Take it to the Carnot limit: Perspectives and thermodynamics of dual-cell electrochemical heat engines

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A B S T R A C T

In electrochemical dual-cell heat engines, the conduction of heat and electricity are fully decoupled, allowing their independent optimisation to maximise the conversion efficiency. Despite this advantage, the dual-cell electrochemical heat engine has only been explored superficially in previous studies. Here we address the in-depth thermodynamic aspects of the heat engines integrated with two electrochemical flow cells and assess the route to achieve a high heat-to-electricity conversion efficiency and system’s power output. Our theoretical analysis revealed for the first time that in the dual-cell electrochemical system, the flow rate must be controlled as a response to the electrical current, and conversion efficiency no longer depend on the conventional thermoelectric figure-of-merit. Based on established principles and considering tremendous advancements for the past 10 years within thermogalvanic materials and flow battery systems, our analysis presents that it is realistic to develop dual-cell electrochemical heat engines that can be operated at conversion efficiencies approaching the Carnot limit, reaching 10.1 % and 19.3 % at maximum power point and maximum conversion efficiency conditions, respectively, under the temperature gradient of 80 °C.

1. Introduction

Heat engines (HEs) are devices that can convert heat energy into other forms of energy (electrical/mechanical) and, in reverse mode, operate as heat pumps (HP). HEs have a breakthrough potential as hybrid energy storage/production units provide sufficient power density and conversion efficiency. This is exemplified in Fig. 1, which shows two integration possibilities of HEs connected to a solar-powered decentralised (i.e., standalone) energy system. In Fig. 1a, the heat harvested from a solar thermal collector is stored in a thermal reservoir and can supply heat and hot water as the existing solar-thermal system provides. In addition to this conventional function, the heat from the thermal reservoir can be converted into electricity when needed by the HE. This can be realised by various means, such as thermoelectric, thermogalvanic and thermally regenerative electrochemical cycle (TREC) [1,2], functioning as a heat-electricity conversion device. Assuming that the hot side temperature (Th) and the cold side temperature (Tc) of the thermal reservoir are 95 °C and 25 °C, respectively, and the HE operates at the Carnot efficiency (~20 %) [3], a hot thermal reservoir of 2.5 m³ of water can be converted into about 10 kWh of electricity if the temperature of the reservoir continuously decreases from 95 °C to 75 °C as the heat conversion progresses. Higher electrical output can be obtained if the thermal reservoir is discharged to even lower temperatures. A conversion efficiency below ~ 20 % may, at first hand appear low, but it should be compared to the theoretical maximum (Shockley-Queisser limit) of 33 % for a single junction photovoltaic (PV) cell [4].

Although the storage reservoir has a higher volumetric footprint than conventional batteries, the important point is that it is an integrated heat-power-storage system that would replace a combined PV, battery and a mechanical heat pump with a large, combined footprint. More importantly, both batteries (400–600 EUR/kWh) [5] and mechanical heat pumps (1400 EUR/kW) [6] have significant capital expenses, while the HE-based system is based on an aqueous thermal reservoir with an obvious low-cost and minimal environmental impact potential.

The other fundamental integration possibility of HEs, often overlooked, is its use as electricity-to-heat-to-electricity storage device, with the same functionality as a battery. Assuming ideal Carnot efficiencies, then the overall electricity-to-electricity round-trip efficiency (ηeto) approaches unity as the heat pump, and the heat-to-electricity mode approaches the Carnot limit (more detailed derivation can be found in

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This integration possibility is shown in Fig. 1b, where surplus electricity from a PV panel powers a HE that pumps heat from outside into a thermal reservoir. Whenever the PV does not produce electricity, the HE operates as a generator that produces electricity from the heat reservoir. Additionally, the thermal reservoir can be used for heating and hot water in the building. This concept is similar to the existing commercial system with PV/heat pump/hot water reservoir/battery; however, the HE integrates the heat pump, hot water reservoir and battery into one hybrid system.

With the versatile integration possibilities of HEs and the potential for large capital cost savings by reduced system complexity, semiconductor-based solid-state thermoelectric materials have been intensively studied over the last several decades. However, the plain fact is that the highest $\eta$ for the commercially available thermoelectric module for low-temperature operation is below 4 % (figure-of-merit $ZT \sim 1$) [7,8], less than 1/5 of the Carnot efficiency. The record $\eta$ for the state-of-the-art lab-scale thermoelectric device is merely over 8 % [9]. In addition, their high costs (ca. 30 $/W for 1 kW unit) [10] have hindered the widespread use of the solid-state HE approach in renewable power applications. Materials with higher efficiencies have been reported in the literature (SrTe, SnSe, CoAsS$_2$, etc.) [11], but the costs and presumably high environmental impact of these materials prevent the wide implication of this technology. For this reason, liquid/solid-state thermogalvanic (i.e., electrochemical) cells have been considered as an alternative inexpensive and scalable route for HEs [12]. The thermogalvanic cells are pure electrochemical analogues to semiconductor thermoelectric materials; however, here, the charges are carried by ions in solution instead of electrons/holes in semiconductor materials. The major advantage of thermogalvanic cells is the relatively high Seebeck coefficient ($\alpha$) (ca. 1 mV K$^{-1}$), which is almost one order of magnitude higher than that of conventional solid-state thermoelectric cells [13].

Among various redox couples used for liquid-based electrochemical systems, the largest values of $\alpha$ have been observed in the Br$_2$/Br$^-$ redox couple, where $\alpha$ varies between 0.5 and 3 mV K$^{-1}$ [14]. For non-aqueous solvents, values up to 10 mV K$^{-1}$ for NaOH-treated polyethyleneoxide was recently reported [15]. Despite these large $\alpha$ values, conversion efficiencies of electrochemical energy conversion systems based on thermogalvanic effect are still relatively low (2 ~ 4 %) [2,16,17], because of low ionic conductivity ($\sigma$) [18]. Conversion efficiencies of thermogalvanic cells are determined by the same dimensionless figure of merit, as for solid-state thermoelectrics, $ZT = \alpha^2 \sigma/kT$, where $T$ is the temperature, $k$ is the thermal conductivity of the electrolyte. Assuming fixed $\sigma = 40$ Sm$^{-1}$ (half of the highest known aqueous values) approximately 30 % sulfuric acid in water, highest known aqueous value) and $k = 0.6$ Wm$^{-1}$K$^{-1}$ (water) values, quite high $\alpha$ reaching 15 mV K$^{-1}$ is required to obtain heat-to-electricity conversion efficiencies above 50 % of the Carnot efficiency, which appears unrealistic based on the currently known $\alpha$ values in aqueous solutions.

From a more fundamental point of view, the most significant challenge for obtaining high efficiency for thermoelectric/galvanic energy conversion systems is that the transport of heat and charge transport are fully coupled. I.e., the transport of heat and charge is along the same path, and if it is attempted to increase electrical conductance by decreasing the distance between the electrodes, this will lead to the concurrent increase of the thermal conductance, whereby the conversion efficiency remains unaltered. This also is the physical explanation of the intensive properties of all the variables that enter the figure-of-merit ($ZT$).

The present analysis work with a perspective study is inspired by recent advancements within redox flow batteries and investigates an efficient approach to heat-to-electricity conversion using a dual-cell model that allows decoupling of the transport of heat and charge by use of heat exchangers (outlined in Fig. 2). The dual-cell model with simultaneous charging and discharge was proposed by Hammond et al. in 1979 [19]. The recent surge of interest toward efficient heat-to-electricity storage technologies led researchers to reconsider the dual-cell concept; however, the latest conversion efficiency milestones (max. 0.54 %) [20,21] are far behind the other thermogalvanic technologies despite the conversion efficiency of the dual-cell was expected to reach 16 % at $\Delta T = 60 ^\circ C$ according to ref. [19], where the performance of the dual-cell system was predicted based on conventional thermoelectric theories.

Herein, we conduct an in-depth theoretical/thermodynamic analysis to address the performance limits in terms of both conversion efficiency and power density of the dual-cell system by rederiving conventional Ioffe’s thermoelectric model [22]. Also, we assess the route to achieve a high heat-to-electricity conversion efficiency and system’s power output by varying the operating parameters of the model dual-cell electrochemical heat engine, which cannot be considered in conventional thermoelectric or thermogalvanic figure-of-merit model studies. Overall, a new figure-of-merit for dual cell thermogalvanic systems is derived, and it is shown that with current state-of-the-art flow battery technology, it is possible to reach conversion efficiencies that approach...
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3. Conversion efficiency and figure-of-merit of dual-cell devices

Detailed thermodynamic analysis of the open-circuited potential of the dual-cell HE ($E_{\text{HE}}$) can be found in Appendix 2, here, it is seen that $E_{\text{HE}}$ has a dependence on the reaction quotient for the combined electrochemical reaction in the cells. An important result from the analysis is that the reaction quotient remains constant during the dual cell operation. It is, at the same time, a parameter that can be controlled externally by normal battery charging of e.g., the cold cell. This is in contrast to recently actively studied thermoelectrochemical topics, such as thermally regenerative batteries [2, 27–29], where a full charging is done at a low temperature, and a full discharging is done at a high temperature or vice versa (i.e., consequence charging/discharging regime). The impact of this difference is well demonstrated by a generic illustration of the cell voltage of the system in the absence of polarisation losses as a function of the reaction quotient in Fig. 2c. Assuming constant charging/discharging rate at both hot and cold cells, the dual-cell HE can operate at a steady open circuit potential state at given temperature conditions (solid line) owing to its concurrent charging/discharging reactions at each cell, while conventional single-cell thermoelectrochemical approaches follow the Nernst behaviour (dotted line) with varying open circuit potential corresponding to reaction quotient (Fig. S1 in Supplementary material). On the basis of the above-described dual-cell HE with concurrent charging/discharging operation, herein, we analyse dual-cell devices’ electrical performance on the basis of thermogalvanic voltage ($\alpha \Delta T$) arising upon a temperature difference ($\Delta T$) between the two cells.

During power generation, the conversion efficiency of HEs ($\eta$) is defined as the ratio between the electrical work extracted ($P_{\text{out}}$) and the amount of consumed heat ($Q_H$) transported out of the hot cell and is given by:

$$\eta = \frac{P_{\text{out}}}{Q_H}$$  

$Q_H$ consists of three contributions; the first is conduction heat ($Q_T$) quantified by $K\Delta T$, where $K$ [Wm$^{-1}$K$^{-1}$] is an empiric thermal conductance (i.e., thermal conductance; not to be confused with the thermal conductivity of the electrolyte, $\kappa$ [Wm$^{-1}$K$^{-1}$]) between the two cells, that includes both conductances in the materials and convective transport of heat in the pumped liquids. The second term is heat transported by entropy ($Q_S$) and can be quantified by $I\alpha T_H$, where $I$ is the electrical current, and $\alpha T_H$ is the Peltier coefficient that quantifies how much heat is displaced.

2. Working principles of dual-cell heat engine

The overall working principle is based on two electrochemical flow cells operating at different temperatures and connected both electrically and hydraulically. As an example, Fig. 2a shows electrolytes with redox pairs $\text{I}_3^+|\text{I}^-$ and $\text{Fe(CN)}_6^{3-}|\text{Fe(CN)}_6^{4-}$, respectively, are circulated between the hot and cold cells and is indicated by the red/blue arrows in the middle. Both redox couples are known to have very small activation overpotential and high reaction rates [23, 24]. Redox potential shift due to the thermogalvanic effect ($\alpha_{\text{TCG}}$ see Appendix 2 for more details) of each of the redox pairs builds a driving force for continuous electrochemical reactions from which electric energy can be harvested. I.e., for $\text{I}_3^+|\text{I}^-$ the thermogalvanic effect ($\alpha_{\text{TCG}}$) has been reported to be approximately $0.9 \text{ mV K}^{-1}$, but can be increased significantly to $2.4 \sim 4.2 \text{ mV K}^{-1}$ by use of additives [25]. For ferro/ferri-cyanide ($\alpha_{\text{Fe(CN)}_6^{3-}|\text{Fe(CN)}_6^{4-}}$) it is reported to be negative $\sim 1.42 \text{ mV K}^{-1}$ [26]. As shown in Fig. 2b, the cell potential of the hot cell ($E_H$) is increased compared to that of the cold cell ($E_C$), and electrochemical reactions will spontaneously occur, i.e., $\text{I}^- \rightarrow \text{I}_3^+$ and Fe($\text{CN}$)$_6^{4-} \rightarrow$ Fe($\text{CN}$)$_6^{3-}$ at anode and cathode, respectively, in the hot cell and vice versa in the cold cell.

As the electrodes in both flow cells are connected electrically, electric work ($P_{\text{out}}$) can be extracted in an external load ($R_L$) due to the cell potential differences between the cold and hot cell. In terms of flow batteries, overall, this process corresponds to charging the liquid electrolytes at low temperature while discharging them at high temperature, and the open circuited potential ($E_{\text{HE}}$) of the dual-cell HE is $E_{\text{HE}} = E_H - E_C$. This is also depicted in the voltage-reaction quotient plot in Fig. 2c (see also Appendix 2), where the coloured area inside the electrochemical cycle represents the electrical work that can be extracted from the cycle.

![Fig. 2. (a) Schematic illustration of the studied HE based on two electrochemical flow cells at different temperatures. We note that dimensions and proportions are not to scale. (b) Open circuit potential shift by electrolyte temperature change leads to cell voltage change (e.g., $E_H > E_C$ for the Fe($\text{CN}$)$_6^{3-}|\text{Fe(CN)}_6^{4-}$ case). (c) Generic schematic cell potential-time plot well illustrates the amount of electric energy converted from thermal energy (i.e., heat-to-electricity conversion).](image)
is transported from the high to the low-temperature cell by reaction entropy of the two redox reactions in the cell. Here a 100 % faradaic efficiency of the cells is assumed. The third one is Joule heating \((Q_H)\), which returns half of the power (i.e., \(\frac{1}{2}P_{\text{in}}\)) to the hot cell, and the rest is transferred to the cold side \([22]\). \(R \) is the total internal resistance of the electrochemical cells \((R = R_H + R_C)\), where \(R_H \) and \(R_C \) are the resistance of the hot and cold cells, respectively. For simplicity, \(R_C = R_H \) is assumed. Hereby the total transported heat from the hot to the cold reservoir can be determined as follows:

\[
Q_H = k\Delta T + 1\lambda - a\Delta T - \frac{1}{2} \gamma^2 R
\]

(2)

The electrical current \(I \) generated by the HE is the open-circuited potential divided by the total circuit resistance according to Ohm’s law which can be quantified as follows:

\[
I = \frac{E_{\text{HE}}}{R_H + R_C} = \frac{aT}{R_H + R_C}
\]

(3)

where \(R_H \) is external electric load and \(E_{\text{HE}} = aT\), where \(a\) is the combined thermogalvanic effect for both sides of the dual-cell, i.e., \(a = a_{\text{conv}} + a_{\text{diff}}\) (see also Appendix 2). The internal resistance \((R)\) of the cell is a complex function of both membrane, electrolyte, electrode charge and mass transfer resistances, while the \(R_H\) (see Fig. 2a) is the external load resistance which determines how much electrical power is transferred from the HE into useful external electric power. As described elsewhere (see also eqs. (3) and (4)) \([30]\), this resistance ratio is the primary variable for power/efficiency mapping of an electrical power-generating device.

It is noted that wire resistance and other external parasitic resistances are not considered here; also, it is assumed that the HE has a linear ohmic electrical response, which is typically the case for flow batteries and discussed in more detail later.

In this case, the output power can be calculated by the following equation:

\[
P_{\text{out}} = R_H \cdot I^2 = \left(\frac{aT}{R_H + R_C}\right)^2 \cdot \frac{R_H}{R_H + R_C}
\]

(4)

With eq. (1) the efficiency can now be stated in terms of measurable transport properties as follows:

\[
\eta = \left(\frac{aT}{R_H + R_C}\right)^2 \cdot \frac{R_H}{R_H + R_C} \cdot L_1 \frac{1}{K\Delta T + \frac{2\Delta T}{R_H + R_C} \cdot \alpha T H - \frac{1}{2} \gamma^2 R}
\]

(5)

Denoting \(R_H/R_C\) ratio as \(m\), the efficiency can be rewritten to:

\[
\eta = \left(\frac{aT}{R_H + R_C}\right)^2 \cdot \frac{m}{(1 + m)} \cdot L_1 \frac{1}{K\Delta T + \frac{2\gamma^2 m}{R_H + R_C} \cdot \alpha T H - \frac{1}{2} \gamma^2 R}
\]

(6a)

\[
= \frac{\Delta T}{T_H} \frac{2}{\gamma^2} \frac{\gamma m}{\gamma^2 m + 1 + \frac{1}{2} \gamma^2 m} \frac{R_H}{R_H + R_C}
\]

(6b)

By using the definition of the thermoelectric figure-of-merit \((Z = a^2 K^{-1} R^{-1})\) and optimising the external load \(R_H\) to maximum power \((R_H/R = m = 1)\), the efficiency at maximum power \((\eta_{\text{max}})\) is found to be:

\[
\eta_{\text{max}} = \frac{1}{2} \frac{\Delta T}{T_H} \frac{1}{1 + \frac{1}{2} \gamma^2}
\]

(7)

The condition for the maximum efficiency can be found at \(m = (1 + Z T)^{-1/2}\) that fulfills the requirement \(\partial \eta / \partial m = 0\) \([31]\), and it follows that the maximum heat-to-electricity conversion efficiency \((\eta_{\text{max, eff}})\) is:

\[
\eta_{\text{max, eff}} = \frac{(T_H - T_C)}{T_H} \cdot (\frac{\sqrt{1 + Z T} - 1}{\sqrt{1 + Z T} + \frac{T_C}{T_H}})
\]

(8a)

where \(\eta_C\) is the maximum theoretical limit quantified by the temperatures at the hot and cold reservoir (i.e., Carnot efficiency; eq. A1-3). \(\eta_{\text{max eff}}\) increases with the dimensionless thermoelectric figure-of-merit \(Z T\) (i.e., \(a^2 K^{-1} R^{-1}\)) and is thus fully equivalent to the one for semiconductor thermoelectric materials. With the exception that \(R\) is the sum of the total internal resistance of both cells and \(K\) is total thermal conductance (mainly convection) between the two cells.

Although eqs. 6, 7, and 8 are fully correct, they lack a description of the effect of different flow rates and the potential use of heat exchangers. There is a major difference between normal state-of-the-art semiconductor/thermogalvanic systems and the dual-cell approach described here. Typically, the flow rate in flow batteries is increased with the current and thereby, the thermal conductance (convexion) is no longer constant but depends on the current. Eqs. (7) and (8) are derived assuming a constant \(K\) value \([W/K]\), and further insight can be obtained if the flow rate is explicitly included in the equations. Assuming that all thermal conductance is convective and there are no diffusive contributions, the rate of heat flow is given by Fourier’s law as follows:

\[
q = \frac{T}{F} \cdot C_p \cdot (1 - \eta_{\text{HX}})
\]

(9)

where \(q\) is the required electrolyte flow rate for both sides of the cells, \(C_p\) is the heat capacity of the electrolyte and \(\eta_{\text{HX}}\) is the heat exchanger efficiency and is assumed to be independent of flow rate. The flow rate \(q\) can be determined by the following equation:

\[
q = \frac{F \cdot C_p \cdot (1 - \eta_{\text{HX}})}{T}
\]

(10)

where \(F\) is the Faraday constant, \(C\) is the concentration of the redox species, and \(F\) is the dimensionless flow rate factor. i.e., in flow batteries, the flow rate typically is at least two or three times higher than the minimum stoichiometric needed for supplying reduced/oxidised redox species to the cells in order to ensure high conversion efficiency. Combining eq. (9) and (10) the following is obtained:

\[
K = 2q \cdot \frac{1}{F} \cdot C_p \cdot (1 - \eta_{\text{HX}})
\]

(11)

An interesting feature is that, unlike conventional thermoelectrics/ thermogalvanics, the thermal conductance of this dual-cell system has an explicit dependence on the electrical current. Naturally, this is valid only if the flow rate is increased proportionally to the electrical current. Combining with eq. (2), this will then change eq. (5) into:

\[
\eta = \frac{1}{1 + m} \cdot \frac{1}{\gamma^2 \alpha_{\text{conv}} - \frac{T_H}{T_C} - \frac{1}{2} \gamma^2 m}
\]

(12)

The conversion efficiency reaches its maximum at \(m \to \infty\), whereby:

\[
\eta_{\text{max conv}} = \frac{1}{\gamma^2 \alpha_{\text{conv}} - \frac{T_H}{T_C} - \frac{1}{2} \gamma^2 m}
\]

(13)

And the efficiency at maximum power (i.e., \(m = 1\)) is:

\[
\eta_{\text{max}} = \frac{1}{2} \cdot \frac{1}{\gamma^2 \alpha_{\text{conv}} - \frac{T_H}{T_C} - \frac{1}{2} \gamma^2}
\]

(14)

To interpret the significance of eqs. (13) and (14), it is important to underline that one unique feature of this system is that the transport of heat and charge is fully decoupled in the dual-cell electrochemical HEs. As illustrated in Fig. 2a, the electrical resistance is associated with the internal resistance of the electrochemical flow cells, while the transport of heat (convexion) is associated with the circulated liquid. This is unlike conventional thermoelectric and thermogalvanic systems, where the transport of heat and charge is coupled because the charge migration/diffusion path and heat transfer path are the same. This opens for
independent optimisation of each transport coefficient, i.e., in the dual cell configuration, the internal resistance can be lowered by methods of e.g., better membranes/electrodes without affecting the thermal transport. In conventional thermogalvanic/thermoelectric systems decrease of the conductivity by e.g. shorter electrical pathway of the device would lead to concurrent increase of the thermal conductivity, whereby the conversion efficiency remains unaltered. In practice, introduction of heat exchangers (indicated by symbols in Fig. 2a) can lower the thermal conductance (K) between the two flow cells, without increasing the electrical resistance, and in principle, the efficiency (eq. (12)) approaches the Carnot limit as the efficiency of the heat exchangers $\eta_{\text{HX}}$ increased. Further, as revealed in eqs. (13) and (14), it is worth noting that conversion efficiency does no longer depend on the conventional thermoelectric figure-of-merit (Z), and the operating parameters, including the flow rate and heat exchanger efficiency, are the critical variables in dual-cell electrochemical systems.

Alternatively, the cell design can be optimised to result in a lower cell resistance, but this leaves the thermal conductance unaffected. It is also interesting to note that, unlike conventional thermoelectric and thermogalvanic energy conversions, the cell resistance does not explicitly enter into eqs. (13) and (14) as a consequence of eq. (11). Furthermore, both the maximum conversion efficiency and the efficiency at maximum power point are independent of the cell resistance. It is also seen that the efficiency at maximum power ($\eta_{\text{max}P}$) for both the conventional thermoelectric figure-of-merit (eq. (7)) and the dual-cell derived here (e.g. 14) approaches the Carnot limit ($\eta_{\text{max}P} = 0.5 \times (T_H/\Delta T - 1/4)^{-1}$) as the $Z \rightarrow \infty$ and $\eta_{\text{HX}} \rightarrow 1$, respectively. In the power density (eq (4)), satisfying the condition for eq. (13), $P_{\text{out}}$ at maximum efficiency ($m \rightarrow \infty$), can be determined as follows:

$$P_{\text{out max}} = \frac{\alpha \Delta T}{4R}$$

while at maximum power ($m = 1$):

$$P_{\text{out max}} = 0$$

4. Modelling and performance quantification

As an example, to highlight the untapped potential of the dual-cell HEs, we plot the power density and conversion efficiency as functions of the resistance ratio ($m = R_i/R$), as shown in Fig. 3. The modelling is based on eqs. (4) and (12), and it is assumed that heat transfer between the hot and cold sides is convective only. The neglected diffusive contributions include thermal conductance through pipes, wires etc. which relies on the heat capacity of electrolytes, i.e., there is no diffusive or other parasitic heat losses between the two sides. Nonetheless, using standard values of the thermal conductivity of materials and Wiedemann–Franz law (electron/charge carrier thermal conductance), it is verified that diffusive contributions only become significant when the resistance ratio $R_i/R \gg 1$ (typically $10^5$ or larger), where the $P_{\text{out}} \approx 0$ (Fig. 3a and b; see eq. (15)) that makes its contribution meaningless. Also, the pump energy losses have not been included as they depend heavily on stack design, but typically, in flow batteries, it varies in the range of $2 \sim 3\%$.

Also, as stated earlier, it is assumed that the total internal dual-cell resistance ($R = R_H + R_C$), which includes ionic/membrane, charge-transfer and mass transfer resistance, has a linear ohmic response. For flow batteries, this is often the case, and in optimised cells, linear response is seen even at current densities > 500 mA cm$^{-2}$ [33]. Furthermore, redox reactions in flow batteries typically present facile reaction kinetics with no activation potentials [23,34-36] that would otherwise lead to a non-linear response around zero current.

Fig. 3a shows a plot for a model with conservative values of the transport coefficients. A combined thermogalvanic effect of 2 mV/K is used and appears fully realistic as it is well established that $\alpha$ of Ferro/
ferri-cyanide is in the range $-1.4$ to $-1.7$ mV/K in water [12,37], implying that $\alpha$ of the redox pair on the other side should only be above approximately $0.3$ to $0.6$ mV K$^{-1}$ in order to reach $|\alpha_{\text{Ox}} - \alpha_{\text{Red}}| > 2$ mV K$^{-1}$. Also, in the modelling an area specific resistance of 0.5 Ωcm$^2$ per cell ($R = 1.0$ Ωcm$^2$) has been used and is fully realistic value as for the redox flow battery cells/stacks values in range of $0.48 - 0.80$ Ωcm$^2$ are reported [38]. As can be seen in Fig. 3a, without heat exchangers, the conversion efficiency at maximum power ($\eta_{\text{maxP}}$) is lower than 1 %, and the maximum conversion efficiency ($\eta_{\text{maxef}}$) only reaches about 1.4 %. However, once heat exchangers with modest efficiencies of 95 % are introduced the corresponding efficiencies increases to almost 6.5 % ($\eta_{\text{maxP}}$) and 12.6 % ($\eta_{\text{maxef}}$), respectively. These values are approaching the Carnot efficiency of 21.4 % and underlines the untapped potential of the dual-cell electrochemical heat engine.

Nevertheless, as can be seen from the power density curve, which is the same with or without heat exchangers, the maximum is only about 8 mW/cm$^2$. Although it is a significantly high value considering previously reported thermogalvanic energy conversion cells [39,40], it is significantly lower than the typical maximum values of about 100–200 mW/cm$^2$ seen in typical redox flow batteries [41]. As stacks constitute a significant part of the cost, such power densities will lead to high capital costs.

A more optimistic future scenario has also been modelled, as shown in Fig. 3b. Here, a thermogalvanic coefficient of 5 mV K$^{-1}$, an area resistance of 0.2 Ωcm$^2$ per cell ($R = 0.4$ Ωcm$^2$), and a heat exchanger efficiency of 98 % are used for the plot in Fig. 3b. Similar to the case in Fig. 3a, it is seen that the maximum efficiency reaches merely 3.3 % without heat exchangers, but once included, the efficiency at maximum power point and maximum conversion efficiency reach 10.1 % and 19.3 %, respectively. This is very close to the maximum achievable Carnot efficiency of 21.4 %. Another notable feature is that the maximum power density reaches 100 mW/cm$^2$ and is comparable to generally accepted values in flow battery cells/stacks. Moreover, this analysis underlines the untapped potential of the dual-cell electrochemical heat engines and would open a pathway to breakthrough in thermoelectric/thermogalvanic energy conversion, providing relevant experimental systems demonstrated previously.

As shown in Fig. 3c, both power density and conversion efficiency vary significantly depending upon the variation in thermogalvanic coefficient in the range of 1 to 5 mV/K. An interesting feature specific to conversion efficiency at maximum power point ($\eta_{\text{maxP}}$, grey lines in Fig. 3c) is that the higher the thermogalvanic coefficient $\alpha$, the lower sensitivity to this resistance ratio is much less for both with and without the heat exchanger (green and blue curves, respectively); however, the sensitivity to this resistance ratio is much less for the case with a heat exchanger. As described elsewhere, the flow factor of the system can be reduced by selecting redox reactions with high electron numbers or increasing the electrolyte concentration to guarantee enough reactants everywhere [42], adopting the assumption that the current applied to the electrodes is the same.

For the sake of completeness of this analysis, contour plots for dual-

![Fig. 4](image-url) Conversion efficiencies at maximum power ($\eta_{\text{maxP}}$) with $\Delta T = 80^\circ$C (a) and $\Delta T = 40^\circ$C (b) as functions of heat exchanger efficiency and flow rate factor. (c) Maximum conversion efficiency (dark) and its ratio to Carnot limit (grey) are plotted as functions of the temperature gradient together with power density change (dark). Note that, for all cases, resistance, thermogalvanic coefficient ($\alpha$), and other chemical parameters (e.g., concentration, reaction rate etc.) are identical to Fig. 3b ($\alpha = 5$ mV K$^{-1}$, $R = 0.40$ Ωcm$^2$, respectively). The Carnot efficiency is plotted in terms of temperature gradient ($\Delta T$) in the supplementary material (Fig. S2).
cell HE system with $\Delta T = 80 ^\circ$C and $\Delta T = 40 ^\circ$C, where the contour plot represents the $\eta_{\max}$ in dependence of both flow rate factor and $\eta_{HX}$, are shown in Fig. 4a and b. For the two temperatures, the Carnot efficiency at maximum power is 12 % and 6.8 %, respectively. In both cases, it can be seen that >80 % of the Carnot efficiency (ca. 10 % and 5.4 %, respectively) can be reached with heat exchanger efficiencies over 90 % and flow rate factors within 3, which are fully realistic considering state-of-the-art devices [43,44]. Considering the fact that extremely high $R_i/R$ ratios are not practical conditions (e.g., extremely low internal resistance) because of the associated low power density, these numbers at maximum power point conditions seem more practical. Notably, the case with a high-temperature gradient (Fig. 4a) exhibits stronger heat-exchanger efficiency than the lower temperature gradient case (Fig. 4b), and this trend becomes more prominent at low flow rate factors. It is worth mentioning that power density remains the same regardless of heat exchanger efficiency (Fig. 4c, red) as derived in eq. (16), where the power density of the dual-cell varies depending upon thermogalvanic coefficient and resistance factors at a given temperature gradient ($\Delta T$). Another interesting feature is that the lower heat exchanger efficiency system, the faster the decline rate of the efficiency relative to the Carnot limit as $\Delta T$ increases (Fig. 4c, grey). This tendency gradually diminishes as the $\eta_{HX}$ increases (Fig. S2 in Supplementary material), highlighting the importance of having a highly efficient heat exchanger to minimise the efficiency loss due to non-electric work (e.g., wasted work transferred to the cold reservoir).

5. Comparison to experimental results.

The theoretical approach and analysis for the present dual-cell heat engine can be applied to performance analysis of other similar systems powered by thermogalvanic phenomena, such as TREC, TEC (thermo-electrochemical cells), and TRAB (thermally regenerative ammonia-based battery) etc. Contrary to the theoretical predictions mentioned above, recent thermogalvanic energy storage techniques (e.g., TREC, TEC, and TRAB) proposed in the literature demonstrated quite moderate efficiencies (Fig. 5 and Table 1). We note that among the recently demonstrated works, only the cases in which the temperature gradient is the main driving force of the conversion, showing reliable thermogalvanic coefficients of the electrolytes, were collected for comparison. As depicted in Fig. 5a, the energy efficiency highly depends on the temperature gap (i.e., $\Delta T = T_H - T_C$), so maximum conversion efficiencies of 5.7 % and 3.52 % were obtained at a 50 °C and 65 °C using the TREC and TEC systems, respectively. Although it is a trend of very few selected cases, data points in the chart clearly shows that the TREC seems relatively promising. Since the $\eta_C$ represents the maximum efficiency for heat-to-power conversion, the steep increase of the conversion efficiency of the TREC systems with respect to $\Delta T$ implies performance that obviously outperforms TECs, where the major thermal driving force is achieved from two different temperatures simultaneously biased at the electrodes.

Unlike their temperature dependency in Fig. 5a, no clear correlation of the conversion efficiency with thermogalvanic coefficient (Fig. 5b) can be found for the TREC systems. This can be, as discussed elsewhere, due to self-discharge caused by ion cross-contamination at high temperatures. Also, the proton exchange across the membrane would gradually shift the pH value of both anolyte and catholyte for some TREC systems with pH gradient, which can result in a decomposition of redox pairs (e.g., HCN and Prussian blue formation from a Fe(CN)$_6^{3-/4-}$) [20]. In the case of TECs, as described elsewhere [45], interelectrode temperature drop in the electrolyte toward the cold electrode, decreases the fraction of the temperature difference between hot and cold sides. This is in generally good agreement with the moderate change of the conversion efficiency with respect to the temperature difference shown in Fig. 5a (red dash). Similarly, TRABs also suffer a self-discharge as a result of ammonia transport across the ion-exchange membrane, and this can lead to a decrease in both coulombic efficiency and energy density [46].

Fig. 5. Conversion efficiencies against temperature gradient ($\Delta T$) (a) and absolute value of $\alpha$ (b) for the selected systems. Systems include thermally regenerative electrochemical cycle (TREC), thermochemical cells (TEC), and thermally regenerative ammonia-based battery (TRAB). Detail performance merits can be found in Table 1.

Although selected studies applied different thermogalvanic cell approaches, the common practical issue that arose is the limited effectiveness of the heat exchangers (i.e. $\eta_{HX}$) [17,47]. Wang et al. claimed in their report that their TEC system with a 5.52 % efficiency (Fig. 5b) could be improved to 4.5 % and above if the $\eta_{HX}$ of 50 % is employed [17]. This was also well predicted using a simplified model in work by Lee et al. [47], where the record TREC efficiency (5.7 % with $\eta_{HX}$ of 50 %; Fig. 5b) was demonstrated. Both cases are in good agreement with our analysis quantified in Fig. 3d.

In terms of architectural similarity to the present dual-cell model, it is worth paying attention to the study demonstrated by Qian et al. [20]. They recently presented a dual-cell type TREC flow system similar to our model cell shown in Fig. 2; however, its overall conversion efficiency is slightly over 0.5 % at a fixed flow rate (4 $\mu$L min$^{-1}$) and internal resistance (8 $\Omega$). They observed significant efficiency loss at increased flow rate due to high mass transfer overpotential, and it may be attributed to the pressure drop at elevated flow rate; but not clearly stated the origin of this mass transfer limit. In relation to the present calculation shown in Fig. 3d, our detailed analysis can be suggestive of how effectively the flow rate needs to be designed. Considering the fact that the required flow rate is proportional to the flow rate factor at a fixed reaction rate and electrolyte concentration, more facile reaction kinetics or lowered electrolyte concentration can be practical approaches to have high conversion efficiency at an increased flow rate.

Unlike the above-listed studies that capture the performance dependency on individual operating factors, the present detailed model provides a basis for quantitatively identifying the key limiting factors...
related to heat-to-electricity conversion and power generation under mixed variable conditions. In addition to the above-mentioned examples based on thermogalvanic effect, the present approach and analysis also can be widely applied to other similar systems operating under larger temperature differences, such as molten salt electrolyte battery or solid oxide electrolyser [48,49] integrated with proton-exchange membrane (PEM) fuel cell [50]. Apart from the fluid chemical selection and electrolyte engineering described above, intense efforts should be made to optimisation of cell resistance and other experimental aspects as explained above, such as membrane crossover and temperature gradient neutralisation, which are quite common issues in thermogalvanic-based energy conversion systems, to make the dual-cell HE system commercially viable.

6. Conclusions

Dual-cell liquid-based electrochemical heat engines have only been superficially described in the literature, despite their huge potential in heat-to-electricity energy conversion. A thermodynamic analysis of the conversion efficiency and power density performances and their dependence on combined conditions of the thermogalvanic effect of the individual redox pairs, flow rate factors, resistance factors, heat recuperation ability (i.e., heat exchanger efficiency) and reaction quotient were, for the first time, derived in this work. It shows that the dual-cell thermogalvanic effect is fully equivalent to the thermoelectric effect in semiconductor thermocouples, where the total thermoelectric effect is the difference between the two materials/redox couples. In contrast to typical thermoelectric/thermogalvanic energy conversion, the conductance of heat and electricity in dual-cell electrochemical HEs is fully decoupled and enables independent optimisation of each in particular by means of heat exchangers to increase efficiency. Two approaches for calculating the conversion efficiency have been particularly addressed. First, the standard approach of thermoelectric materials where the thermal conductivity is constant. It is shown that the conversion efficiency depends on the figure-of-merit, as seen for normal thermoelectric energy conversion. However, in dual-cell electrochemical heat engines, the flow rate must be controlled as a response to the electrical current in the system, and conversion efficiency does, in this case, no longer depend on the thermoelectric figure-of-merit. Our analysis revealed that the conversion efficiency at both maximum power point and maximum efficiency conditions only depends on the thermogalvanic effect and thermal conduction. Using optimistic, but fully realistic values of transport properties, the analysis showed that the dual-cell electrochemical heat engines can operate with efficiencies close to the Carnot limit. Another important aspect is that the power density is comparable to that of flow batteries and is orders of magnitude higher than that of current thermogalvanic energy conversions reported so far, except for a few works demonstrated using a compact pouch type cell. The theoretical approach and analysis for present dual-cell heat engines have general validity that is applicable to other similar electrochemical cells, which work at higher temperature ranges. We believe that these analyses and insights contribute to the development of solid pathways for reassessing the merit of electrochemical thermogalvanic heat engines, which are being back into the spotlight as waste heat energy storage systems.

CRediT authorship contribution statement

Dowon Bae: Conceptualization, Methodology, Writing – original draft, Visualization. Anders Bentien: Conceptualization, Methodology, Writing – original draft, Visualization.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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Appendix 1. Heat pump and round-trip efficiency

In the heat pump operation, the coefficient-of-performance (COP), i.e., the ratio between the heat pumped into the hot side (Q_H) and the electrical work (P_e). Here the theoretically maximum Carnot efficiency (COP_C) is given by:

$$\text{COP} = \frac{Q_H}{P_e}$$

However, in real systems, there are irreversible losses resulting in lower COP values and can be represented by the following equation:

$$\text{COP} = \frac{\eta_{\text{th}}}{}$$
\[ \text{COP} = \eta_{\text{2nd}} \cdot \text{COP}_c = \frac{\eta_{\text{2nd}}}{(1 - \eta_{\text{2nd}})} (A1-2). \]

where \( \eta_{\text{2nd}} \) is the thermodynamic 2nd law efficiency with respect to the ideal Carnot COP value.

Equally, the conversion efficiency for power generation is defined as the ratio between the electrical work extracted (\( P_{\text{out}} \)) and the amount of heat consumed (\( Q_h \)). For the ideal Carnot cycle, the efficiency is given by:

\[ \eta_c = \frac{\text{w}_{\text{out}}}{\text{w}_{\text{in}}} = \frac{1}{T_{\text{High}}} - \frac{1}{T_{\text{Low}}} (A1-3). \]

Again, due to irreversible losses, the efficiency is decreased in real power generation systems and can be represented by:

\[ \eta = \eta_{\text{2nd}} \cdot \eta_c = \frac{\eta_{\text{2nd}}}{(1 - \eta_{\text{2nd}})} (A1-4). \]

where \( \eta_{\text{2nd}} \) again is the thermodynamic 2nd law efficiency.

If a system is used for electricity-to-electricity storage, electricity is initially converted to heat (i.e., heat pump regime) with a COP value given by eq. A1-2 and then it is converted back to electricity with an efficiency given by eq. A1-4. Thus, the total round-trip efficiency (\( \eta_{\text{rt}} \), electricity-to-electricity) is, therefore:

\[ \eta_{\text{rt}} = \eta \cdot \text{COP} = \eta_{\text{2nd}} \cdot \frac{(1 - \eta_{\text{2nd}})}{(1 - \eta_{\text{2nd}})} \cdot \eta_{\text{2nd}} (A1-5). \]

For simplicity, it has been assumed that \( \eta_{\text{2nd}} \) is the same for both heat pumping and power generation. As an example, the round-trip efficiency for an electricity-to-electricity storage system is approximately 60% if its 2nd law efficiency is over 75%. Also, it is seen that \( \eta_{\text{rt}} \) approaches 100% as \( \eta_{\text{2nd}} \) also approaches 100%.

The qualitative explanation is that \( \eta_c \) can approach 100% is that the COP value of the heat pump is always > 1 and compensates for the less than 1 heat-to-electricity conversion efficiency.

**Appendix 2. Thermodynamic description of open circuit potential**

The Gibbs free energy change (\( \Delta G(T) \)) in each of the cells is given by:

\[ \Delta G(T) = \Delta G^0(T) + RT\ln Q (A2-1). \]

where \( \Delta G^0(T) \) is the standard reaction Gibbs Free energy for the redox reactions in the cell and is related to the standard reaction enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) as follows:

\[ \Delta G^0(T) = \Delta H^0 - T\Delta S^0 (A2-2). \]

where \( Q \) is the reaction quotient for the redox reactions. For instance, in the hot cell, the chemical (i.e., discharging) reaction in Fig. 2 is:

\[ \begin{align*}
2\text{Fe}^3+ + \text{Fe}(CN)_6^{3-} &\to 2\text{Fe}^2+ + \text{Fe}(CN)_6^{4-} \\
\text{and its reaction quotient is given by:}
Q &= \frac{[\text{Fe}^2+]^2}{[\text{Fe}^3+]^2} (A2-3).
\end{align*} \]

The total Gibbs free energy of the system is given by the sum of the Gibbs Free energy from both cells:

\[ \Delta G_{\text{ref}} = \Delta G(T_h, Q_h) + \Delta G(T_c, Q_c) = \Delta G^0(T_h) + \Delta G^0(T_c) + RT_h\ln Q_h + RT_c\ln Q_c (A2-5). \]

To a first approximation, \( \Delta H^0 \) and \( \Delta S^0 \) are temperature independent, whereby:

\[ \Delta G^0(T) = \Delta H^0 - T\Delta S^0 - (\Delta H^0 - \Delta H^0 - T\Delta S^0) = -\Delta S^0(T_h - T_c) (A2-6). \]

Here the minus sign before the bracket is because the reactions are reversed (charging) in the hot cell. Furthermore, if the concentration of the reactants and products are the same in both cells, whereby \( Q = Q_h = Q_c \), the change in Gibbs free energy can be derived as follows:

\[ RT_c\ln Q_c + RT_h\ln Q_h = (T_h - T_c)RT\ln Q (A2-7). \]

The Soret effect (i.e., thermal diffusion) can make a small shift in the reaction quotients, but is assumed to be negligible. Considering equations (A2-5 to 7), we have:

\[ \Delta G_{\text{ref}} = -\Delta S^0(T_h - T_c) + (T_h - T_c)RT\ln Q = -(T_h - T_c) \cdot (\Delta S^0 - RT\ln Q) (A2-8). \]

Assuming that the dual-cell system is closed, the Gibbs free energy (\( \Delta G_{\text{ref}} \)) is the maximum amount of extractable work, which is dependent on the temperature difference \( \Delta T \), the reaction entropy, and the reaction quotient. \( \Delta G_{\text{ref}} \) can be related to the open-circuited thermogalvanic/thermolectric voltage (\( E_{\text{cell}} = E_{\text{cell}}(T_h) - E_{\text{cell}}(T_c) \)) that can be measured in the wires between the two cells in Fig. 2a and is related to \( \Delta G_{\text{ref}} \) through:

\[ E_{\text{cell}} = \frac{-\Delta G_{\text{ref}}}{RT} = \Delta T(\Delta S^0 - RT\ln Q) (A2-9). \]

where \( n \) is the number of electrons in the redox reaction, and \( F \) is the Faraday constant. By defining the thermogalvanic (Seebeck) coefficient (\( \alpha = \Delta E/\Delta T \)), where \( \Delta E \) is an electrical potential difference, eq. (A2-9) can be rewritten:

\[ \alpha = \frac{\Delta E}{\Delta T} - \frac{\Delta S^0 - RT\ln Q}{RT} (A2-10). \]

For the electrochemical process, in general, eq. A2-10 can be rewritten as \( \Delta G_{\text{ref}} = \Delta G_{\text{ref}} \cdot \Delta S^0/RT \ln Q, \) where \( \Delta G_{\text{ref}} \) and \( Q \) are the reaction entropy and the reaction quotient for the half cell reactions, respectively. Thus, large \( \Delta S_{\text{ref}} \) and of opposite sign for the half-cell results in a high \( \alpha \). This is fully equivalent to the case for thermoelectric materials with n- and p-type semiconductors.

The reaction quotient \( Q \) is related to the molar fraction of the reduced species (x), i.e., \( \text{Fe}(CN)_6^{3-} \). For the flow batteries, this corresponds to the state-of-charge (SOC) of the flow battery solution. It can be defined in many ways; however, here, the following is used:

\[ x_{\text{red}} = \frac{c_{\text{Red}}}{c_{\text{Total}}} = 1 - \frac{c_{\text{ox}}}{c_{\text{Total}}} = 1 - \frac{1}{x_{\text{red}}^0} (A2-11). \]

where \( c_{\text{Total}} \) is the initial ferricyanide concentration, and is assumed that the initial \( x \) concentration is stoichiometrically balanced to the ferricyanide. In this case, on the basis of conservation of mass, eq. A2-4 for the reaction quotient can be derived as follows:

\[ Q = \frac{2}{3} \frac{x_{\text{red}}^{2/3}}{c_{\text{Total}}(1 - x_{\text{red}}^{2/3})} (A2-11). \]

Consequently, eq. A2-9 can be plotted as a function of x (see Figure S1 in the Supplementary material). In practice, it is very simple to vary the reaction quotient experimentally by electrical ‘charging/discharging’ on one of the cells.
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