



Ecological analysis of a thermally regenerative electrochemical cycle



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ABSTRACT

The performance of a TREC (thermally regenerative electrochemical cycle) has been investigated based on the finite time analysis. The impacts of the cell material, heat exchangers, and heat sources on the maximum ecological objective function and its corresponding power output and efficiency have been analyzed. For prescribed heat sources, the efficiency corresponding to the maximum ecological criterion is always less than that corresponding to the maximum power. Results also reveal that materials with larger isothermal coefficient and specific charge/discharge capacity and lower internal resistance and specific heat lead to a larger maximum ecological objective function and the corresponding power output and efficiency. Heat exchangers with much higher performance are of no practical use to enhance the performance of the TREC system, and the characteristics of the heat sources also present significant impacts on the performance of the TREC under the maximum ecological criterion. As the ecological criterion considers both the energy benefit and loss, the results in this paper may contribute in designing high performance TREC devices.

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1. Introduction

The utilization of low-grade waste heat has attracted much interest following concerns regarding the shortage of fossil energy, the depletion of fossil fuels, and global warming. Thermodynamic cycles such as the ORC (organic Rankine cycle), Kalina cycle, supercritical CO₂ cycle, Stirling engine and those involving heat pipe technology and TE (thermoelectric) devices can alleviate such issues by converting low-grade heat resources into electricity [1–7]. For optimizing the performance of those cycles, MP (maximum power) output is the main figure of merit. Considering finite time durations of the heat transfer processes between heat reservoirs and working fluid, Curzon-Ahlborn [8] proposed the concept of endoreversible Carnot heat engine, and deduced its efficiency at maximum power output. That is the well-known CA efficiency $\eta_{CA} = 1 - \sqrt{T_c/T_h}$. It opens the era of finite time thermodynamics [9,10]. Based on the CA model, by considering different heat transfer laws between the working medium and the heat reservoirs and the internal dissipations, many revisions have been made to describe the real life heat engines more accurately, and some good results have also been obtained [11–19]. However, actual heat

engines may not work in the MP condition, but under a compromise between energy benefits and losses. Angulo-Brown [20] proposed an optimization criterion for Carnot heat engines as $E = \dot{W} - T_c \dot{\sigma}$ to consider both the energy benefits and losses, where \dot{W} is the power output, and $\dot{\sigma}$ is the entropy production rate. Actually it is the Ω criterion for heat engines defined later by Hernández et al. [21]. Based on the Ω criterion, de Tomas et al. [22] and Long et al. [23] obtained the efficiency bounds of the heat engines through the low dissipation model and the minimally nonlinear irreversible model. To step further, Yan [24] declared that it is more reasonable to use $E = \dot{W} - T_0 \dot{\sigma}$ for heat engines, representing the best compromise between the power output \dot{W} and the power loss $T_0 \dot{\sigma}$, which stems from entropy generation in the system and its surroundings, where T_0 is the temperature of the ambient. Many researches had been focused on the irreversible Carnot heat engines under the ecological optimization criterion [25–32]. And the ecological criterion has also been applied to optimize some practical cycles, such as Stirling engine [33], Brayton cycle [26,34–36], and even the quantum heat engines [37]. Yasin et al. [35] conducted a performance analysis based on an ecological performance criterion for an endoreversible regenerative Brayton heat-engine. Abdul et al. [38] ecologically optimized the power output of an endoreversible and regenerative gas-turbine power-cycle for infinite thermal-capacitance rates to and from the reservoirs. Based on the exergy-based ecological criterion, Chen et al. [29] studied a class of generalized irreversible universal steady-

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flow heat-engine cycle models consisting of two heating branches, two cooling branches and two adiabatic branches with the consideration of the losses of heat-resistance, heat leak and internal irreversibility. Furthermore, under the ecological criteria, the performance of many other thermodynamic cycles has also been systematically investigated [39,40].

For energy harvesting, thermoelectrics is a promising technology, however the main disadvantage is the relatively low conversion efficiency and figure-of-merit (ZT) compared to other technologies [41], and the value of ZT is usually less than 2 [42]. What is more, the Seebeck effect in an electrochemical system has also been investigated for energy harvesting systems; the problem is that its efficiency achieved is much lower than the corresponding Carnot efficiency [43,44]. An alternative approach to an electrochemical system for thermal energy harvesting is to explore a thermodynamic cycle as a heat engine. An electrochemical cycle based on the thermogalvanic effect and temperature dependence of electrode potential has been proposed: discharging a battery at temperature T_H and charging back at temperature T_L [45]. If the charging voltage at T_L is lower than the discharging voltage at T_H , net energy is produced by the voltage difference that originates from heat absorbed at the higher temperature. To enhance the efficiency, regenerators have been adopted as in the case of Stirling engines. This is the TREC (thermally regenerative electrochemical cycle), which shows an efficiency of 40–50% of the Carnot limit for high-temperature applications [43]. Recently, TREC has been applied to recovery low-grade thermal energy. Long et al. [46] adopted the TREC to harvest waste heat from the PEMFC (proton exchange membrane fuel cell), and found that the power output of the hybrid system is 6.85%–20.59% larger than that of the PEMFC subsystem, and the total electrical efficiency is improved by 2.74%–8.27%. Lee et al. [44] conducted an experiment on an electrochemical system for efficiently harvesting low-grade heat energy, and found that the electrical efficiency reaches 5.7% when cycled between 10 °C and 60 °C. Yang et al. [47] proposed a charging-free TREC system, and the electrical efficiency of 2.0% is reached for the TREC operating between 20 and 60 °C. Besides, a membrane-free battery for the TREC has been also investigated [48]. Furthermore, multi-objective optimization of a continuous TREC for waste heat recovery has been conducted [49], and the refrigeration system based on reversed TREC has also been studied [50].

However, most the aforementioned literature about the TREC are dedicated to studying the maximum efficiency the TREC can achieve by investigating high performance electrode materials. As a thermodynamic cycle, its performance has not been widely studied. Finite time thermodynamics could offer an alternative method to investigate the performance of the TREC with irreversibility. In this paper, we conduct an analysis of the TREC with imperfect regenerator, internal dissipations and finite heat capacity of external reservoirs based on the ecological criterion. The analytic expressions of the ecological objective function have been deduced. And the impacts of the cell material, heat exchangers and the heat source on the maximum ecological criterion and the corresponding power and efficiency have been studied. And some useful results have been drawn for TREC devices.

2. Mathematical model

As shown in Fig. 1, the TREC consists of four processes: heating, charging, cooling, and discharging. In processes 1–2, the cell is heated from T_L to T_H under an open circuit condition. The cell is then charged at a lower voltage at T_H in process 2–3, and the entropy of the cell increases through heat absorption during the electrochemical reaction. In process 3–4, the cell is cooled down from T_H to T_L in the open circuit state, thus increasing the open circuit

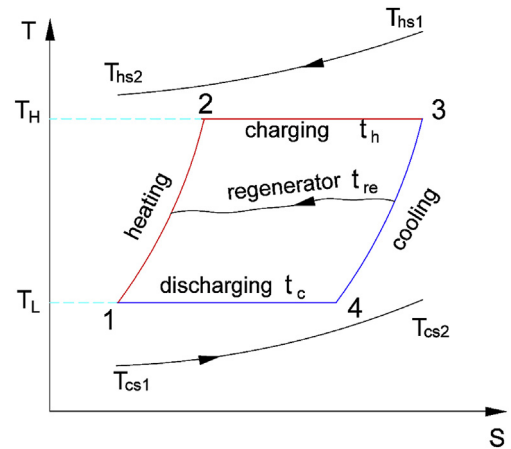


Fig. 1. Schematic T-S diagram for the TREC.

voltage. In the final process (4–1), the cell is discharged at a higher voltage at T_L and the entropy of the cell increases though the ejection of heat into the cold reservoir. After the cycle, the cell returns to its initial state. Furthermore, as the TREC is a Stirling-like cycle, a regenerator should also be adopted to improve its performance, as depicted in Fig. 1. Since the charging voltage is lower than the discharging voltage, the net work (W) equal to the difference between charging and discharging energy is extracted.

In an electrochemical reaction, an isothermal temperature coefficient may be defined when both electrodes are at the same temperature. The isothermal coefficient for the full cell can be defined as [51]

$$\alpha_c = \left(\frac{\partial V_{oc}}{\partial T} \right)_{iso}, \quad (1)$$

where V_{oc} is the open circuit voltage of the full cell in the isothermal condition. α_c has opposite signs in the charging and discharging processes. For a full cell with an electrode reaction $\Sigma A \rightarrow \Sigma B$, the spontaneous reaction in the isothermal cell can be written as $\sum v_j C_j = 0$, where C_j is the j th chemical involved and v_j is its stoichiometric number. v_j is positive for A and negative for B. We then obtain

$$\alpha_c = \left(\frac{\partial V_{oc}}{\partial T} \right)_{iso} = \frac{\sum v_j s_j}{nF}, \quad (2)$$

where s_j is the partial molar entropy of the j th chemical involved, n is the number of moles of electrons passed per v_j mole of C_j reacted, and F is the Faraday constant. The entropy change of the charging process at T_H can thereby be expressed as

$$\Delta S_H = \int_i^f \sum s_j dn_j, \quad (3)$$

where i and f represent the initial state (ΣA) and the final state (ΣB), respectively. It is well known in physical chemistry that the extent of reaction is equal for all chemicals involved in the reaction, as $\xi = (n_j - n_{j0})/v_j$, where n_{j0} is the amount of j th chemical at the initial state, and n_j is the amount of j th chemical at a certain time during the reaction. The substitution of Eq. (2) into Eq. (3) yields

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