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Review of osmotic heat engines for low-grade heat harvesting

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HIGHLIGHTS

- The architectures of the osmotic heat engines are presented and reviewed.
- The main components of osmotic heat engine system are overviewed.
- Outlook and technological challenges outlining the research perspectives are discussed.
- Some other state-of-art heat-to-work thermodynamic systems are introduced.

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ABSTRACT

Osmotic heat engines (OHEs) consisting of a separation unit for separating the salt solution into two solutions with different concentrations and a power generation unit for extracting electricity from the mixture of the two solutions generated in the separation unit has attracted increasing attention as an emerging “low-grade heat to power” technology. In this study, a comprehensive review of OHEs is presented for the first time. The common types and characteristics of the main component of osmotic heat engine system are overviewed. The architectures of the OHEs classified as reverse electrodialysis heat engines, pressure retarded osmosis heat engines are presented and reviewed. Some other state-of-art heat-to-work thermodynamic systems are also introduced briefly. Furthermore, the potential application of osmotic heat engines is discussed and a critical assessment of osmotic heat engines is conducted. Outlook and technological challenges outlining the research perspectives are also discussed in this review, and the results reveal that practical application of OHE considering the distinct characteristics of application scenarios should be further emphasized. Substantial improvement in membrane performance and cost would favor the emergence of OHE in a commercial scale.

1. Introduction

Securing a robust energy supply has been identified as a prerequisite for sustainable development. The major energy supply originates from the combustion of non-renewable primary energy under the current energy structure. In addition, the anticipated population growth will bring two billion new energy consumers by 2050 and the global energy consumption will increase by 48% between 2012 and 2040 as estimated [1,2]. However, the primary energy resources are finite and the excessive combustion of fossil fuels induces severe environmental problems, hence improving energy utilization efficiency and exploiting renewable and sustainable energy are urgently required [3]. It is estimated that 72% of the primary energy is lost as waste heat and emitted into environment due to the inefficient conversion in the thermodynamic cycle, and 63% of the waste heat arises below 100 °C [4]. Moreover, vast waste heat also can be obtained from renewable energy resource such as solar energy, geothermal energy and biomass energy [5]. It is evaluated that the conventional hydro-geothermal resources in China are equivalent to 1.25 trillion tons of standard coal [6], and most of which are utilized as low temperature water below 150 °C. Therefore, developing efficient thermodynamic system to harvest low-grade heat contributes to alleviating the energy resources shortage and environmental deterioration.

Traditional “heat to electricity” technologies include Organic Rankine Cycle (ORC), Kalina Cycle (KC), which are both suitable for operation temperatures ranging from 100 to about 300 °C due to the vapor-liquid characteristics of their working fluids [7]. Some innovative technologies for utilizing low-grade heat have also been proposed, such as thermoelectric generator (TEG) [8], Carbon Carrier Cycle (CC) [9], Piezoelectric Generator (PG) [10] and Stirling Engine (SE) [11]. Osmotic heat engine (OHE) also as a novel waste heat to electricity technology,

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which is based on the regeneration and mixing of two solutions with different concentrations, has been attracted considerable attention recent years. In an osmotic heat engine, salt solution is separated into two streams with different concentrations, then the Gibbs free energy of mixing of the two generated solutions is converted into electricity, meanwhile the working solution is restored to the initial concentration to prepare for the next cycle. Among the technologies mentioned above, OHE is more superior due to the following advantages [12,13]: They have no environmental risk even if employing toxic working fluids thanks to the closed-loop configuration. In addition, the closed-loop allows the use of a certain amount of artificial solution and system performance optimization by selecting salts and solvents. The artificial working fluid also minimizes the corrosion and scaling in system. Moreover, OHEs can operate under ultra-low temperature of 40 °C, which surpasses any other technologies. In a recent review, Brogioli et al. [14] proposed a framework based on energy efficiency and power density of the novel proposed low-grade heat harvesting technologies to compare the performances reported in the literature. A detailed discussion of the physical limitations, possible improvements and future research lines is also discussed. Different performance of similar system reported in previous papers can be attributed to the different assumptions about heat exchangers [14]. To give a fair comparison of different technologies for exploiting low-temperature, homogeneous assumptions on the heat exchangers is necessary. Performance comparison of low-grade heat harvesting technologies reported in previous literatures under a uniform basis of assuming a temperature difference across heat exchangers of 5 K is depicted in Fig. 1 [14].

In this study, we focus on the system architectures and a detailed review for architectures of osmotic heat engine, which is an emerging "low-grade heat to work" technology, is discussed and evaluated for the first time. The common types and characteristics of the main component of OHE system are stated. The architectures of the OHEs are reviewed based on numerous relevant literatures recapitulated in this study. Some other state-of-art heat-to-work thermodynamic systems are also introduced briefly. Furthermore, the potential application of OHEs is discussed and a critical assessment of OHEs is conducted. Outlook and technological challenges outlining the research perspectives are also discussed in this review.

2. Main components of OHE system

The Osmotic heat engine generally consists of a separation component that separates the salt solution into two solutions with different concentrations driven by heat or power and a power generation component that extracts electricity from the mixture of the two solutions generated in the separation component. The common types and characteristics of the two main components will be further detailed in this section.

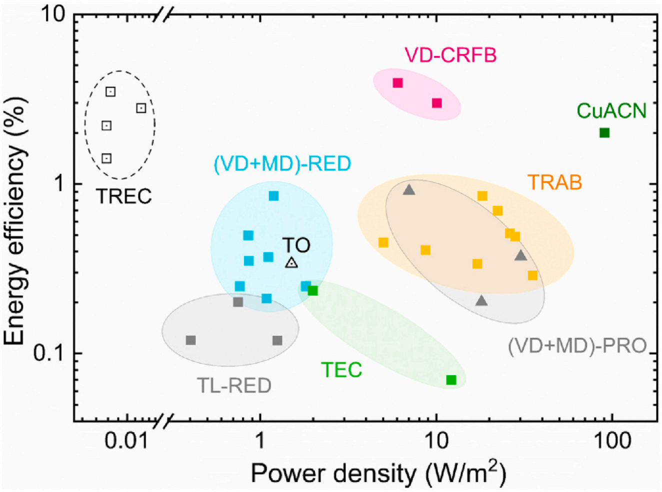

Fig. 1. Performance comparison of low-grade heat harvesting technologies reported in previous literatures under a uniform basis of assuming a temperature difference across heat exchangers of 5 K [14].

2.1. *Separation component*

The main categories for salt solution separation in the osmotic heat engines can be classified into thermal-driven and power-driven separation according to the type of energy employed to drive the process. In the thermal process, separation can be accomplished by either extracting pure solvent from salt solution with the phase change of evaporation or removing the thermolytic salts in the thermal regenerative solutions which are easily decomposed by heat [7]. And the power-driven separation process is usually associated with membrane technology.

2.1.1. *Thermal-driven separation*

Compared with power-driven separation, thermal-driven technologies require lower electric consumption and can operate with low temperatures which allow for efficiently harvesting low-grade heat and expanding the potential application range [16]. Multi-effect distillation (MED) is a well-established commercial technique with a desalination market share of 7% by 2019 and the highest efficiency among all thermal desalination technologies, the electrical and thermal specific energy consumption of per m^3 water production for MED at below 70 °C are 1.5 kWh and 6 kWh, respectively [17–20]. In MED system, the salt solution is thermally evaporated with the aid of a heat source in the first stage, then the latent heat of the vapor is utilized in the following stage for evaporation and the condensed steam from each stage is collected to produce diluted solution, therefore, the heat is reused by stage sequentially [21]. Membrane distillation (MD) is a thermal-driven separation process combined with membrane technology. The advantages of low operation temperature, low technical complexity and low construction cost make MD a competitive technology for small scale separation component of OHE. In MD process, the membrane allows water vapor to pass through while preventing the liquid solution, and the phase changing of liquid solution into vapor at feed stream side caused by thermal energy results in a vapor pressure difference across the hydrophobic membrane interfaces, which drives the vapor to pass through and condense at the permeate stream side, realizing the extraction of pure solvent [22–24]. According to the different mechanisms of vapor condensation at permeate side, MD can be generally divided into four different subtypes: Direct Contact Membrane Distillation (DCMD), Vacuum Membrane Distillation (VMD), Air Gap Membrane Distillation (AGMD) and Sweeping Gas Membrane Distillation (SGMD) [18]. Recently, adsorption desalination (AD) as a novel desalination technology, which can utilize even lower temperature waste heat down to 40 °C than MED and MD, has become a preferred separation component of OHE [25]. In AD, the solvent transforms the phase into vapor in the evaporator driven by hydrophilic adsorption particles and is adsorbed by adsorbent, then the vapor is repelled from the adsorption material by a heat source and travels into the condenser, generating diluted solution [26–28]. All of the technologies mentioned above are achieved by extracting pure solvent from salt solution, salt extraction can be another scheme for thermal separation, where the ammonium bicarbonate (NH_4HCO_3) is always employed as thermolytic salt [29]. Ammonium bicarbonate-based solution can be decomposed into carbon dioxide and ammonia gases and removed with low-grade heat around 60 °C to produce diluted solution, meanwhile the concentrated solution can be prepared by dissolving the gaseous species. The energy consumption in thermolysis-based regeneration process was further explored by McGinnis et al. [30], and the relationship between the quantity of the energy required and the heat quality (i.e. temperature of the heat) is revealed.

Several papers [31–33] have performed thermodynamic analysis of distillation-based techniques to evaluate the efficiencies of thermal-driven desalination process and emphasized the role of the boiling point elevation that working solutions with higher boiling point elevation favored higher energy efficiency. Ref. [32] revealed that for a single-effect distiller, the efficiency of single-effect distiller is constrained by a function of boiling point elevation and a large boiling point elevation results in higher efficiency. For multiple-effect distillation, the efficiency is limited by the ratio between the boiling point elevation and the temperature drop across the heat exchangers, where the efficiency advantage of higher boiling point elevation still persists. A detailed thermodynamic analysis of representative distillation process using temperature-entropy graph for qualitatively interpreting the physical limitation can be found in ref. [31]. It is also stressed that high concentration working solution is required to improve the performance of thermal-driven desalination process [14], and highly soluble salts is promising as they provide higher boiling point elevation [34].

2.1.2. Power-driven separation

Another separation technology in OHE requires external power input. Reverse osmosis (RO) has been a most widely adopted desalination technology accounting for 69% of the global desalination capacity [19]. In reverse osmosis (RO) process, a hydrostatic pressure is applied artificially to the concentrated side to counter the nature osmotic pressure, resulting in an opposite direction of solvent flux to that dictated by natural osmosis. Then a semi-permeable membrane which allows solvent to permeate into the diluted stream while preventing salts to pass through is employed, achieving separation. Electrodialysis (ED) is a power-driven separation technology with the aid of the external direct current (DC), which is in commercial over 10 years prior to reverse osmosis [18]. When electrodes are connected to an external DC power supply, cations/anions are forced to directionally pass through the alternately installed cation/anion exchange membrane (CEM/AEM) driven by the electrical current and then blocked by the adjacent membrane in the electrodialyser, thus separating the ions from the main stream, producing diluted and concentrated solutions in the alternating channels.

Compared with thermal-drive separation, the electric consumption of power-drive separation is relatively high. A detailed comparison between all the separation technologies mentioned above are summarized in Table 1, where gain output ratio (GOR) reflects the energy efficiency of the thermal separation technology driven by external heat source, which is defined as the ratio of water production to heat consumption. Distillation efficiency of some thermal-drive separation technologies in distillation-SGP (salinity gradient power) processes defined as the ratio of Gibbs free energy of mixing to the heat consumption has also been reported in some literatures [15,31,32]. The distillation efficiency fulfils the fundamental physical limitations and is related to the working solution type, system configuration and heat recovery.

Table 1
A detailed comparison between the separation technologies.

Technology	Separation principle	GOR	Electricity consumption (kWh/m^3)	Ref.
MED	Thermal-driven	9–18	2–2.5	[35–37]
MD	Thermal-driven	2.1–11.2	0.6–1.8	[35]
AD	Thermal-driven	0.43–1.43	Around 1.38	[38–41]
Thermolytic separation	Thermal-driven	4.4–20.2	Less than 0.25	[30]
RO	Power-driven	–	2.5–7	[35]
ED	Power-driven	–	0.7–5.5	[37,42,43]

2.2. Power generation component

The fundamental of the power generation component in OHE is to convert the Gibbs free energy released by mixing the two solutions of different concentrations generated in separation component into electricity. Several technologies are reported to capture energy from Gibbs free energy, among them, reverse electrodialysis (RED) and pressure retarded osmosis (PRO) are the most representative and best developed.

The concept of RED is first proposed by Pattle in 1954 and then wildly investigated over the past decades [44]. A typical RED configuration consists of an anode chamber, a cathode chamber and a membrane stack where CEMs and AEMs are alternatively assembled to form flow channels of concentrated solution and diluted solution [45,46]. In RED process, anions and cations in high concentration compartment are transferred to the low concentration compartment in opposite directions through AEMs and CEMs driven by salinity gradient, which can be directly converted into electricity via the redox reaction on the electrodes and further extracted by an external load [47]. Many works on RED have been conducted, which covered the key research topics of modeling and simulation [48–50], stack design [51,52], membrane development [53–56], performance optimization [57–61] and hybrid applications [7,62–64], indicating the great potential for harvesting salinity gradient energy. Recently charged nanochannels are also employed to function as the CEMs or AEMs, thus to augment the power extracted [65–69]. PRO was first proposed by Leob [70] in 1973 as an osmotic process to convert Gibbs free energy into electricity, and the development has been hindered by the lack of adequate membrane for many years [71]. With the development of membrane technology, the performance of PRO has been greatly improved, and according to the review of Lee et al. [72], it has higher power density and greater efficiency than other salinity energies. In the PRO system, concentrated and diluted solutions are separated on both sides by a semi-permeable membrane [73]. Taking advantage of the inherent osmotic potential due to the salinity gradient, the solvent in the low concentration side permeates to the pressurized high concentration side, then a hydro-turbine is employed to generate electricity while depressurizing [74].

Recently, a relatively novel family of SGP technologies based on alternately injected high and low concentration solutions are also proposed to exploit salinity gradient energy: capacity mixing (CapMix) based on electrical double layer [75–77] and mixing entropy battery (MEB) based on electrode reaction with specific ions [78–80]. Since batteries and capacitors are collectively known as accumulators, the whole technique family is called accumulator mixing (AccMix). At variance with RED and PRO, in which the high and low concentration solutions simultaneously flow on both sides of the membrane, two solutions is sequentially filled in the cell of AccMix device with two electrodes dipped in it. The power generation process consists of four steps [81]: (1) the electrodes dipped in high concentration solution is charged by external device. (2) The circuit is opened and the high concentration solution in the cell is substituted with the low concentration solution. (3) The cell is discharged through an external load and the flow direction of current is opposite to step (1). (4) The circuit is opened and the low concentration solution in the cell is substituted with the high concentration solution. Currently the performance of AccMix is slightly inferior to RED and PRO in terms of efficiency and power density, however it is still in the research stage and is very promising, especially MEB can overcome the dilemma of reduced efficiency at extremely high concentrations due to the weakened membrane permselectivity [82]. The application of such technique for power generation component of OHEs is worthy of further evaluation and development.

3. Osmotic heat engine architectures

In this section, different osmotic heat engine architectures classified as reverse electrodialysis heat engines and pressure retarded osmosis heat engines are presented and reviewed based on numerous relevant literatures recapitulated.

3.1. RED heat engines

The idea of converting low-grade heat into electricity via a closed-loop RED heat engine was first proposed in 1979 by Loeb [83]. Thanks to the progress of membrane technologies in recent years, RED heat engine has attracted more and more attention and has been extensively studied.

In the RED heat engine, the types of salts in the system impact not only RED process but also thermal separation process, which further determines the performance of the entire system, thus selecting an appropriate salt solution with specific properties is significant. Most literatures reported mainly focused on NaCl as working solution employed in RED heat engine, the researches of system performance with salts other than NaCl were also indispensable. Micari et al. [84] experimentally investigated the behavior of pure uni-univalent salts (LiCl, NH_4Cl and NaCl) and salt equimolar binary mixtures (NaCl-NH_4Cl, NH_4Cl-LiCl and NaCl-LiCl) in the RED unit of the OHE, the results showed that for pure salt-water solutions, NH_4Cl performed best in the experimental concentration range (0.5–5 M), while LiCl led higher power density at larger concentration. And as regards the salt mixtures, the stack electrical resistance was lower than that of the two corresponding pure salts in some cases, resulting in higher power density. Giacalone et al. [33] theoretically analyzed the effect of non-conventional working salts (LiCl, NaAc, CsAc and KAc) on the performance of the RED heat engine, which combined RED and single or multi stage evaporative regeneration unit. The key parameters of the molality related activity and osmotic coefficient for these salts in the Pitzer's model were reported though experiment at temperature range of 20–90 °C, which expended the application scope of Pitzer's model for acetate salts. A highest thermal efficiency of 13% and a corresponding exergy efficiency of 50% were observed for LiCl and KAc with concentration of 15–17 mol/kg. Luo et al. [85] compared artificially prepared $NaHCO_3$, Na_2CO_3 and NH_4Cl solutions with river-sea nature solution to investigate the effects of ion composition on the potential across ion exchange transmembrane, results indicated the potential of RED has a greater potential for recovery salinity gradient energy with artificially prepared mixed solutions than with natural seawater, and a higher power density of 0.174 W/m^2 was obtained with 0.49 M NaCl+0.01 M NaHCO3|0.01 M $NaHCO_3$. Ortega-Delgado et al. [34] introduced a performance analysis of a RED-MED osmotic heat engine with a comprehensive mathematical model, two different working salts (NaCl and KAc) were comparatively evaluated and the impacts of the operation temperature and the MED effects number are investigated. Results showed that under the operation temperature of 80 °C and 12 MED effects, KAc with a thermal efficiency of 9.4% is a better working salt for RED heat engine than NaCl with a thermal efficiency of 6.3%, which can be attributed to the higher activity coefficient and solubility of KAc under 80 °C and 12 MED effects.

For integrated system like osmotic heat engine, operation and structure conditions play an important and complex role in determining system performance and some works have been conducted to investigate the influence of operation conditions. Long et al. [63] presented a hybrid MD-RED system for converting low-grade heat into electricity as shown in Fig. 2, the impacts of relative permeate/feed solution flow rate in MD on the system performance in terms of power output, mass recovery rate and specific heat duty were systematically evaluated. The effects of working concentration of NaCl solution and heat source temperature, were also discussed. Results indicated that there existed an optimal relative flow rate to maximum the electrical efficiency, larger concentration elevated the electrical efficiency and when operated with 5 mol/kg NaCl solution under heat source temperature ranging from 20 to 60 °C, an electrical efficiency of 1.15% was obtained. Hu et al. [86] conducted a detailed mathematical simulation of a MED-RED heat engine as shown in Fig. 3 to investigate the influence of structure and operation parameters on system performance. Results showed that the increase of initial concentration, heat source temperature and MED effects number all contributed to enhancing the system performance. The energy conversion efficiency can reach to 1.01% when operated under hot and cooling water temperature of 80 and 20 °C with 10 effects and 5.40 mol/kg NaCl solution. Despite the obtained efficiency of MED-RED system was lower than that of the MD-RED system mentioned above, the performance of MED, which required lower specific heat duty, still better than that of MD in the literature [63]. The low efficiency can be attributed to the resistance correction factor and permselectivity correction factor considered in RED model. Hu et al. [87] further considered adopting multi-stage reverse electrodialysis (MSRED) structure instead of traditional RED in order to alleviate the internal resistance loss caused by the decrease of the concentration difference at downstream of RED feed solution [88]. Two MSRED control schemes of independent control strategy and serial control strategy were theoretically studied, and the effects of high concentration (HC) compartment thickness, feed solution velocity, concentration and flow arrangement on the performance of the MSRED were discussed. The results demonstrated that reducing the thickness of the HC compartment, increasing the concentration and employing counter-flow arrangement all enhanced the performance, and serial control can be more suitable for practical application. Palenzuela et al. [89] also evaluated the impact of working concentration, velocity of the solution on a MED-RED heat engine through sensitivity analyses, results indicated that the increase of high salinity feed concentration induced higher total energy required and power generation, which was consistent with the conclusion of the previous literature.

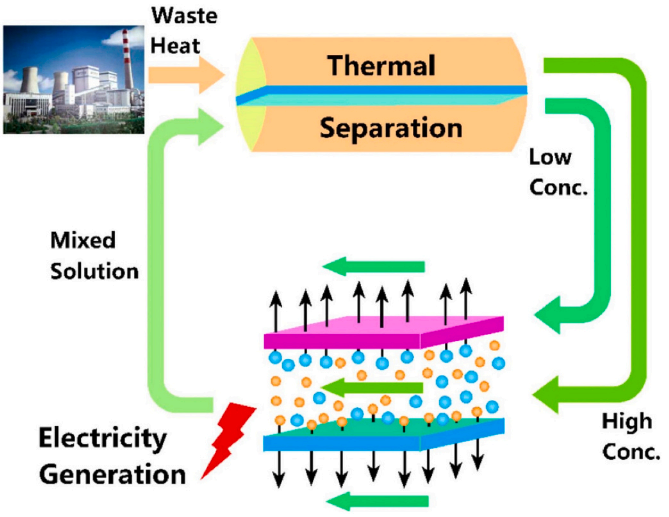

Fig. 2. Schematic diagram of a hybrid MD-RED system [63]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Adsorption desalination is also a great candidate for the thermal separation component in OHE due to the advantage of low temperature required and low electricity consumption. No literatures about AD-RED configuration have been reported until 2018, Olkis et al. [25] explored the combination of AD and RED for converting low-grade heat into electricity for the first time. A steady-state model was established to analyze the system performance with 300,000 different combinations of 227 salts and 10 adsorbents and the optimal combination was screened. The results showed that an exergy efficiency of about 30% can be obtained with the optimized system. Then they further develop the investigation of AD-RED osmotic heat engine which harvested waste heat from power plant [90]. A dynamic AD model validated with experimental data in their work combined a validated RED model was employed. The results of the simulation under different heat integration

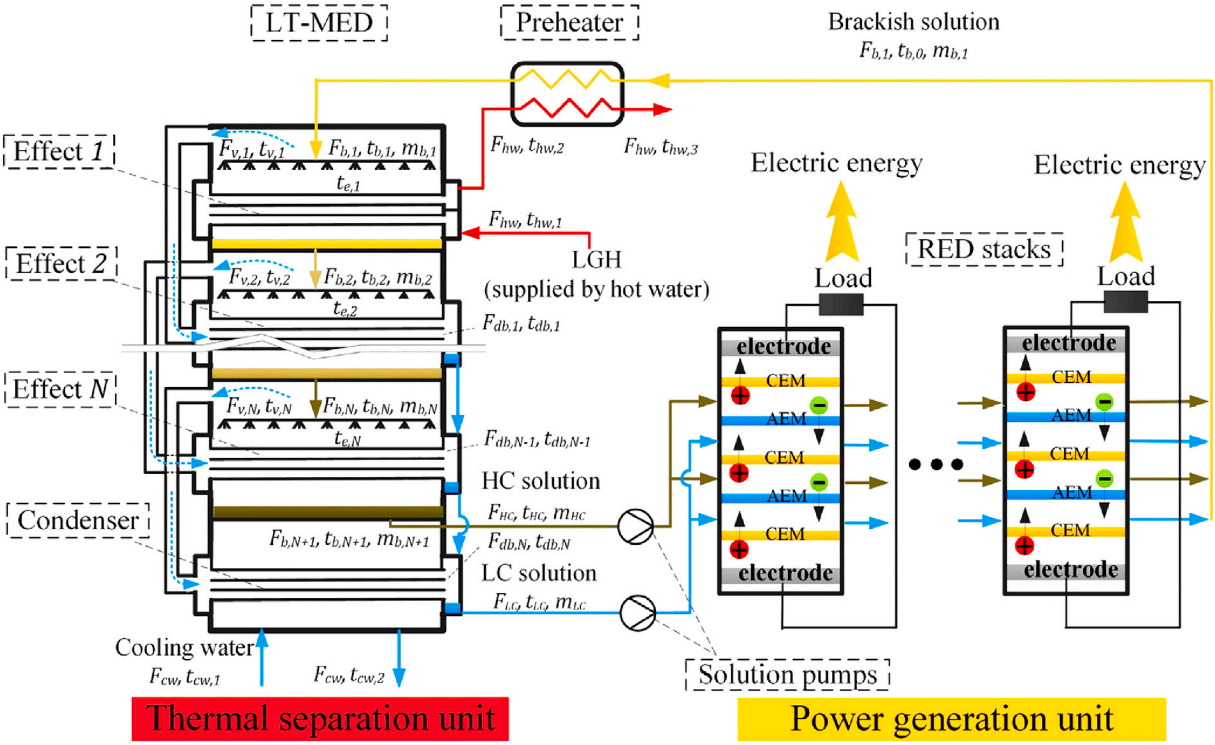

Fig. 3. Schematic diagram of a hybrid MED-RED system [86]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

scenarios presented exergy efficiencies of 10%–15% and energy efficiencies of 0.35–0.55%. At almost the same time, dynamic modeling and analysis of a power and cooling cogeneration AD-RED system as shown in Fig. 4 was conducted by Zhao et al. [62]. In their study, cooling power produced in AD unit was not ignored, but considered as system output. The effects of working concentration, solution mass, adsorption/desorption time, switching time and adsorbent types on the system performance, which was characterized in terms of electric efficiency, exergy efficiency and coefficient of performance (COP), were investigated. Results revealed that longer adsorption/desorption time led to degraded electrical efficiency and exergy efficiency, and upgraded COP. Extended switching time contributed to COP and exergy efficiency, however, decreased the electric efficiency. Larger salt concentration improved the electric efficiency, however degraded the exergy efficiency and COP. Increasing working solution mass can augment the electrical efficiency, exergy efficiency and COP. CUA-10 performed best

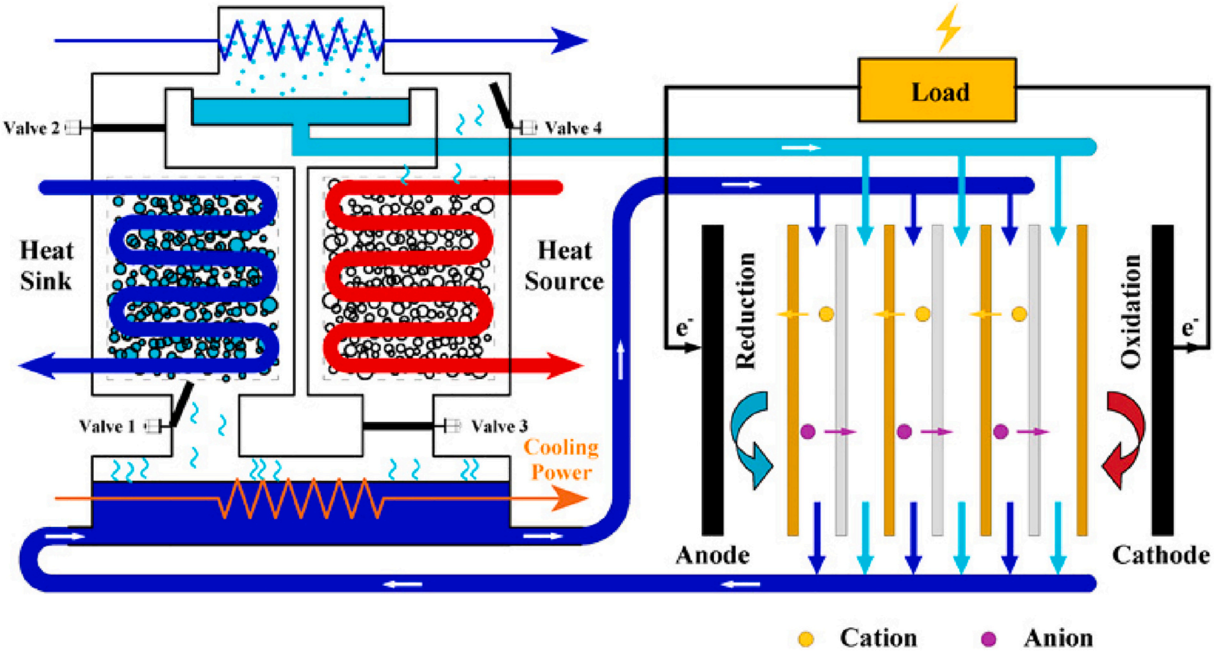

Fig. 4. Schematic diagram of an AD-RED system [62]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

among the selected adsorbents, which led to a maximum exergy efficiency of 30.04%, and the corresponding COP and electric efficiency were 0.84 and 0.39%, respectively. As a follow-up investigation, Zhao et al. [91] further proposed two heat recovery configurations based on the original AD-RED system in ref. [62] to improve the heat-to-power performance. Configuration I dumped the cooling power generated in the evaporator into the condenser for aiding condensation and Configuration II coupled the condenser inside the evaporator. The results showed that both configurations elevated the work extracted. At smaller desorption time and working concentrations, electrical efficiency was improved via configuration II, while the electrical efficiency was hindered at larger desorption time and working concentrations.

In the RED heat engines mentioned above, the thermal separation process is based on extracting pure solvent from salt solution. Another strategy that can be applied to thermal separation process is to remove the thermolytic salts in the thermal regenerative solutions. The most common thermolytic salt employed in OHE is NH_4HCO_3 due to its high solubility, high diffusivities and easy removal by heat, which was first proposed as a thermal regenerable solution for closed-loop forward (direct) osmosis system in 2005 [29]. Subsequently, thermolytic RED heat engines are widely investigated. The experimental study of RED coupled with ammonium bicarbonate is first conducted by Luo et al. [92], which validate the feasibility of RED using NH_4HCO_3 as the working solution for power generation. In their study, the flow rate of feed solution for a specific RED stack was optimized to be 800 mL/min to achieve a maximum power density of 0.33 W/m^2 under an optimal high and low concentrations of 1.5 M and 0.02 M, and the ionic flux efficiency and energy efficiency of 88% and 31% can be obtained. The power reported was relatively insufficient for applications, further efforts on enhancing the power are appealing. Kwon et al. [93] Experimentally characterized the effects of concentration differences, flow rates, membrane types, and intermembrane distances on the performance of RED with NH_4HCO_3 as working solution. The results revealed that the power density monotonously increases with the decreasing intermembrane distances and increasing flow rate. Considering the quadratic increase of the pumping consumption, there existed an optimal inlet flow rate corresponding to the maximum net power density. An excellent power density of 0.77 W/m^2 compared to the previous studies on RED Thermolytic OHEs was obtained with concentrated and diluted solutions of 1.5 and 0.01 M and intermembrane distance of 0.2 mm. A fully operation prototype of RED-NH_4HCO_3 system containing a thermal separation unit as shown in Fig. 5 was first constructed and tested by Giacalone et al. [94], the results showed a continuous and stable operation of over 55 h, which successfully demonstrated the concept of RED-NH_4HCO_3 osmotic heat engine. And in the case of 1.9 M–0.05 M NH_4HCO_3 solutions, a highest exergy efficiency of 1.1% was achieved. The above studies on closed-loop RED-NH_4NO_3 system are based on experiments, while the numerical simulation of the system still faced the challenge due to unclarified NH_4NO_3 electrochemical parameter for traditional RED model which uses NaCl as working solution. Kim et al. [95] developed the RED-NH_4NO_3 model, in which the electrical conductivity in the Planck-Henderson equation was employed to replace the activity of NH_4HCO_3 in the Nernst equation and an actual permselectivity calculated from the membrane potential obtained by a simple experiment was applied. The simulation results agreed well with the experimental results especially at high concentration above 1 M, and a maximum power density of 0.84 W/m^2 was achieved at the flow rate of 3 mL/min, concentrated and diluted solutions of 2 and 0.01 M and intermembrane distance of 0.1 mm. The performance under detailed operation conditions of some RED heat engines can be found in Table 2.

3.2. 3.3 PRO heat engines

The generalized concept of closed-loop PRO heat engine for harvesting waste heat was theoretically proposed by S. Loeb in 1975 [103] and then many efforts have been made to fill the relevant knowledge

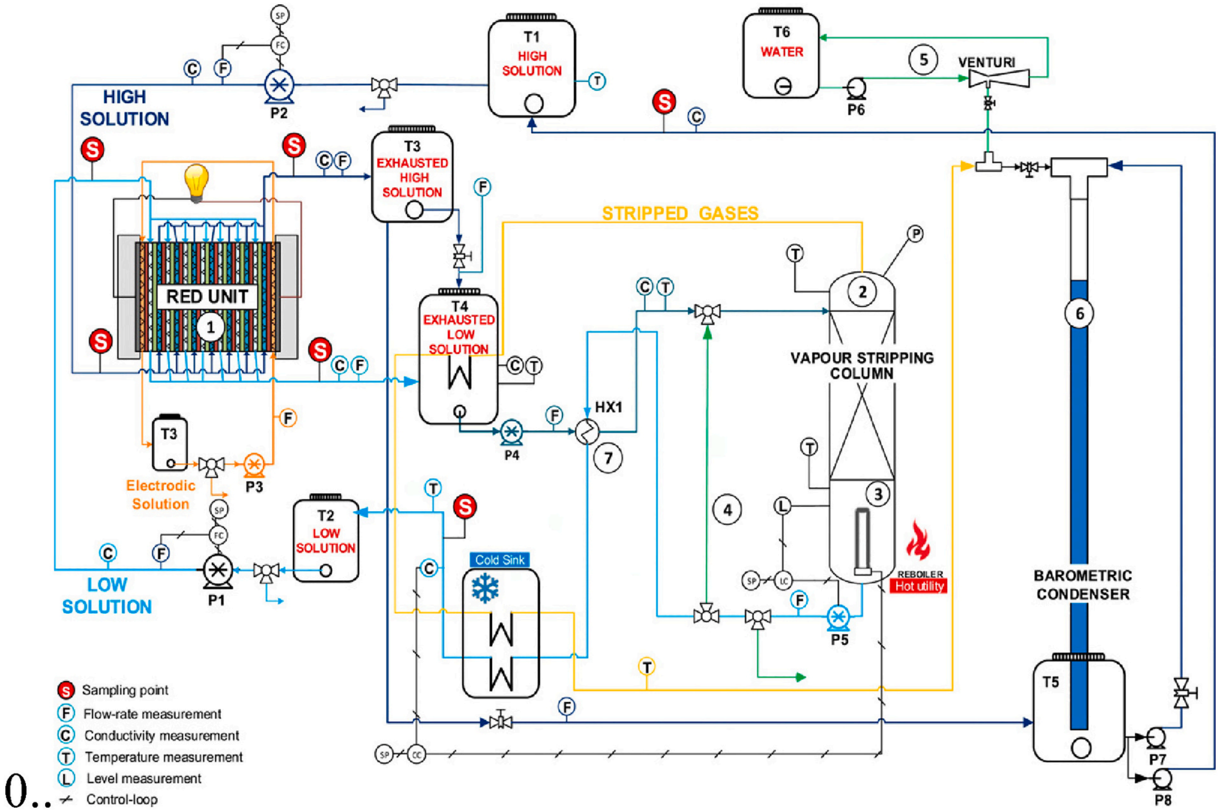

Fig. 5. Schematic diagram of the RED-NH_4NO_3 thermolytic osmotic heat engine prototype. ((1) RED unit; (2) stripping column; (3) reboiler; (4) auxiliary circuit; (5) Venturi ejectors; (6) barometric condenser; (7) thermal integration heat exchanger; (S) sampling points) [94].

Table 2
Performance of some osmotic heat engine architectures.

Architecture	High and low temperature [°C]	Working solution	Working concentration	Energy/electrical efficiency	Exergy efficiency	COP	Ref.
MED-RED	80 and 15	Kac-water	7 mol/L	9.40%	43%	N/A	[34]
MED-RED	80 and 20	NaCl-water	5.4 mol/kg	1.01%	N/A	N/A	[86]
MED-RED	100 and 20	NaCl-water	4.5 mol/L	6.60%	31.00%	N/A	[89]
MD-RED	60 and 20	NaCl-water	5 mol/kg	1.15%	N/A	N/A	[63]
AD-RED	60 and 30	LiCl-water	20 mol/kg	4%	33%	N/A	[25]
AD-RED	40 and 25	NaCl-water	5 mol/L	0.55%	15%	N/A	[90]
AD-RED	70 and 20	NaCl-water	8 mol/kg	0.39%	30.04%	0.84[b]	[62]
AD-RED	70 and 20	NaCl-water	7 mol/kg	1.08%	7.40%	N/A	[91]
AD-RED	N/A and 20	NaCl-water	7 mol/kg	1.04%	N/A	N/A	[96]
Thermolytic RED	78–85 and 23–27	NH4HCO3-water	1.9 mol/L	N/A	1.10%	N/A	[94]
MD-PRO	60 and 20	NaCl-water	1.0 mol/L	9.80%	81.6%[a]	N/A	[97]
MD-PRO	45 and 20	LiCl-Methanol	3 mol/L	around 2.7%	Around 45%[a]	N/A	[98]
AD-PRO	50 and 15	LiBr-Water	3 mol/L	1.63%	33.90%	0.87[b]	[99]
AD-PRO	60 and 20	LiBr-methanol	5 mol/kg	6.68%	N/A	N/A	[3]
AD-PRO	80 and 20	LiCl-Methanol	6 mol/kg	6.30%	N/A	N/A	[100]
Thermolytic PRO	50 and 25	NH4HCO3-water	6 mol/L	N/A	16%[a]	N/A	[101]
Thermolytic PRO	50 and 20	NH4HCO3-water	2 mol/L	4.61%	17.90%	N/A	[102]

[a] Efficiency relative to the Carnot efficiency.
[b] Cooling effect can only be available in OHEs with AD unit.

gap.

Diverse from the traditional open loop PRO, the PRO heat engines avoid the limitation of fouling membrane, low concentration difference and geography, and PRO as an important unit of the PRO heat engines, the research on improving its performance is crucial. Anastasio et al. [104] experimentally investigated the impact of working temperature and concentration on the performance of PRO with a commercial forward osmosis membrane, the results indicated that the power density increase with the increase of temperature and concentration in general, and a highest power density of around 20 W/m^2 was obtained when measured at system temperature of 40 °C using 1.5 M NaCl solution. Both the diffusivity of the solute and selectivity of the semipermeable membrane solute in PRO determine the performance of the PRO heat engine. To find better solutes, Gong et al. [105] tested three inorganic salts (NaCl, $MgCl_2$ and $MgSO_4$) on their potential for application in PRO heat engine. The results showed that smaller and more diffusive salts tend to led higher water flux, although the salt flux was also higher. A highest power density of over 13 and 14 W/m^2 are achieved with $MgCl_2$ at 20 °C and with NaCl at 40 °C, respectively. Altaee et al. [106] analyzed the performance of the single stage and dual stage PRO in a closed loop system with MED as the regeneration component. The impact of membrane area, draw solution flow rate and pressure were investigated. The results predicted that the dual stage PRO is superior to the single stage PRO by 18% higher power generation though a computer model and the most influential parameter in the first stage was the pressure of the draw solution while in the second stage was the flow rate. The performance of MED was also assessed, proving the feasibility of harvesting low-grade heat to generate electricity. The semi-permeable membrane is the core component of PRO and the membrane transport properties directly affect the water flux, thus the electricity generation of the whole heat engine. So far, the lack of appropriate membrane is still the obstacle to improving the technology. Tong et al. [107] synthesized a freestanding graphene oxide membrane (GOM) and investigated the application in the osmotic heat engine. Duo to the elimination of the support layer of the membrane, the internal concentratio0n polarization was significantly reduced, which led to higher water flux and power density. Moon et al. [108] first adopted novel one-step direct fluorination to increase the hydrophilicity of the electrospun membranes fabricated by poly(benzoxazole-co-imide) (PBO) polymer, forming the thin film composite membrane of PBO-TFC-F5. As a result, an unprecedented power density of 87 W/m^2 was achieved with PBO-TFC-F5 and 3 M NaCl solution under hydraulic pressure of 27 bar. And when in OHE, the power generation cost of the OHE with PBO-TFC-F5 was only 203 $ MW/h, which was less than half of that with commercial membrane.

Many researches on the performance of the whole system containing the separation unit and PRO have been conducted. Lin et al. [97] presented a novel MD-PRO system and evaluated the Thermodynamic performance and energy efficiency of the OHE. The relative flow rate of MD distillate and feed flow was defined as an important operation parameter and there existed an optimal relative flow rate to maximum the energy efficiency of the system. A theoretical energy efficiency of 9.8% can be obtained with 1.0 M NaCl as working solution at heat source and heat sink temperature of 60 and 20 °C, respectively. Shaulsky et al. [98] proposed to employ methanol as the solvent in an MD-PRO system due to the advantage of high volatility, low specific heat capacity and vaporization enthalpy compared with water (see Fig. 6). A maximum power density of 72.1 W/m^2 was achieved with 3 M LiCl-methanol as working solution, and the energy efficiency was higher than that with LiCl-water solution. Zhao et al. [99] first proposed a novel closed loop AD-PRO heat engine to harvest waste heat for cooling and power cogeneration as presented in Fig. 7. The effects of heat source temperature, concentration of working solution, types of adsorbents, salts, and solvents on the performance of the system were comprehensively investigated. Considering the energy quality difference between cooling power and electricity, exergy efficiency was employed to reflect the degree of energy utilization. When operated under desorption temperature of 50 °C with AC MAXSORB3 as adsorbent and 3 M LiBr-methanol as working solution, the maximum exergy efficiency of 33.9% can be achieved, meanwhile the corresponding COP and electric efficiency were 0.87 and 1.63%, respectively. Long et al. [3] also investigated a methanol-based AD-PRO heat engine with activated carbons and metal-organic as adsorbents. In their study, heat recovery between heat source and heat sink were considered to improve the system efficiency, the exergy analysis was conducted and the potential applications were discussed.

Thermolytic PRO heat engines with NH_4HCO_3 as working salt as the follow-up investigation of the desalination system in Ref. [29] was first presented by McGinnis et al. [101]. In their study, the thermolytic PRO heat engine is modeled. The results revealed a fairly low overall probable actual operating efficiency of 5–10% and a power density of 200 W/m^2 (of membrane area) can be obtained. The study provided a direction for further optimization and development of the thermolytic OHE. A thermolytic PRO heat engine as show in Fig. 8 was also systematically investigated by Tong et al. [102] in terms of thermodynamic efficiency, system performance and suitable application circumstances. The Results showed that when operated at heat source temperature of 323 K and concentrated and diluted solutions of 2 and 0.01 M, energy efficiency and exergy efficiency can reach 4.61% and 17.90%. In addition, the investigation of the PRO-NH_4NO_3 harvesting energy from solar energy

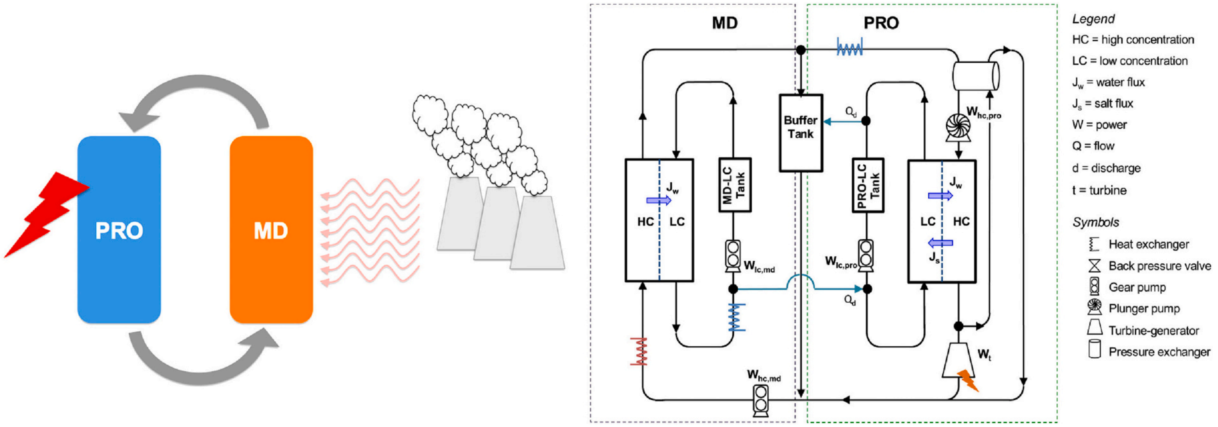

Fig. 6. Schematic diagram of an MD-PRO system [109].

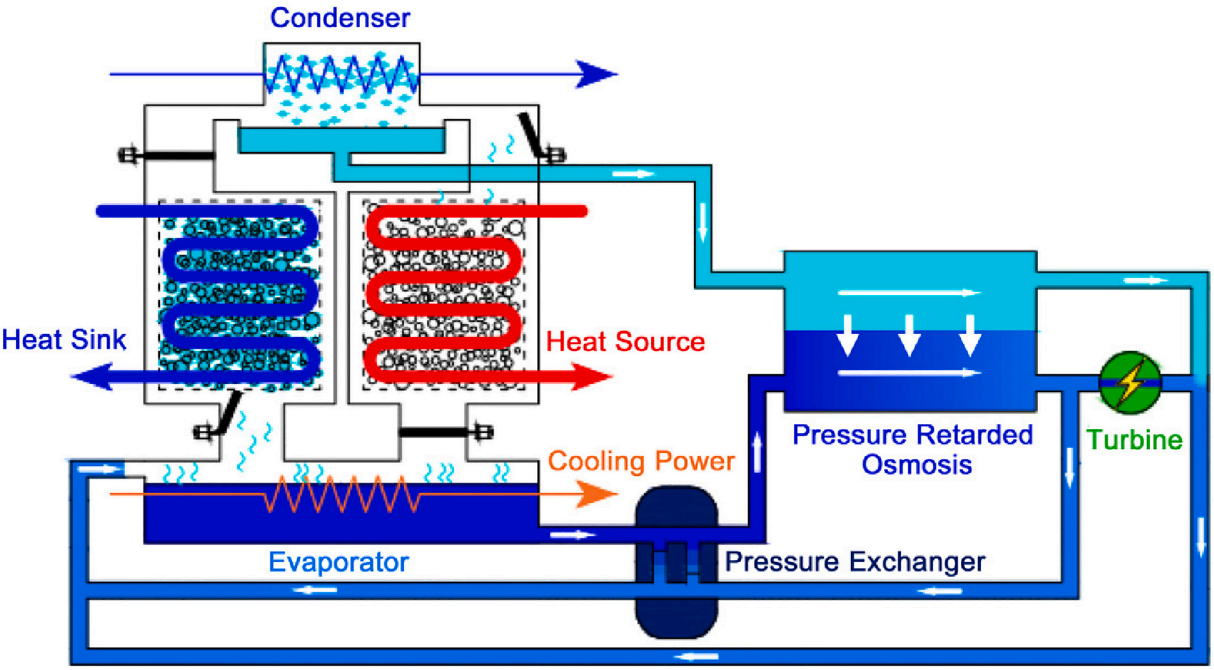

Fig. 7. Schematic diagram of an AD-PRO system [99].

and industrial waste heat was conducted for the first time, indicating the feasibility of such OHE in practical application. One of the challenges with NH_4HCO_3 as working solution in thermolytic PRO heat engines is that the free ammonia in the solution can cross through the membrane relatively easy, resulting in reverse solute diffusion, which undermines the water flux, thus the power density of the system. Xia et al. [110] evaluates the performance of the PRO thermolytic OHE with trimethylamine–carbon dioxide (TMA-CO_2) as working solution and a power density of 18.6 W/m^2 was obtained at pressure of 10 bar and working concentration of 5 M. The results showed that the water flux was equivalent and the reverse solute flux was significantly reduced compared with NH_3-CO_2 due to the larger solute size, while the water flux was 20% lower compared with NaCl due to the lower diffusion coefficient and higher solution viscosity. The performance under detailed operation conditions of some PRO heat engines can be found in Table 2.

4. Other state-of-art heat-to-work thermodynamic systems

Some other less investigated osmotic heat engine architectures are also presented in some literatures, and we will briefly introduce these architectures in this section.

Different from the osmotic heat engine introduced above, low-grade heat is directly applied to the power generation unit of the thermo-osmotic energy conversion (TOEC) devices. In TOEC, the operating principle is similar to MD, except that the permeate stream is pressurized. When low-grade heat is supplied to the solution on one side of the hydrophobic porous membrane, the water vapor diffuses through the membrane and condenses in the permeate side, resulting in a pressurized flow, which can be depressurized by a turbine to generate electricity. Some studies highlighting the system operating conditions, membrane characteristics have been reported [111,112]. Straub et al. [111] developed a framework to investigate the realistic mass and heat transport in TOEC process, and the results revealed that a heat-to-electric conversion efficiency of 4.1% (34% of the Carnot efficiency) can be achieved by an optimized TOEC system with cold and hot working temperature of 20 and 60 °C, respectively, and operation pressure of 5 Mpa (see Fig. 9).

Thermoelectric materials offer an alternative way for converting heat into electricity, and the application in OHEs has been proposed.

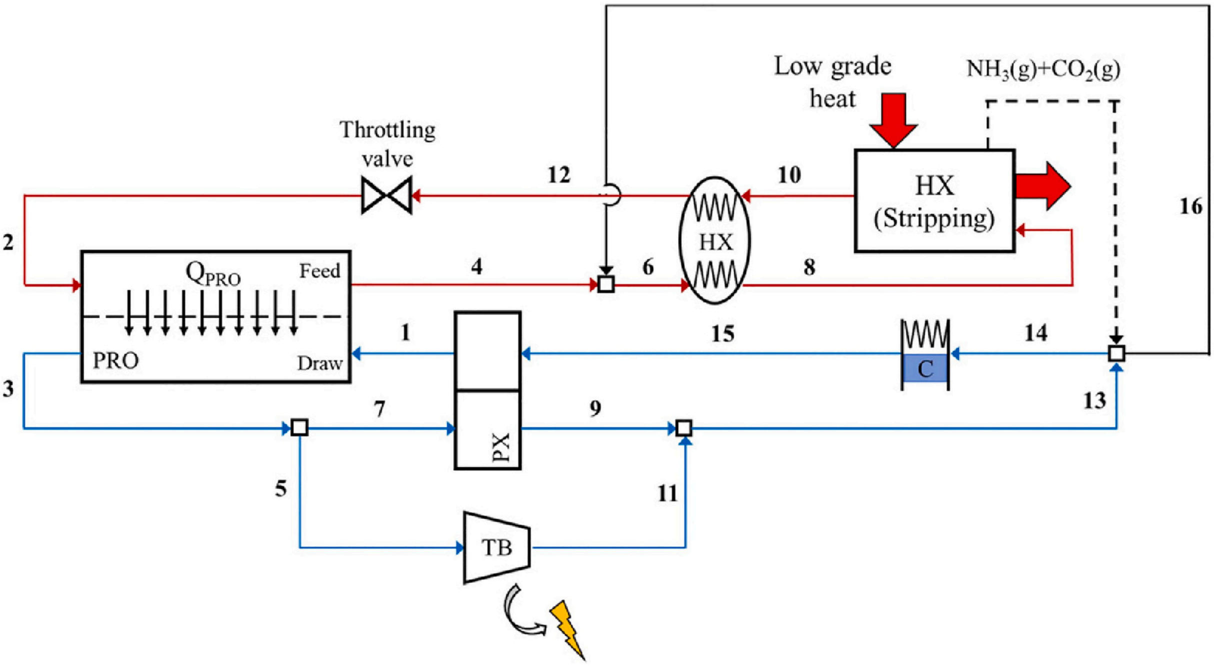

Fig. 8. Schematic view of the thermolytic PRO heat engine [102].

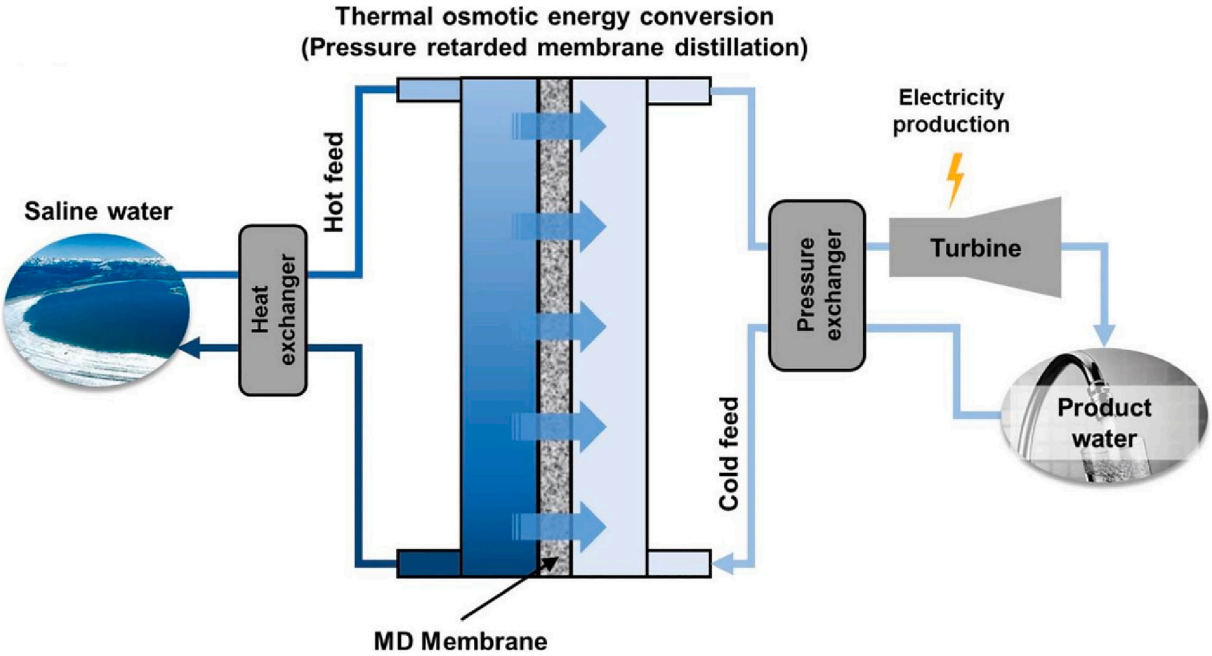

Fig. 9. Schematic diagram of a TOEC process [113].

Thermally regenerative electrochemical cycles (TREC) are a Stirling-like cycle. In TREC process, the electrodes are discharged at a low temperature (T_L) and recharged at a high temperature (T_H), where the voltage of discharging at T_L is higher than that of charging at T_H, resulting in a net power generated by the difference of the voltage [114–118]. An anion exchange membrane is employed to separate the cations in the electrolyte of the two electrodes [119,120]. Lee et al. [121] developed a TREC system with CuHCF and Cu/Cu^{2+} electrodes for low-grade heat harvesting, the results indicated that a cycle efficiency of 5.7% can be achieved when 50% heat recuperation is considered (see Fig. 10).

Thermally regenerative battery (TRB) is a new approach to convert low-grade heat into electricity via redox and heat-based fractionation. In TRB, a ligand such as ammonia is added in one electrolyte to make it the anolyte, which is separated from the catholyte via an anion exchange membrane, generating metal ammine complexes. Then oxidative dissolution occurs at the anode and the metal ions at the cathode are reduced and attached to the electrode, meanwhile the potential difference between the cathode and the anode is discharged. Finally, the ligand is separated through heat-based technology and added to another electrolyte for the next stable cycle [122,123]. Wang et al. [124] developed a bimetallic thermally-regenerative ammonia-based flow battery system for low-grade heat recovery, a thermoelectric conversion efficiency of 0.34% can be achieved. Recently, an innovative TRB based on a flow cell with solid-state ion conductors has been designed by

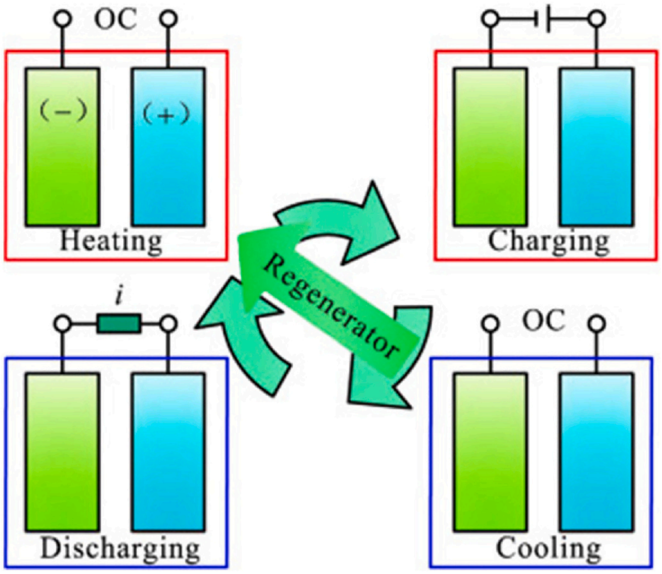

Fig. 10. Schematic diagram of a TREC process [118].

Facchinetti et al. [125,126], which presents a remarkable improvement in the performance of thermoelectric conversion. They first proposed and experimentally investigated a novel system consisting of an electrochemical cell for generating electricity from the mixing free energy of two NaI aqueous solutions with different concentrations and an unconventional liquid-liquid extraction device named "through-liquid-exchanger (LTE)" for rebalancing the concentration [125]. The results showed that an unprecedented energy efficiency of 3% and a power density of 10 W/m^2 can be achieved with a heat source <100 °C. Then they further improved this technique by replacing the chemical species with LiBr/Br$_2$ [126], resulting in a highest heat-to-electricity efficiency of around 4% (see Fig. 11).

A novel OHE configuration called thermal regenerative osmotic heat engine (TROHE) with power-driven separation unit instead of thermal-driven separation unit was proposed by Long et al. [127] and the TROHE is composed of RO for power-driven separation and PRO for electricity generation. In the TROHE process, RO is operated under a lower temperature, then the generated concentrated and diluted solutions are heated before entering the PRO to extract more electricity than the RO consumes, thereby providing net power. In their study, a maximum energy efficiency of 1.4% can be achieved with the proposed TROHE when operating between high and low temperature of 60 and 20 °C, respectively (see Fig. 12).

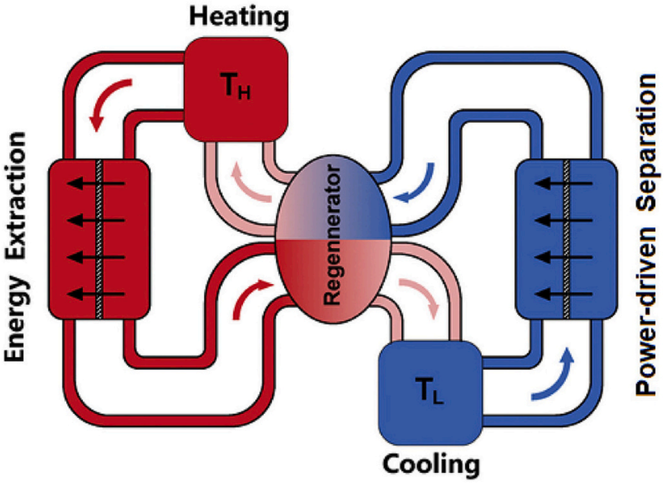

Fig. 12. Schematic diagram of a TROHE process [127].

5. Potential application and assessment

Some literatures about the potential application of the OHEs have been reported. Tong et al. [102] explored the feasibility of a thermolytic osmotic heat engine to harvest low-grade industrial heat for power generation and a high energy return on investment of 54.7 is resulted, which indicates the potential of such OHE to utilize industrial waste heat. Zhao et al. [96] presented a solar-driven osmotic heat engine combining AD and RED for electricity generation, the dynamic characteristics of the OHE under varying direct solar irradiation intensity during a day was investigated and a highest energy efficiency of 1.04% was obtained when operating under 60 cycles with 7 mol/kg NaCl as working fluid. The assessments of the OHEs have also been carried out in many studies. Catrini et al. [128] evaluated the energy, economic and environment benefits of integrating the OHE into cogeneration plants by proposing two potential applications and investigating three illustrative case studies, and the results indicated the feasibility of the OHE exploiting waste heat available from prime mover and process operation. A techno-economic assessment of a MD-PRO osmotic heat engine was conducted by Hickenbottom et al. [109]. Net power output, system efficiency and electricity generation costs were calculated by an OHE system model based on experimental data and well-established model. The result indicated that the high electricity generation cost of $0.48/kWh for base-case is not competitive with not only the conventional grid electricity costs ($0.04/kWh in the United States) but also the cost of organic Rankine cycle ($0.08–0.13/kWh). Besides, A commercial-scale

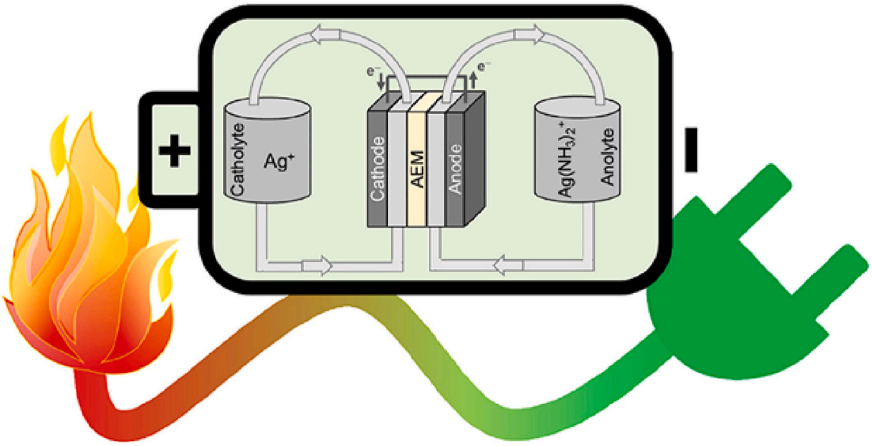

Fig. 11. Schematic diagram of a TRB process [122].

OHE occupies a footprint of about 920 m^2, which is much larger than ORC of about 120 m^2. While substantial improvements in system operation and the performance of membrane were the keys to reducing the cost of power generation, approaching $0.10/kWh. They then performed a comparative life-cycle assessment of a MD-PRO osmotic heat engine and ORC [129], the results showed that the environmental impact of OHE during both construction and operation was higher than that of ORC and the conclusion of the sensitive analysis was that the impacts can be reduced by 80% with the improvement of the membrane performance. Papapetrou et al. [130] evaluated the economic and environmental performance of a MED-RED osmotic heat engine, they also emphasized the effects of improving membrane performance and reducing cost on the large-scale market uptake in the future. The calculation of the levelized cost of electricity indicated that at least the medium to large system scale (heat input of 5 MW) can be competitive. The results of the life-cycle environmental analysis presented the same solution with the smallest environmental impact and the best economic performance.

6. Outlook and conclusion

Despite many studies have been devoted to OHEs, there are still limitations and challenges constraining the commercialization of this technology. As discussed in Section 4, the practical application of OHE operating under different heat sources should be further emphasized according to the distinct characteristics of application scenarios. Moreover, improving system efficiency and reducing power generation cost would favor the emergence of OHE in a commercial scale, both of which are highly dependent on the properties of the membrane. Membrane plays a very important role in osmotic heat engines, thermal separation technology MD and most power generation technologies (including PRO, RED and Membrane-based AccMix) are all membrane-based technologies. Therefore, improving the performance of membrane can be beneficial for system performance, thus the commercialization of OHEs. Studies showed that the power density can be improved from 2 W/m^2 to 47 W/m^2 with the development of membrane technologies [37]. Although it is proposed in many literatures that the use of unconventional artificial solutions contributes to improving the efficiency of the system, most of the membranes available on the market are designed for NaCl-water solutions. New membranes maintaining high permselectivity and low electrical resistance for different salts and solvents still need to be developed. From an economic point of view, the cost of the system largely depends on the cost of the membrane modules. It is reported that the membrane cost is expected to fall from the current (2020) 5 €/m^2 to 2 €/m^2 within a few years, which will reflect on the price of the electricity production directly. The separation unit can be also further enhanced according to the regeneration characteristics of different separation technologies. For example, the adsorption desalination process can be optimized by screening high-performance adsorbents to improve the working capacity and designing suitable adsorbent bed configurations to elevate heat and mass transfer [131]. Long et al. [100] conducted a high-throughput computational screening via grand canonical Monte Carlo simulations to screen high-performance metal-organic frameworks (MOF) adsorbents for AD-PRO heat engine, machine learning was employed for further accelerating the screening and the optimal structure properties of the adsorbent were identified based on genetic algorithm. In addition, the importance of heat recuperation and heat exchanger power density should be also emphasized. To improve the performance of the technologies for exploiting low-temperature, various methods have been applied into the system by means of heat recuperation, where multiple units are connected and work at different temperatures, allowing heat to flow through "multi-effect" before being released to heat sink [15]. The schemes of recuperation to improve the efficiency of the technologies are highly dependent on the performance of heat exchangers. Further studies on high-performance heat recuperation and satisfied heat exchanger power density are appealing. Moreover, finite time thermodynamics (FTT) as a powerful theoretical tool for performance analysis and optimization of various thermodynamic processes and cycles has been applied into generalized objects [132–135]. For example, Chen et al. [136–138] explored the power output and thermal efficiency optimal performances of isothermal chemical engines based on FTT, they also applied FTT to Brayton cycles for system analysis and optimization [139–142]. Therefore, FTT is potential for OHE thermodynamic optimization with investigating the effect of internal heat and mass transfer irreversibilities on system performance.

In this study, a comprehensive review of osmotic heat engine as an emerging "low grade heat to power" technology is presented for the first time. The common types and characteristics of the main component of OHE system are overviewed. The architectures of the OHEs classified as RED heat engines, PRO heat engines are presented and reviewed based on numerous relevant literatures recapitulated in this study. Some other state-of-art heat-to-work thermodynamic systems are also introduced briefly. Furthermore, the potential application of OHEs is discussed and a critical assessment of OHEs is conducted. Outlook and technological challenges outlining the research perspectives are also discussed in this review.

Declaration of competing interest

The authors declare no competing financial interest.

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