

The energy storage/release density and net energy density of the electrochemical Brayton cycle: A thermodynamic derivation

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ABSTRACT

The power density and thermal efficiency of the electrochemical Brayton cycle (EBC) have been addressed through the conservation of energy. However, it remains a gap to determine the energy density of charging and discharging processes, a crucial aspect tied to energy storage/release density in EBC systems with integrated energy storage. This study derives the energy storage/release density and net energy density of the ideal EBC system, confirming key parameters including the change in state of charge ΔSOC and the dimensionless figure of merit $\alpha q_v/c_v$ (α : temperature coefficient, q_v : specific charge, c_v : specific heat) are confirmed. The theoretical energy storage/release density approximates 10 W h L^{-1} , and the net energy density is expected to reach 1.0 W h L^{-1} . This study provides a valuable framework for assessing the energy storage performance of EBC systems.

Keywords: energy storage, energy density, electrochemical Brayton cycle, thermodynamic cycle, electrochemical heat engine, flow battery

1. INTRODUCTION

Low-grade heat ($< 100^\circ\text{C}$) is widely available in solar energy, geothermal energy [1], ocean thermal energy, and industrial waste heat [2], with an immeasurable reserve. Therefore, its efficient utilization is promising to meet energy challenges and realize carbon neutrality [3].

Recently, the emerging electrochemical approaches for heat harvesting provided a novel route for the efficient utilization of low-grade heat due to the simple structure, low cost, good portability, and environmental

friendliness [4]. Among them, the thermally regenerative electrochemical cycle (TREC) based on the temperature effect of electrode potential receives great attention because of its outstanding efficiency [5]. The temperature coefficient α in TREC is a thermodynamic property [6], determined by the entropy change of electrode reaction $\alpha = \partial V/\partial T = \Delta S/nF$, where V is the voltage, T is the temperature, ΔS is the entropy change of reaction, n is the number of electrons transferred and F is Faraday's constant [7]. Combined with temperature changes of electrolytes, TREC could be constructed. TREC with a positive temperature coefficient consists of four typical processes: heating, isothermal discharging, cooling, and isothermal charging [8].

TREC is also known as an electrochemical Stirling cycle because it consists of two isothermal processes (charging and discharging) and two isobaric processes (heating and cooling) [7]. According to our previous theoretical research, TREC is the result of retaining the isothermal reaction processes in the ideal cycle and replacing the isentropic reaction processes with isobaric heat exchange processes [9]. Also, cycles with other configurations may be feasible, depending on the availability of actual devices.

Starting from the ideal cycle of the electrochemical Carnot cycle and the decoupling of heat transfer and charge transport, the authors proposed the electrochemical Brayton cycle (EBC) for power generation, in which the charging and discharging processes were adiabatic [10]. Apart from this, the EBC and TREC have the same system structure, as shown in Fig.1.

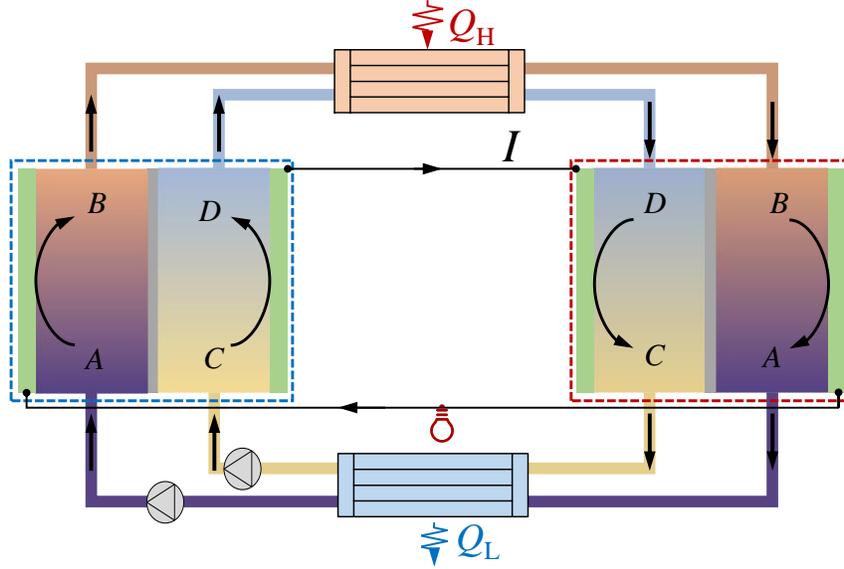


Fig. 1 Schematic of the EBC system

The EBC is more feasible than TREC because the isothermal processes require good heat transfer performance of reactors [11]. In the previous study, the authors preliminarily investigated the performance of the EBC systems based on a two-dimensional model coupling mass transfer and electrode kinetics, showing that the performance of EBC was very promising to compete with existing TRECs, especially in terms of thermal efficiency [12].

On the downside, the system performance of the previous studies was obtained by energy conservation based on solving the temperature of each state point of the cycle. Although this treatment was sufficient to give the power density and thermal efficiency of EBC, it cannot give a specific amount of work transfer during the charging and discharging processes. As the authors pointed out before, the economic improvement of EBC systems depended on their integration with flow battery energy storage [10]. This conceive has been described by the authors. Specifically, in the energy storage mode, the electrolytes are cooled by the heat sink, allowing the charging process to occur at a lower voltage, and then return to the storage tank. In the energy-use mode, the discharging process occurs at a higher voltage because the electrolytes are heated by the heat source as it flows through the heat exchanger. From this point of view, the energy density in the charging and discharging process is particularly important because it is closely related to the performance of energy storage.

In recognition of the above shortcomings, this study strictly deduces the energy storage density, energy release density, and net energy density of the ideal EBC

system are derived. Key parameters are pointed out to provide useful guidance for the integration of EBC systems with flow battery energy storage.

2. MODELING

2.1. Work exchange in EBC

For a general half-cell reaction, its equilibrium potential is governed by the Nernst equation

$$E_{\text{eq}} = E^0 - \frac{RT}{nF} \sum_i \nu_i \ln a_i \quad (1)$$

where E^0 is the standard electrode potential, R is the molar gas constant, T is the temperature, n is the number of electrons transferred, F is the Faraday's constant, ν_i is the stoichiometric coefficient of species i , taking negative values for the reactants and positive values for the products, and a_i is the activity, expresses as $\gamma_i C_i$, where γ_i is the activity coefficient and C_i is the dimensionless concentration. Note that E^0 is a function of temperature, written as

$$E^0 = E^0(T_0) + \alpha_0(T - T_0) \quad (2)$$

where T_0 is the standard temperature and α_0 is the standard temperature coefficient of electrode reaction, which relates to the temperature coefficient α through

$$\alpha = \frac{\Delta_r S_m}{nF} = \alpha_0 - \frac{R}{nF} \sum_i \nu_i \ln a_i \quad (3)$$

where $\Delta_r S_m$ is the entropy change of reaction. The dependence of the activity coefficient on temperature is ignored here. The work exchange during the charging and discharging processes could therefore be expressed as

$$W = - \int_{q_{\text{ini}}}^{q_{\text{fin}}} E dq = -V q_v \int_{\text{SOC}_{\text{ini}}}^{\text{SOC}_{\text{fin}}} E d\text{SOC} \quad (4)$$

where q stands for the quantity of charge, V is the volume of the electrolyte, and SOC is the state of charge. SOC is appointed as 1 as the concentrations of reactants for the discharging reaction approach their maximum operating concentrations, and the concentrations of products approach zero. q_v is the volume specific charge of the electrolyte, calculated through the Faraday's law as

$$q_v = nF \frac{\Delta c_{i,\max}}{V_i} \quad (5)$$

where $\Delta c_{i,\max}$ is the maximum concentration change when SOC changes from 1 to zero. Note that $\Delta c_{i,\max}/V_i$ is constant for the given reaction. The concentration of species could relate to SOC by

$$c = c_{\text{SOC}1} + \Delta c_{\max} (1 - \text{SOC}) \quad (6)$$

It must be noted that in the adiabatic charging and discharging processes of EBC, the temperature of the electrolyte T is a variable that changes with the extent of reaction, making it difficult to integrate Eq. (4). On the other hand, the work exchange W can be determined by the enthalpy change of the electrolyte through the conservation of energy [13]

$$W = -\Delta H_{\text{adi}} \quad (7)$$

$$\Delta H_{\text{adi}} = \int_{\xi_{\text{ini}}}^{\xi_{\text{fin}}} \Delta_r H_m d\xi + C_p (T_{\text{fin}} - T_{\text{ini}}) \quad (8)$$

where $\Delta_r H_m$ is the enthalpy change of reaction, C_p is the total heat capacity of the electrolyte, and ξ is the extent of reaction, relating to SOC by

$$\xi = \frac{V \Delta c_{i,\max}}{V_i} (1 - \text{SOC}) \quad (9)$$

$\Delta_r H_m$ could be expressed as a function of standard electrode potential and temperature coefficient by

$$\Delta_r H_m = \Delta_r G_m^\ominus (T_H) + T_H \Delta_r S_m^\ominus = -nF [E^0 (T_0) - \alpha_0 T_0] \quad (10)$$

It is independent of temperature and activity because the specific heat of species is assumed to be constant before and after the reaction. Therefore, the solution of the work comes down to the solution of the final temperature of the electrolyte during the charging/discharging process.

2.2. Energy density and thermal efficiency

The total differential of the entropy of electrochemical systems is written as [11]

$$dS = \frac{C_p}{T} dT + \Delta_r S_m d\xi \quad (11)$$

Under reversible and adiabatic conditions, there is $dS = 0$. Then Eq. (11) can be rewritten as

$$\left(\frac{\partial T}{\partial \text{SOC}} \right)_S = \frac{T}{C_p} \frac{V \Delta c_{i,\max}}{V_i} \Delta_r S_m = \frac{\alpha q_v}{c_v} T \quad (12)$$

where c_v is the volumetric specific heat. Note $\alpha q_v/c_v$ is a dimensionless figure of merit of the electrolyte, denoted as Y , which characterizes the ratio between the maximum entropic driving force (αq_v) that drives the change in electrolyte temperature and the thermal inertia of the electrolyte (c_v) that opposes that change during the adiabatic reaction process. The solution of Eq. (12) is

$$T = T_{\text{ini}} \exp[Y (\text{SOC} - \text{SOC}_{\text{ini}})] \quad (13)$$

Combining with Eqs. (8)-(10) and (13), the work exchange during the adiabatic charging/discharging processes could be solved as

$$W = V q_v \Delta \text{SOC} [E^0 (T_0) - \alpha_0 T_0] + V c_v T_{\text{ini}} [1 - \exp(-Y \Delta \text{SOC})] \quad (14)$$

where ΔSOC is the change in SOC during the process ($\text{SOC}_{\text{ini}} - \text{SOC}_{\text{fin}}$). For a redox reaction with a positive temperature coefficient, the discharging process occurs at high temperature and the charging process occurs at low temperature. The initial temperatures of the discharging/charging processes are equal to those of heat/cold source T_H and T_L , respectively. Therefore, there is

$$W_{\text{dis}} = V q_v \Delta \text{SOC}_{\text{dis}} [E^0 (T_0) - \alpha_0 T_0] + V c_v T_H [1 - \exp(-Y \Delta \text{SOC}_{\text{dis}})] \quad (15)$$

$$W_{\text{cha}} = V q_v \Delta \text{SOC}_{\text{cha}} [E^0 (T_0) - \alpha_0 T_0] + V c_v T_L [1 - \exp(-Y \Delta \text{SOC}_{\text{cha}})] \quad (16)$$

where W_{dis} is positive and W_{cha} is negative, and there is $\Delta \text{SOC}_{\text{dis}} = -\Delta \text{SOC}_{\text{cha}} > 0$. Further, the net work output by EBC could be determined by

$$W_{\text{net}} = W_{\text{dis}} + W_{\text{cha}} = V c_v [T_H + T_L - T_H \exp(-Y \Delta \text{SOC}) - T_L \exp(Y \Delta \text{SOC})] \quad (17)$$

where ΔSOC refers to $\Delta \text{SOC}_{\text{dis}}$. The net work under the ideal condition is only related to the temperatures of hot and cold sources and the degree to which the reaction proceeds. The volumetric energy density of energy storage/release in the EBC system and the energy density of the EBC system can also be obtained by dividing the above equations by the electrolyte volume V , written as

$$e_v = \frac{W}{V} \quad (18)$$

Without regard to heat regeneration, the heat absorbed by the EBC system from the heat source should be

$$Q_H = Vc_v [T_H - T_L \exp(Y\Delta SOC)] \quad (19)$$

which takes into account the temperature of the electrolyte at the inlet of the heat exchanger is that at the outlet of the adiabatic charging reactor. The thermal efficiency of EBC could be obtained by

$$\eta_{th} = \frac{W_{net}}{Q_H} = 1 - \frac{T_H \exp(-Y\Delta SOC) - T_L}{T_H - T_L \exp(Y\Delta SOC)} \quad (20)$$

Compared with the thermal efficiency expression previously studied by the authors [10], this equation is more concise, with variables of only two temperatures (T_H and T_L) and two dimensionless parameters (Y and ΔSOC).

3. RESULTS AND DISCUSSION

To evaluate the performance of the ideal EBC system, the constraints of electrolyte properties should be considered. Here the standard electrode potential at the standard temperature $E^0(T_0)$ and the standard temperature coefficient α_0 are set to 1.26 V and -2.4 mV K^{-1} respectively according to the vanadium redox reaction [14,15]. The specific heat capacity of the vanadium electrolyte is 4.2 kJ $L^{-1} K^{-1}$ and its specific charge with a concentration of 1 M is 48243 C L^{-1} [16,17], so the dimensionless figure of merit Y is calculated as -0.028. The temperatures of hot/cold sources are considered as 60°C and 20°C respectively to simulate the conditions of a low-grade heat source. Based on the above parameters, the energy density for energy storage and energy release of the ideal system could be assessed.

Fig. 2 shows the energy density of energy storage/release $e_{v,s}$ and $e_{v,r}$ and the energy density of the EBC system $e_{v,EBC}$ as functions of ΔSOC . According to Eq. (17), $e_{v,EBC}$ is the difference between $e_{v,r}$ and $e_{v,s}$. It is informed from Eqs. (15) and (16) that this difference originates from the different operating temperatures of the charging reactor and the discharging reactor. Combined with the operation of flow batteries, an ΔSOC of 0.6 is realistic. Under this condition, the $e_{v,s}$ and $e_{v,r}$ are respectively 9.5 W h L^{-1} and 10.2 W h L^{-1} , corresponding to a $e_{v,EBC}$ of 0.67 W h L^{-1} . If the active species is completely converted ($\Delta SOC = 1$), the $e_{v,s}$ and $e_{v,r}$ could increase to 15.9 W h L^{-1} and 16.9 W h L^{-1} , while the $e_{v,EBC}$ could reach 1.0 W h L^{-1} .

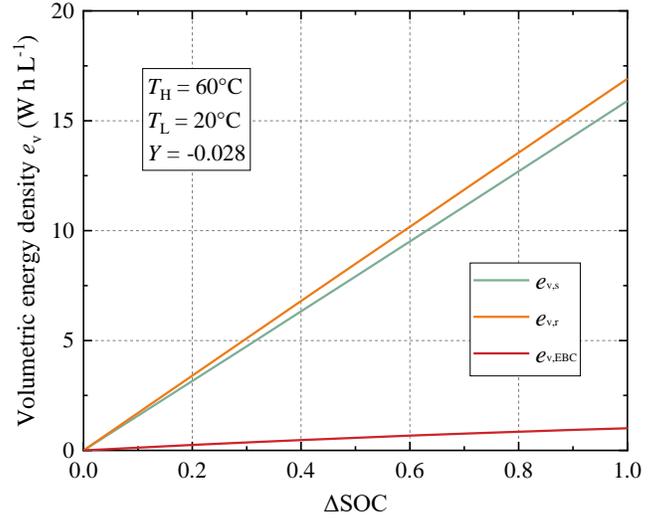


Fig. 2 The energy density of energy storage/release and the EBC system as a function of ΔSOC

With the given ΔSOC and c_v , the $e_{v,s}$ and $e_{v,r}$ is dominated by the volume specific charge q_v and temperature coefficient α . According to Eqs. (15) and (16), the q_v and ΔSOC have the same mechanism of action on $e_{v,s}$ and $e_{v,r}$, while the q_v and α have the same mechanism of action on Y and $e_{v,EBC}$. Therefore, the effect of q_v on energy density is no longer discussed here. Fig. 3 presents the $e_{v,s}$, $e_{v,r}$, and $e_{v,EBC}$ as functions of α with a given ΔSOC of 0.6. Interestingly, the $e_{v,r}$ almost remains unchanged at 10.1 W h L^{-1} as the α increases from 0.5 mV K^{-1} to 5 mV K^{-1} , while the $e_{v,s}$ decreases from 10.0 W h L^{-1} to 8.9 W h L^{-1} . Consequently, the $e_{v,EBC}$ increase from 0.16 W h L^{-1} to 1.2 W h L^{-1} . The different effects of α on $e_{v,s}$ and $e_{v,r}$ is due to the difference in operating temperature of charging and discharging reactors T_H and T_L . At the temperature of T_L , the first and second terms in Eq. (15) cancel each other out, resulting in a basically unchanged $e_{v,r}$. In contrast, at the temperature of T_H , the second term increases faster, so $e_{v,s}$ decreases with the increasing α .

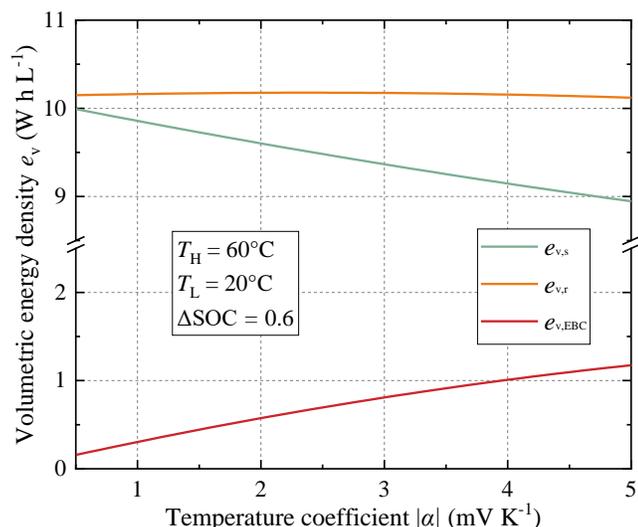


Fig. 3 The energy density of energy storage/release and the EBC system as a function of the temperature coefficient α

It is known from Eq. (20) that the thermal efficiency of the ideal EBC system is only determined by Y and ΔSOC (in addition to the two temperatures). Fig. 4 shows the relative efficiency to the Carnot efficiency of EBC as a function of Y and ΔSOC . Undoubtedly, they have a positive effect on relative efficiency. The relative efficiency could exceed 40% if the $|Y|$ increases to 0.05 and ΔSOC increases to 1. However, with the given Y of -0.028 and ΔSOC of 0.6, the relative efficiency is only 13.8%. Such a fact indicates heat regeneration is necessary to further improve the efficiency of current EBC systems.

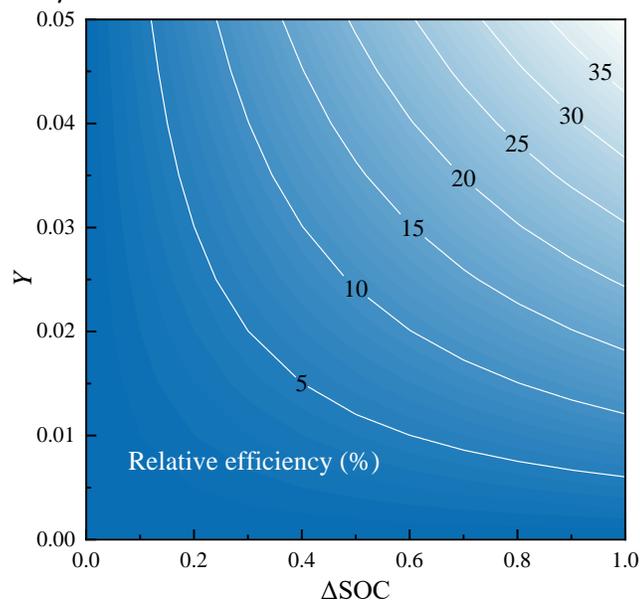


Fig. 4 The relative efficiency of EBC as a function of Y and ΔSOC

4. CONCLUSIONS AND FUTURE DEVELOPMENT

In this study, the energy storage density, energy release density, and net energy density of the ideal EBC

system are derived from a thermodynamic perspective. Key parameters of energy storage/ release density, including the standard electrode potential E^0 , temperature coefficient α , change in the state of charge ΔSOC , specific charge q_v , and specific heat c_v , are confirmed. The net energy density and thermal efficiency are determined only by the dimensionless figure of merit $\alpha q_v/c_v$ and ΔSOC . Parameter analysis shows that the theoretical energy storage/ release density is approximately 10 W h L^{-1} , and the net energy density is expected to reach 1.0 W h L^{-1} . Future research should focus on the energy storage performance of actual EBC systems with irreversible losses caused by overpotentials and internal resistance, which is in progress.

ACKNOWLEDGEMENT

The work is supported by the National Natural Science Foundation of China (No. 52176017) and the China Postdoctoral Science Foundation (No. 2021TQ0237).

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