



# Performance analysis of a thermally regenerative electrochemical cycle for harvesting waste heat



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## ABSTRACT

The performance of a (TREC) thermally regenerative electrochemical cycle for harvesting waste heat has been investigated based on finite time analysis. The impacts of cell material and heat exchangers on the maximum power extracted and its corresponding efficiency have been analyzed. Results reveal that materials with larger isothermal coefficients, specific charge/discharge capacities, and lower internal resistances correspond to larger maximum power that can be extracted from them. If both power and efficiency are considered, materials with larger isothermal coefficients, specific charge/discharge capacities, appropriate internal resistances, and lower specific heats are more appealing. A better heat exchanger performance increases maximum power output; however, it does not guarantee higher efficiency. This work is expected to contribute in choosing appropriate materials and heat exchangers to improve the performance of 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 CO<sub>2</sub> cycle, and those involving heat pipe technology and (TE) thermoelectric devices can alleviate such issues by converting low-grade heat resources into electricity [1–8]. Among them, thermoelectric materials and devices have been studied extensively in the past few decades [9–14]. Thermoelectric technology is considered to have several advantages; notably, it has no moving parts, has an ability to function in harsh environments, and it has substantially less maintenance requirements than comparable technologies. The main disadvantage of thermoelectrics is the relatively low conversion efficiency and figure-of-merit (ZT) compared to other technologies [15]. Current thermoelectric efficiencies are between 5% and 10% [16], and the value of ZT is usually less than 2 [14]. Besides, the Seebeck effect in an electrochemical system has also been investigated for energy harvesting systems; however, the efficiency achieved is considerably lower than the corresponding Carnot efficiency due to the poor ionic conductivity

of electrolyte that is more than three orders of magnitude smaller than the electronic conductivity [17,18].

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  $T_L$  [3]. 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 concept of a (TREC) thermally regenerative electrochemical cycle that shows an efficiency of 40–50% of the Carnot limit for high-temperature applications [17]. The conversion of thermal energy into electrochemical energy requires that the electrochemical voltage hysteresis during charging/discharging at a fixed temperature must be considerably smaller than the voltage difference caused by the temperature change [18]. Therefore, highly reversible electrochemical electrodes are preferred and significant attention has been focused on investigating high performance electrodes [19,20]. In practice, instead of transport property limited TE devices, the efficiency of a TREC is limited by the heat capacity of materials and the effectiveness of heat exchangers [21]. Recently, TREC has been applied to recovery low-grade thermal energy. Lee et al. [18] conducted an experiment on an electrochemical system for efficiently harvesting low-grade

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heat energy, and found that the electrical efficiency reaches 5.7% when cycled between 10 °C and 60 °C. While most TREC systems still require external electricity for charging, Yang et al. [22] proposed a charging-free TREC system. The two electrochemical processes at both low and high temperatures in a cycle are discharging. The electrical efficiency of 2.0% is reached for the TREC operating between 20 and 60 °C. In addition, a membrane-free battery for the TREC has been also investigated, and the electrical efficiency of 3.5% is obtained when the battery is discharged at 15 °C and recharged at 55 °C [23].

However, all aforementioned studies have focused on studying the maximum efficiency a TREC can achieve by investigating high performance electrode materials. In terms of the actual application, the maximum obtainable power should be considered since larger efficiency needs longer cycle durations that result in vanishing power output. Finite time analysis, i.e., taking into account the cycle duration, can offer a method to mitigate such an issue [24–26]. This paper focuses on the performance of a TREC for harvesting waste heat based on finite time analysis. The impacts of a cell material's characteristics and the heat exchangers on the maximum power output and the corresponding efficiency have been studied. Some useful results have been drawn for recovering waste heat by using 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 (OC) 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 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 through the ejection of heat into the cold reservoir. After the cycle, the cell returns to its initial state. 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 as depicted in Fig. 1(c).

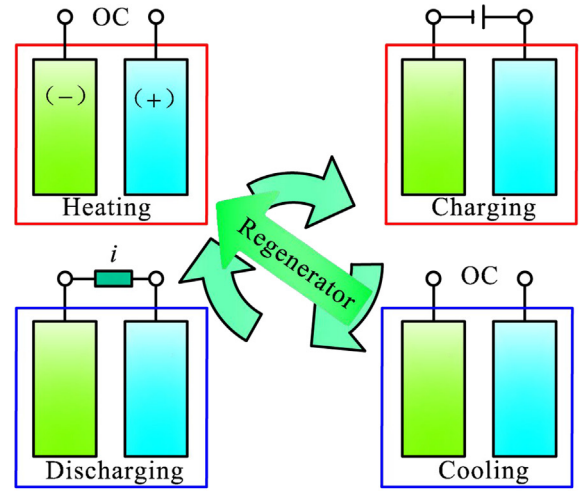
In an electrochemical reaction, an isothermal temperature coefficient may be defined when both electrodes are at the same temperature. The isothermal coefficient for the full cell can be defined as [27]

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

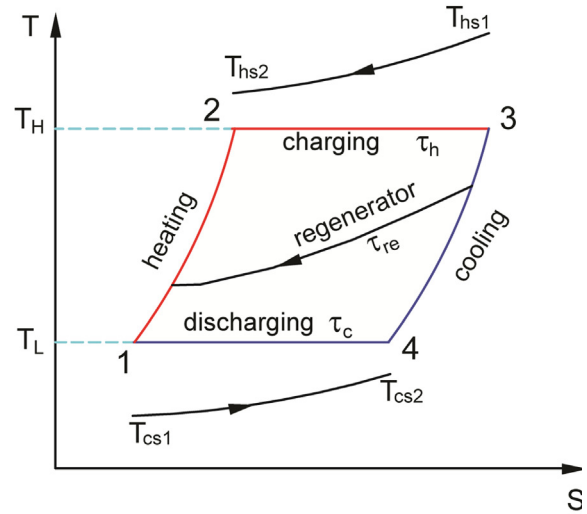
where  $V_{oc}$  is the open circuit voltage of the full cell in the isothermal condition.  $\alpha_c$  has opposite signs in the charging and discharging processes. For a full cell with an electrode reaction  $\Sigma A \rightarrow \Sigma B$ , the spontaneous reaction in the isothermal cell can be written as  $\Sigma v_j C_j = 0$ , 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

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

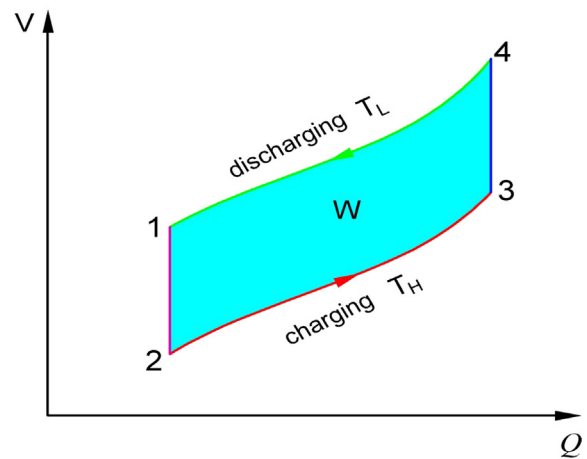
where  $s_j$  is the partial molar entropy of the  $j$ th chemical involved,  $n$  is the number of moles of electrons passed per  $v_j$  mole of  $C_j$  reacted, and  $F$  is the Faraday constant. The entropy change of the charging process at  $T_H$  can thereby be expressed as



(a)



(b)



(c)

**Fig. 1.** Schematic diagram (a) T-S diagram (b) and voltage-quantity of electric charge (c) for the TREC.

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