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# Osmotic heat engine using thermally responsive ionic liquids

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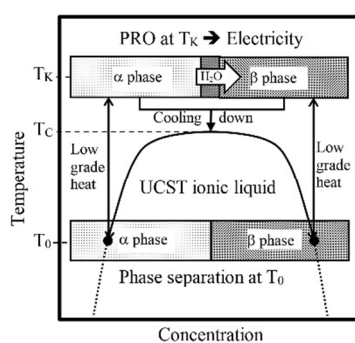
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**ABSTRACT:** The osmotic heat engine (OHE) is a promising technology for converting low grade heat to electricity. Most of the existing studies have focused on thermolytic salt systems. Herein, for the first time, we proposed to use thermally responsive ionic liquids (TRIL) that have either an upper critical solution temperature (UCST) or lower critical solution temperature (LCST) type of phase behavior as novel thermolytic osmotic agents. Closed-loop TRIL-OHEs were designed based on these unique phase behaviors to convert low grade heat to work or electricity. Experimental studies using two UCST-type TRILs, protonated betaine bis(trifluoromethyl sulfonyl)imide ([Hbet][Tf<sub>2</sub>N]) and choline bis(trifluoromethylsulfonyl)imide ([Choline][Tf<sub>2</sub>N]) showed that (1) the specific energy of the TRIL-OHE system could reach as

20 high as 4.0 times that of the seawater and river water system, (2) the power density measured  
 21 from a commercial FO membrane reached up to  $2.3 \text{ W/m}^2$ , and (3) the overall energy efficiency  
 22 reached up to 2.6% or 18% of the Carnot efficiency at no heat recovery and up to 10.5% or 71%  
 23 of the Carnot efficiency at 70% heat recovery. All of these results clearly demonstrated the great  
 24 potential of using TRILs as novel osmotic agents to design high efficient OHEs for recovery of  
 25 low grade thermal energy to work or electricity.

## 26 TOC ART



27

28 **KEYWORDS:** Osmotic heat engine, thermally responsive ionic liquid, low grade heat, pressure-  
 29 retarded osmosis, osmotic pressure

## 30 INTRODUCTION

31 Low grade heat with a temperature below  $120 \text{ }^\circ\text{C}$  is available in abundance not only from various  
 32 industrial processes but also from solar heating, geothermal energy, nuclear power and so on. It  
 33 is estimated that more than 50% of the energy in industry eventually ends up as low grade heat  
 34 due to process inefficiency.<sup>1, 2</sup> The concept of using OHE to recover low grade heat was first  
 35 proposed by Loeb in 1975 based on a pressure-retarded osmosis (PRO) process that uses a  
 36 semipermeable membrane to harvest the salinity gradient energy (SGE) and then uses low grade  
 37 heat to regenerate the salinity gradient.<sup>3</sup> Compared with other technologies that are currently  
 38 under development such as the Rankine cycle, Sterling engines and solid-state devices based on

39 the Seebeck effect, and so on, OHE is easy scalability, requires no addition of chemicals, and  
40 produces zero discharge.<sup>1,4</sup>

41 The osmotic agent is the working medium of OHE. The first proposed osmotic agent is simply a  
42 sodium chloride solution. Due to a small change in the boiling point of NaCl solution with  
43 concentration, this approach is limited by its low efficiency.<sup>5</sup> Hence, most OHE studies have  
44 focused on thermolytic salt systems for which solubility changes dramatically with temperature.<sup>6</sup>

45 The most famous example is probably the NH<sub>3</sub>-CO<sub>2</sub> system developed by Elimelech et al. By  
46 using a conventional steam stripping system to regenerate the solution, the overall efficiency was  
47 improved to around 1%.<sup>7</sup> A broader range of OHE devices include also electrochemical  
48 concentration cells and capacitive mixing or mixing entropy batteries.<sup>8-16</sup> Ammonia has a low  
49 molecular weight, which on the one hand offers the advantage of high solubility and therefore a  
50 high power density, whereas on the other hand it causes a high membrane cross-over rate which  
51 reduces the efficiency. Furthermore, its toxicity and unpleasant odor make it difficult to handle.

52 Hence, developing a good osmotic agent is still a large challenge in OHE development.

53 Herein, we propose a novel idea of using thermally responsive ionic liquids (TRILs) as the  
54 osmotic agent. Ionic liquids (ILs) are electrolytes with a melting point typically lower than room  
55 temperature.<sup>17</sup> They are often considered as green solvents and have found broad applications in  
56 catalysis, separation, food and pharmaceutical processes, and so on.<sup>17, 18</sup> Thermally responsive  
57 ionic liquids have phase diagrams with either an upper critical solution temperature (UCST) or a  
58 lower critical solution temperature (LCST). In our previous reports we demonstrated that both  
59 UCST- and LCST-types of ILs can be used as novel draw solutions in the forward osmosis  
60 processes for water desalination.<sup>19,20</sup> As an osmotic agent, ILs have a number of advantages. ILs  
61 are electrolytes that can dissociate into ions and generate higher osmotic pressure. ILs are

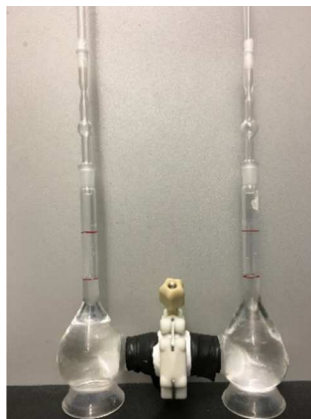
62 typically large molecules, which minimize the crossover issue. ILs are liquids. The phase  
63 separation is much faster than other thermally responsive agents such as polymers, and it will not  
64 cause membrane fouling or flow blocking.<sup>21</sup> ILs have high boiling points and low vapor  
65 pressures, reducing the potential material loss during heating/cooling cycles. Hence, TRILs are  
66 expected to be a very promising type of osmotic agent. The disadvantages of ILs are high cost,  
67 high viscosity, and low diffusion coefficient that may leads to large concentration polarization.

68 The specific energy (SE) and power density (PD) are two figure-of-merit parameters for an  
69 OHE. The specific energy is determined by the Gibbs energy of mixing, which is determined by  
70 the maximum osmotic pressure difference. Power density is a property primarily related to  
71 membrane performance, but it is also related to the maximum osmotic pressure difference  
72 because from process design studies it was found that the maximum power density occurs  
73 typically at the condition when the retarded pressure is equal to half of the maximum osmotic  
74 pressure difference.<sup>22</sup> Hence, the maximum osmotic pressure difference is a critical value.  
75 Herein, we use two UCST-type ILs, protonated betaine bis(trifluoromethylsulfonyl)imide  
76 ([Hbet][Tf<sub>2</sub>N]) and choline bis(trifluoromethylsulfonyl)imide ([Choline][Tf<sub>2</sub>N]), to illustrate the  
77 OHE concept and to demonstrate the potential performance from osmotic pressure  
78 measurements.

## 79 MATERIALS AND METHODS

80 **Materials.** [Hbet][Tf<sub>2</sub>N] (> 99%) and [Choline][Tf<sub>2</sub>N] (> 99%) were purchased from Shanghai  
81 Chengjie Chemical Co., Ltd. Sodium chloride (>99.5%) was purchased from Sigma-Aldrich. All  
82 chemicals were used as received without further purification. Water purified by a Milli-Q (Milli  
83 Pore) system was used as fresh water in all experiments.

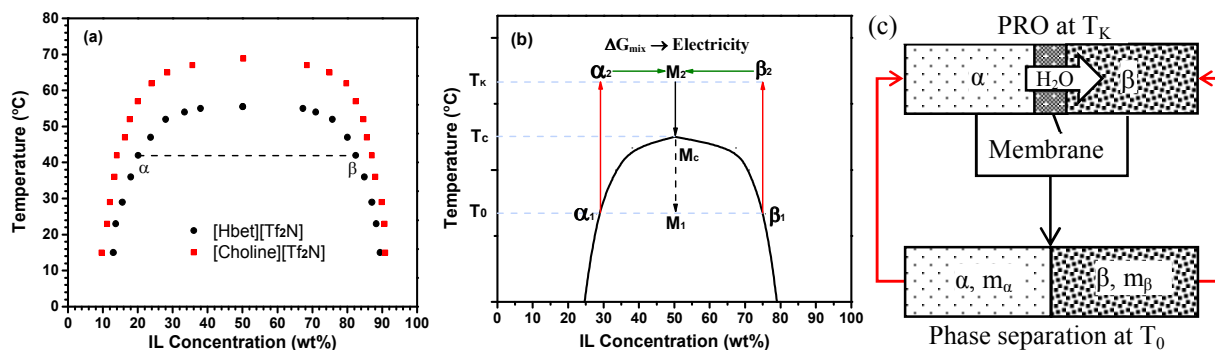
84 **Measurements.** The primary method to measure the concentration of IL and NaCl solutions is  
85 through conductivity (Thermo Scientific™ Orion™ 5 STAR and Orion™ 013005MD  
86 Conductivity Cell). The solution needs to be diluted to low down the concentration to the linear  
87 response region. For mixtures containing both IL and NaCl, the conductivity measurement gives  
88 the total ionic concentration. In this case the concentration of NaCl is determined through  
89 measurement of chloride by an Aquakem 250 photometric analyzer (Thermo Scientific). The  
90 concentration of IL was also verified by two methods: (1) UV-vis spectra (Cary 5000) if it is UV  
91 sensitive, and (2) for the  $\beta$  phase (IL-rich phase), the water content was measured by a standard  
92 Karl Fischer Titrator (Mettler Toledo, C30X). The heat capacity of IL solution was detected by a  
93 differential scanning calorimetry (Mettler Toledo DSC 1). The heat of mixing was measured by a  
94 C80 calorimeter (Setaram). The solution density was determined from weight and volume  
95 measurements. The osmotic pressure was measured by a custom-designed forward osmosis setup  
96 as shown in Fig. 1. The setup contains two glass chambers, one filled with IL solution and the  
97 other with NaCl solution. A polyamide reverse osmosis membrane (Toray, UTC-73AC), which  
98 has a good salt rejection rate, was placed in the middle of the two chambers. The whole setup  
99 was maintained at the working temperature  $T_K$  by immersion in a water bath. An equivalent  
100 NaCl solution having the same osmotic pressure as the IL solution was found by adjusting the  
101 concentration of the NaCl solution until water transport through the membrane in both ways was  
102 observed. The concentrations of NaCl and IL in both solutions were measured after the  
103 experiment to ensure that the leakage rate across the membrane was negligible.



104

105 **Figure 1.** A custom-designed apparatus for osmotic pressure measurement.106 **RESULTS AND DISCUSSION**

107 Fig. 2a shows the phase diagrams of the two ILs. Both phase diagrams exhibit a critical  
 108 temperature  $T_c$ , above which the IL is completely miscible with water but under which the  
 109 mixture separates spontaneously into a water-rich phase (denoted as  $\alpha$  phase) and an ionic  
 110 liquid-rich phase (denoted as  $\beta$  phase).



111

112 **Figure 2.** (a) Phase diagrams of [Hbet][Tf<sub>2</sub>N] and [Choline][Tf<sub>2</sub>N] aqueous solutions; (b)  
 113 Illustration of an TRIL-OHE loop on the phase diagram; (c) illustration of an TRIL-OHE by a  
 114 PRO process.

115 Based on the UCST phase behavior, a novel closed-loop TRIL-OHE was designed as illustrated  
 116 in Fig. 2b and Fig. 2c. The most studied pressure-retarded osmosis (PRO) process was used to

117 demonstrate the energy conversion process in Fig. 2c, but other commonly studied processes  
 118 such as reverse electro dialysis (RED) and capacitance mixing (CM) can also be used. All of  
 119 these processes have 100% ideal efficiency if conducted reversibly<sup>4, 11, 23</sup>. The TRIL-OHE loop  
 120 includes three stages. The first stage starts from a temperature  $T_0$  (for example, room temperature  
 121 23°C) which should be lower than the critical temperature  $T_c$ . The equilibrium pair of  $\alpha$  and  $\beta$   
 122 solutions obtained at  $T_0$  are heated separately to a working temperature  $T_K$  that should be above  
 123 the critical temperature and then placed in the two sides of a semipermeable membrane which  
 124 allows the transport of water only. The second stage is the PRO process that is conducted  
 125 reversibly at  $T_K$  by applying a pressure equal to the osmotic pressure difference of the two  
 126 solutions to the  $\beta$  phase. Water is drawn from the  $\alpha$  phase to the  $\beta$  phase by osmotic pressure  
 127 which increases the volume of the  $\beta$  phase and in turn generates either mechanical work or  
 128 electricity. Because  $T_K$  is above the critical temperature, a single phase will eventually form after  
 129 mixing. The mixture is then cooled in the third stage to the initial temperature  $T_0$ , regenerating  
 130 the original two phases. Table 1 lists all the operation parameters of the TRIL-OHE loop  
 131 assuming to generate 1000 kg mixture after the PRO process.

132 **Table 1.** Operation conditions of the TRIL-OHE loop for the two IL systems

IL	$T_c$ (°C)	$W_c$ (wt%)	$\mu$ (Pa·s)	$T_0$ (°C)	$W_\alpha$ (wt%)	$W_\beta$ (wt%)	$m_\alpha$ (kg)	$m_\beta$ (kg)	$T_K$ (°C)
[Hbet][Tf <sub>2</sub> N]	55.6	50.1	0.030	23.0	13.7	88.3	512.06	487.94	60.0
[Choline][Tf <sub>2</sub> N]	68.9	50.2	0.024	23.0	11.2	90.7	509.43	490.57	74.0

133  $T_c$ , critical temperature;  $W_c$ , critical concentration;  $\mu$ , viscosity measured at  $T_K$ ;  $T_0$ , initial  
 134 temperature;  $W_\alpha$ , concentration of  $\alpha$  phase at  $T_0$ ;  $W_\beta$ , concentration of  $\beta$  phase at  $T_0$ ;  $m_\alpha$ , amount  
 135 of  $\alpha$  phase;  $m_\beta$ , amount of  $\beta$  phase;  $T_K$ , working temperature.

136

137 The maximum energy that can be extracted out of SGE is the Gibbs mixing energy, which in  
 138 principle can be calculated from thermodynamic models.<sup>24-26</sup> Most of these models, however,



139 contain empirical parameters which are not available due to the limit of experimental data.  
140 Hence, herein the Gibbs mixing energy was obtained through experimental measurement of the  
141 osmotic pressure based on the following equation:

$$142 \quad \Delta G_{mix} = - \int_0^V \Delta \pi dV \quad (1)$$

143 where  $\Delta \pi$  is the osmotic pressure difference between the  $\alpha$  and  $\beta$  phases, and  $V$  is the total  
144 amount of water drawn from the  $\alpha$  to  $\beta$  phase during the PRO process. Unfortunately, the  
145 osmotic pressure of TRILs cannot be measured by commercial osmometers because they  
146 typically utilize colligative properties such as the decrease in melting point. Therefore, a custom-  
147 designed forward osmosis (FO) setup was built as shown in Fig. 1.

148 The mechanism of measurement was to use the sodium chloride solution as a reference to find  
149 the equivalent osmotic pressure of the ionic liquid solution by observing the transport of water in  
150 a trial-and-error fashion. If the osmotic pressures of the two solutions are equal, then no water  
151 should pass through the membrane. Otherwise water will be extracted from the solution with a  
152 lower osmotic pressure to the solution with the higher one. During the experiment, one container  
153 was filled with sodium chloride solution with a known concentration while the other was filled  
154 with an ionic liquid solution with a known concentration. The whole setup was immersed into a  
155 circulation bath to maintain the temperature at the working temperature  $T_K$ , which was selected  
156 as approximately 5 °C above the critical temperature in this study. The osmotic pressures of the  
157 NaCl solution at different salt concentrations are available from a reference<sup>27</sup> and shown in Fig.  
158 3a.

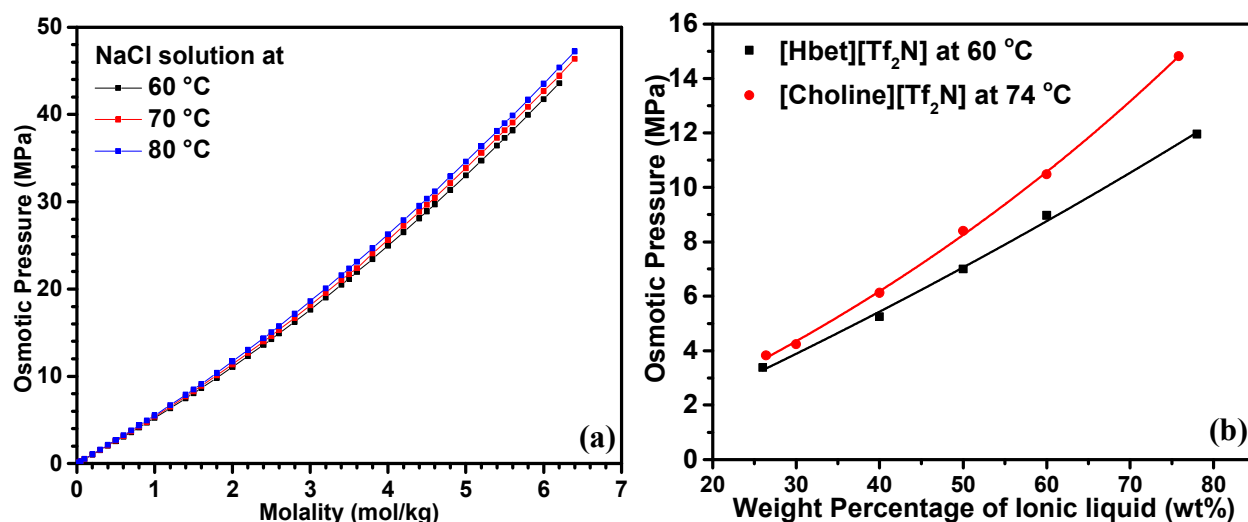
159 Table 2 shows an example of how the equivalent osmotic pressure of a 1.14 M (40 wt%)  
160 [Hbet][Tf<sub>2</sub>N] solution was determined at  $T_K = 60$  °C. A 1.035 M NaCl solution was first tested.

161 After 22 hours, it was found that 0.792 g of water was extracted from the ionic liquid to the NaCl  
 162 solution, indicating that the equivalent osmotic pressure of the ionic liquid solution should be  
 163 lower. Hence, the concentration of the NaCl solution was lowered to 1.0 M, then to 0.937 M, and  
 164 finally to 0.92 M. The amount of water extracted from the ionic liquid to NaCl became  
 165 increasingly lower until a reverse transport of water was observed at the last measurement. The  
 166 average value of the last two measurements was used as the final result. The error of  
 167 measurement of this approach is estimated to be less than 1%. Table 2 also showed the total  
 168 conductivity ( $\kappa$ ) of the solutions before and after each trial, and the conductivity in parenthesis  
 169 showed the contribution from the minor component, i.e. NaCl in IL solution or IL in NaCl  
 170 solution. As the data shown, the changes in total conductivities before and after each trial  
 171 matched very well with the direction of water transport, verifying the accuracy of our  
 172 measurements. For example, when water was extracted from IL solution to NaCl solution, the  
 173 conductivity of IL solution increased while that of NaCl solution decreased, or vice versa. The  
 174 minor component is due to leakage during experiment. Their conductivities were less than 0.5%  
 175 of the total conductivity, indicating that the leakage rate was very small. Based on the FO  
 176 measurements, the equivalent osmotic pressure of the two ILs at different IL concentrations are  
 177 shown in Fig. 3b.

178 **Table 2.** Osmotic pressure detection for a 1.14 M (40 wt%) [Hbet][Tf2N] water solution at 60 °C

Trial	IL Conc. (M)	NaCl Conc. (M)	Time (h)	Water Pass (h)	Water Flux (LMH)	IL side (dilute 5 times)			NaCl side (dilute 100 times)		
						$\kappa$ _before (ms/cm)	$\kappa$ _after (ms/cm)	(0.047)	$\kappa$ _before ( $\mu$ s/cm)	$\kappa$ _after ( $\mu$ s/cm)	(1.10)
1	1.14	1.035	22	0.792	0.068	19.57	20.27	(0.047)	1322	1307	(1.10)
2	1.14	1.000	22	0.509	0.044	20.27	20.94	(0.046)	1196	1182	(1.19)
3	1.14	0.937	21	0.057	0.006	20.03	20.12	(0.043)	1013	1005	(1.14)
4	1.14	0.920	20	-0.055	-0.006	20.06	19.98	(0.042)	965	974	(1.15)

179



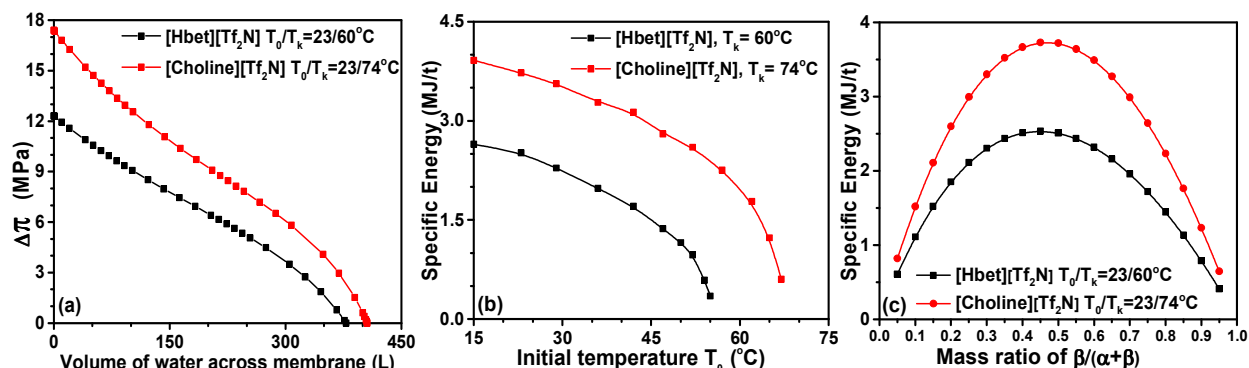
180  
181 **Figure 3.** (a) Osmotic pressure of NaCl aqueous solution at different molality and temperature.  
182 Data obtained from a reference;<sup>27</sup> (b) osmotic pressures of the two IL solutions at different  
183 weight percentage measured at  $T_K$ .

184 The Gibbs mixing energy can then be calculated as follows. Assuming  $f(x)$  is the function of the  
185 equivalent osmotic pressure at weight percentage  $x$ , which can be data fitted from Fig. 3b, and  $V$   
186 is the amount of water extracted from the  $\alpha$  phase to the  $\beta$  phase, then the osmotic pressure  
187 difference of the two phases  $\Delta\pi$  can be calculated from the following equation:

$$188 \quad \Delta\pi = f\left(\frac{m_\beta W_\beta}{m_\beta + \rho V}\right) - f\left(\frac{m_\alpha W_\alpha}{m_\alpha - \rho V}\right) \quad (2)$$

189 where  $m_\alpha$ ,  $W_\alpha$ ,  $m_\beta$ , and  $W_\beta$  are the amount and the weight percentage of the  $\alpha$  and  $\beta$  phases,  
190 respectively, and  $\rho$  is the density of pure water. The total amount of ionic liquid  $m_\alpha + m_\beta$  was  
191 fixed at 1000 kg. The concentrations of the  $\alpha$  and  $\beta$  phases were determined by the initial  
192 temperature  $T_0$ . It was further assumed that after mixing the mixture had the same concentration  
193 as the critical concentration. Then  $m_\alpha$  and  $m_\beta$  in Equation (2) can be calculated accordingly. Fig.  
194 4a shows the relationship of  $\Delta\pi$  vs.  $V$  of the two ionic liquid systems when the initial  
195 temperature was fixed at room temperature (23 °C). The areas under the curves are the maximum

196 Gibbs mixing energy per 1000 kg of the total mixed ionic liquid solutions, or the specific energy,  
 197 SE, of the system. Fig. 4b shows the specific energies at different initial temperatures.  
 198 Obviously, the lower the initial temperature, the higher is the concentration difference between  
 199 the  $\alpha$  and  $\beta$  phases and thus the higher the specific energy. At 23 °C, the specific energy was  
 200 approximately 2500 kJ/t for [Hbet][Tf<sub>2</sub>N] and 3700 kJ/t for [Choline][Tf<sub>2</sub>N]. It is worthy to note  
 201 that the specific energy between regular seawater and river water was approximately 912 kJ/t.<sup>28</sup>  
 202 Thus, the specific energy of the two ionic liquids are approximately 1.74 and 3.06 times higher.  
 203 The specific energy can be further optimized in terms of the mass ratio of two phases. Fig. 4c  
 204 shows the specific energy at different  $m_{\beta}/(m_{\alpha}+m_{\beta})$ . The optimal ratio was found to be 1.157 for  
 205 [Hbet][Tf<sub>2</sub>N] and 1.075 for [Choline][Tf<sub>2</sub>N]. Interestingly, these ratios were exactly the same  
 206 values after mixing when the concentration of the mixture was equal to the critical concentration.



207  
 208 **Figure 4.** (a) Osmotic pressure difference at different amounts of water drawn across the  
 209 membrane from the  $\alpha$  to  $\beta$  phase at the working temperature  $T_K$ , (b) specific energy at different  
 210 initial temperature  $T_0$ , and (c) the specific energy at different  $m_{\beta}/(m_{\alpha}+m_{\beta})$  ratios from the room  
 211 temperature  $\alpha/\beta$  pair.

212 Power density (PD) is a measure of the energy generated per unit time and unit membrane area.  
213 It is an important performance index of the PRO process. The gross power density can be  
214 calculated as the product of water flux  $J_w$  and the hydraulic pressure difference  $\Delta P$ .

$$215 \quad PD = J_w \Delta P \quad (3)$$

216 In the ideal case,

$$217 \quad PD = A(\Delta\pi - \Delta P)\Delta P \quad (4)$$

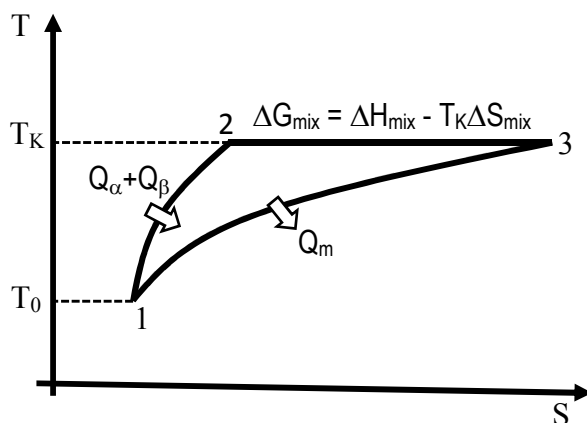
218 It reaches the maximum when  $\Delta P = \pi_{max}/2$ <sup>22</sup> and thus,

$$219 \quad PD_{max} = \frac{1}{4} A \Delta\pi_{max}^2 \quad (5)$$

220 The maximum osmotic pressure difference  $\Delta\pi_{max}$  in Equation (5) can be read directly from Fig.  
221 4a, but the water permeability coefficient,  $A$ , is a membrane property. From the osmotic pressure  
222 measurements, it was found that the commercial HTI© membrane, which is made from cellulose  
223 acetate and often used for FO or PRO processes, was not stable in the ionic liquid. Hence, during  
224 the osmotic pressure measurement a commercial polyamide membrane (Toray, UTC-73AC) that  
225 is typically used for reverse osmosis was used as the semipermeable membrane. The membrane  
226 was found to be very stable even after hundreds of hours of testing. It has a good salt rejection  
227 rate, which is beneficial for our fundamental studies to obtain the maximum Gibbs mixing  
228 energy. However, the disadvantage of this membrane is its low water flux which will lead to low  
229 power density. Another commercial FO membrane HTI OsMem™ TFC-ES Membrane was  
230 found stable and gave relatively higher water flux. The measured water flux between the  $\alpha$  and  $\beta$   
231 phases were 1.71 LMH for [Hbet][Tf<sub>2</sub>N] at 60 °C and 1.95 LMH for [Choline][Tf<sub>2</sub>N] at 74 °C.  
232 Using the ideal equation (4) the  $A$  values were calculated to be 0.014 LMH/bar for [Hbet][Tf<sub>2</sub>N]  
233 and 0.011 LMH/bar for [Choline][Tf<sub>2</sub>N]. Correspondingly, the maximum power density  
234 calculated from Equation (5) gives 1.5 W/m<sup>2</sup> for [Hbet][Tf<sub>2</sub>N] and 2.3 W/m<sup>2</sup> for

235 [Choline][Tf<sub>2</sub>N]. These values are comparable to many reports for the seawater-river water  
236 system.<sup>29, 30</sup> It should be noted that the A values were estimated without considering  
237 concentration polarization, which is a well-known issue in FO and PRO processes that leads to  
238 reduced driving force across the membrane.<sup>31</sup> Hence, the intrinsic A values without centration  
239 polarization should be larger and the corresponding power density should be higher.<sup>32</sup> Recently,  
240 a number of high-flux polyamide type of thin film composite (TFC) membranes have been  
241 successfully developed for the PRO process with A value reached up to 1 LMH/bar.<sup>33</sup> Hence,  
242 there should be a big room for further improvement of the power density for the TRIL-OHE  
243 system in order to meet the economic requirements.<sup>34</sup>

244 The temperature vs. entropy of the TRIL-OHE cycle is shown in Fig. 5. In the first stage, the  
245 system requires  $Q_{\alpha} + Q_{\beta}$  amount of heat to increase the temperature from  $T_0$  to  $T_K$ . The entropy  
246 of the system will increase with temperature roughly by amount of  $(C_P^{\alpha} + C_P^{\beta}) \ln \frac{T_K}{T_0}$ . In the  
247 second stage, the PRO process operates isothermally, thus temperature will keep constant, but  
248 since it is a spontaneous mixing process, so entropy will increase by amount of  $\Delta S_{mix}$ . The  
249 system in this stage may adsorb or release heat depending on the heat of mixing  $\Delta H_{mix}$ . In the  
250 third step, the mixture is cooled down from  $T_K$  to  $T_0$ , and the system recovers back to the original  
251 state. The heat released from the third stage,  $Q_m$ , should be able to be recovered by a heat  
252 exchanger coupling with the first stage.



253  
254 **Figure 5.** Temperature-Entropy diagram of a TRIL-OHE cycle  
255

256 Based on the above T-S diagram, the energy balance of each step and the overall energy  
257 efficiency can be calculated as below. The heat required for stage one is calculated by,

$$258 \quad Q_{\alpha} + Q_{\beta} = m_{\alpha} \int_{T_0}^{T_K} C_p^{\alpha} dT + m_{\beta} \int_{T_0}^{T_K} C_p^{\beta} dT \quad (6)$$

259 and the heat released in stage three is calculated by,

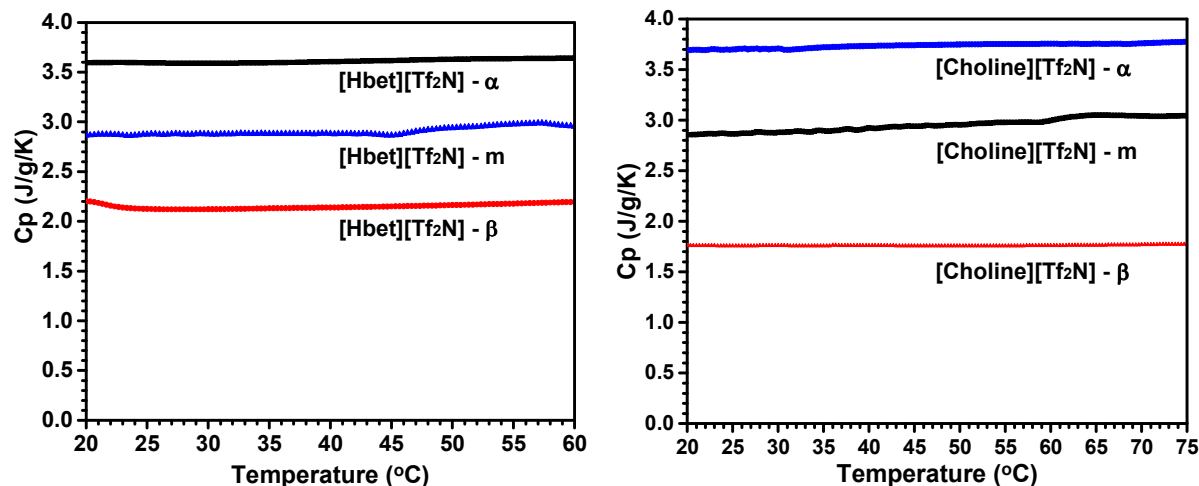
$$260 \quad Q_m = (m_{\alpha} + m_{\beta}) \int_{T_0}^{T_K} C_p^m dT \quad (7)$$

261 where  $C_p^{\alpha}$ ,  $C_p^{\beta}$  and  $C_p^m$  are the heat capacities of the  $\alpha$  phase,  $\beta$  phase and mixture, respectively,

262 and their values at different temperatures are shown in Fig. 6a and 6b. It is noted that the mixture

263 will undergo phase separation during cooling. Hence,  $C_p^m$  is the overall value of the two phases.

264 The energies involved in each step of the TRIL-OHE loop are listed in Table 3.



265  
 266 **Figure 6.** (a) Heat capacity of [Hbet][Tf<sub>2</sub>N] in the process temperature range, (b) Heat capacity  
 267 of [Choline][Tf<sub>2</sub>N] in the process temperature range.

268 **Table 3.** Energy at each step of the TRIL-OHE loop. All calculations are based on 1000 kg of  
 269 mixture and the operation conditions listed in Table 1.

IL	$\Delta G_{mix}$ (kJ)	$\Delta H_{mix}$ (kJ)	$Q_{\alpha}+Q_{\beta}$ (kJ)	$Q_m$ (kJ)
[Hbet][Tf <sub>2</sub> N]	$-2.52 \times 10^3$	44	$1.072 \times 10^5$	$1.075 \times 10^5$
[Choline][Tf <sub>2</sub> N]	$-3.73 \times 10^3$	-190	$1.412 \times 10^5$	$1.507 \times 10^5$

270  
 271 It is interesting to find  $(m_{\alpha} + m_{\beta})C_P^m \approx m_{\alpha}C_P^{\alpha} + m_{\beta}C_P^{\beta}$ , and  $Q_m \approx Q_{\alpha} + Q_{\beta}$ . It implies that  
 272 the heat released from the third stage can be largely recovered through a heat exchanger coupling  
 273 with the first stage. Assuming the recovery rate is  $\eta$ , then the overall energy efficiency is,

$$274 \quad E = -\Delta G_{mix} / (Q_{\alpha} + Q_{\beta} - \eta Q_2 + \Delta H_{mix}) \quad (8)$$

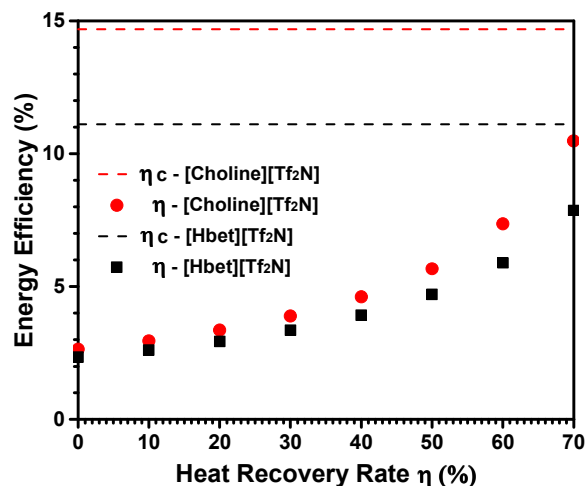
275 Carnot efficiency is calculated by,

$$276 \quad E_C = (T_K - T_0) / T_K \quad (9)$$

277 The Carnot efficiency for [Hbet][Tf<sub>2</sub>N] system is around 11.1% and for [Choline][Tf<sub>2</sub>N] system  
 278 around 14.7%. Fig. 7 shows the energy efficiency at different heat recovery rate. If assuming the  
 279 average temperature difference of the heat exchanger is about 10°C, it is estimated that about



280 70% heat of the [Hbet][Tf<sub>2</sub>N] system and about 80% heat of the [Choline][Tf<sub>2</sub>N] system can be  
281 recovered. As can be seen in Fig. 7, without heat recovery the energy efficiency is about 2.4%  
282 for [Hbet][Tf<sub>2</sub>N] system and about 2.6% for [Choline][Tf<sub>2</sub>N] system, or 21% and 18% of their  
283 Carnot efficiency, respectively. While at 70% heat recovery, the efficiencies can reach as high as  
284 7.9% and 10.5%, or 71% and 71% of the Carnot efficiency for the two IL systems, respectively.



285

286 **Figure 7.** The energy efficiency at different heat recovery rate.

287 Based on the unique phase diagrams of two UCST type of ionic liquids, [Hbet][Tf<sub>2</sub>N] and  
288 [Choline][Tf<sub>2</sub>N], a novel closed-loop TRIL-OHE was designed to convert low grade thermal  
289 energy to electricity. The osmotic pressures of the two ionic liquids were measured using a  
290 custom-designed FO setup using NaCl solution as a reference. From the osmotic pressure data,  
291 the specific energy and the power density, two performance metric parameters of OHE, were  
292 estimated. The specific energy increases when the initial temperature decreases. When the initial  
293 temperature is set at room temperature (23 °C), the specific energy of the [Hbet][Tf<sub>2</sub>N] system  
294 was around 2500 kJ/t and that of the [Choline][Tf<sub>2</sub>N] system around 3700 kJ/t, which are 2.7 and  
295 4.0 times the seawater and river water system, respectively. The maximum power density  
296 measured from a commercial FO membrane is about 1.5 W/m<sup>2</sup> for the [Hbet][Tf<sub>2</sub>N] system and

297 2.3 W/m<sup>2</sup> for the [Choline][Tf<sub>2</sub>N] system. The power density is obtained from a relatively low  
298 permeable membrane. There should be still a big room to improve the power density if highly  
299 permeable membranes are used. During the experiment, it was found that the cellulose acetate  
300 type of membranes were not stable in ionic liquid solutions, but this was not an issue for  
301 polyamide type of membranes. The temperature-entropy diagram of the TRIL-OHE loop was  
302 analyzed. A notable advantage of the TRIL-OHE was revealed from the energy balance, that is,  
303 the heat released from the cooling stage can be largely recovered. A rigorous energy balance  
304 showed without heat recovery the energy efficiency was about 2.4% or 21% of the Carnot  
305 efficiency for the [Hbet][Tf<sub>2</sub>N] system, and about 2.6% or 18% of the Carnot efficiency for the  
306 [Choline][Tf<sub>2</sub>N] system, while at 70% heat recovery, the energy efficiency increased to 7.9% or  
307 71% of the Carnot efficiency and 10.5% or 71% of the Carnot efficiency for the two ionic liquid  
308 systems, respectively. All of these results clearly demonstrated the superior performance of the  
309 TRIL-OHE system. Therefore, this concept provided a very promising way to design efficient  
310 OHEs for waste heat recovery.

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327 Y. Zhong and X. Wang did most of the experimental measurements and data analyses. S.  
328 Telalovic contributed to the heat of capacity measurements. Z. Lai prepared the manuscript. Z.  
329 Lai, and X. Hu conceived the TRIL-OHE concept. X. Feng, K-W. Huang and Y. Gnanou  
330 contributed to the design of the thermally responsive ILs.

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**333 ABBREVIATIONS**

334  $\alpha$  phase, water-rich phase;  $\beta$  phase, ionic liquid –rich phase; CM, capacitance mixing; FO,  
335 forward osmosis; IL, Ionic liquids; TRIL, thermally responsive ionic liquid; LCST, lower critical  
336 solution temperature; UCST, upper critical solution temperature; OHE, osmotic heat engine; PD,  
337 power density; RED, reverse electro dialysis; SE, specific energy; SGE, salinity gradient energy;  
338  $T_c$ , critical temperature;  $T_0$ , initial temperature;  $T_K$ , working temperature; TFC, thin film  
339 composite.

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419 **Table of Contents and Graphic Synopsis**

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