highest with $T_g$ below 86 °C.

The CATES performance (COP and ESD) characteristics shown here are comprehensively affected by the refrigerant solubility, heat capacity, mixture density and compression ratio. The refrigerant solubility in the solution determines the circulation ratio and operating temperature.
range, the heat capacity determines the generation heat load (energy input for COP calculation), the density determines the solution volume and thus the ESD, while the compression ratio determines the pressure improvement and compressor power.

3.3. Performance under various condensation temperatures

In this section, $T_c$ is fixed at 90 °C, $T_e$ is fixed at 5 °C, and $T_g$ varies from 30 °C to 50 °C. The effect of $T_c$ on the COPs and ESDs of the ATES and CATES cycles are compared in Figs. 8 and 9. Compared with the ATES, the CATES can operate under higher condensation temperatures. This is because a high enough concentration difference can be obtained under increased condensation temperature with the help of compression. For the CATES, $H_2O$/[DMIM][DMP] has the highest COP and performs better than $H_2O$/LiBr with $T_c$ below 42 °C. When $T_c$ is above 47 °C, $H_2O$/[EMIM][EtSO_4] shows the highest COP among all the working fluids. This is mainly due to the lowest circulation ratio of [EMIM][EtSO_4] among all the working fluids under higher condensation temperatures.

The conventional $H_2O$/LiBr has a risk of crystallization with $T_c$ below 40 °C and has lower ESDs than $H_2O$/[EMIM][EtSO_4] with $T_c$ below 47 °C. Among the $H_2O$/IL mixtures, $H_2O$/[DMIM][DMP] shows the highest ESD with $T_c$ below 37 °C, $H_2O$/[EMIM][EtSO_4] shows the highest with $T_c$ above 43 °C, while $H_2O$/[EMIM][Ac] shows the highest with $T_c$ in between.

3.4. Performance under various evaporation temperatures

In this section, $T_e$ is fixed at 90 °C, $T_c$ is fixed at 40 °C, and $T_g$ varies from 2 °C to 20 °C. The effect of $T_e$ on the COPs and ESDs of the ATES and CATES cycles are compared in Figs. 10 and 11. As $T_e$ increases, the COP and ESD of both cycles increase. This is because a higher evaporation means a higher absorption pressure, thus enlarging the concentration
difference for both cycles. For the ATES, H$_2$O/[DMIM][DMP] shows the lowest COP with $T_e$ below 3 °C, due to the lowest circulation ratio. For the CATES, H$_2$O/[DMIM][DMP] has the highest COP and performs better than H$_2$O/LiBr with $T_e$ above 3 °C. H$_2$O/[DMIM][DMP] obtains larger improvement from the compression technique.

Given a high $T_e$ of 20 °C, the ESD is 146.1, 130.7, 116.8 and 156.9 kWh/m$^3$ for H$_2$O/[DMIM][DMP], H$_2$O/[EMIM][Ac], H$_2$O/[EMIM][DEP] and H$_2$O/[EMIM][EtSO$_4$], respectively. Among the H$_2$O/IL mixtures, H$_2$O/[EMIM][Ac] shows the highest ESD with $T_e$ below 8 °C, while H$_2$O/[EMIM][EtSO$_4$] shows the highest with $T_e$ above 8 °C.

4. Optimization of the compression ratio of the CATES

The above analysis uses a fixed compression ratio of 1.5, and the effect of CR on the performance is investigated to identify the optimal CR for the CATES. With CR varying from 1.0 to 3.0, the COPs and ESDs of the CATES using H$_2$O/[DMIM][DMP] under different generation temperatures are presented in Fig. 12. Fig. 12(a) indicates that the COP increases first and decreases later with the CR. This can be explained by that a higher CR strengthens the absorption process and contributes to a larger concentration difference, but a too high CR leads to an increased compressor power per cooling capacity. As a result, there is an optimal CR at which the COP of the CATES reaches the maximum. The optimal CR is 1.6, 2.1 and 2.8 under the generation temperature of 90, 80 and 70 °C. The corresponding maximum COP is 0.758, 0.744 and 0.727, respectively. When the generation temperature is low, the optimal CR is high due to higher compression required for absorption strengthening. For lower generation temperatures, the CATES cannot work if the CR is too low.

Fig. 12(b) indicates that the ESD increases significantly as the CR increases. The ESD reaches 110.9, 92.7 and 62.5 kWh/m$^3$ under the
generation temperature of 90, 80 and 70 °C. If a higher ESD is more desired, a higher CR can be used with a slight sacrifice of COP.

It is summarized that the CR greatly affects the charging temperature, COP and ESD. Therefore, an optimal CR can reduce the operating cost due to maximized COP. In the meanwhile, it can reduce the volumes of storage tanks (and thus initial cost of tanks) due to increased ESD.

5. Conclusions

A hybrid CATES cycle using IL-based working fluids is investigated to avoid crystallization, enhance performance and lower charging temperature of the existing ATES cycles. Models for mixture property and cycle performance are established with verified accuracies. Four ILs ([DMIM][DMP], [EMIM][Ac], [EMIM][DEP], and [EMIM][EtSO4]) are compared with the conventional H2O/LiBr. The main conclusions are as follows:

1. The CATES effectively avoid the crystallization, decreases the circulation ratio, lowers the charging temperature, as well as improves the COP and ESD of the conventional systems;
2. With varying Te, H2O/[DMIM][DMP] has the highest COP and performs better than H2O/LiBr with Te above 86 °C, while H2O/[EMIM][EtSO4] shows the highest COP with Te below 75 °C. Among the H2O/IL mixtures, H2O/[EMIM][Ac] shows the highest ESD with Te above 86 °C, while H2O/[EMIM][EtSO4] shows the highest with Te below 86 °C.
3. With varying Tc, H2O/[DMIM][DMP] has the highest COP and performs better than H2O/LiBr with Tc below 42 °C, while H2O/[EMIM][EtSO4] shows the highest COP with Tc above 47 °C.
Among the H$_2$O/IL mixtures, H$_2$O/[DMIM][DM][DMP] shows the highest ESD with $T_0$ below 37 °C, H$_2$O/[EMIM][EtSO$_4$] shows the highest with $T_0$ above 43 °C, while H$_2$O/[EMIM][Ac] shows the highest with $T_0$ in between.

(4) With varying $T_0$, H$_2$O/[DMIM][DMP] has the highest COP and performs better than H$_2$O/LiBr with $T_0$ above 3 °C. Among the H$_2$O/IL mixtures, H$_2$O/[EMIM][Ac] shows the highest ESD with $T_0$ below 8 °C, while H$_2$O/[EMIM][EtSO$_4$] shows the highest with $T_0$ above 8 °C.

(5) There is an optimal CR to maximize the COP. The optimal CR is 1.6, 2.1 and 2.8 under generation temperatures of 90, 80 and 70 °C with the corresponding maximum COPs of 0.758, 0.744 and 0.727, respectively. The ESD increases significantly with the CR. If a higher ESD is more desired, a higher CR can be used with a slight sacrifice of COP.

It is worth noticing that the viscosities of ILs are typically higher than conventional working fluids, future work includes reducing pressure drop by design optimization and strengthening heat/mass transfer by fluid additives.

Declaration of Competing Interest

The authors declare that they have no known actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations that could have appeared to influence the work reported in this paper.

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