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Energetic, exergetic and ecological (3E) evaluations of a hybrid system based on a phosphoric acid fuel cell and an organic Rankine cycle

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Abstract: The waste heat from phosphoric acid fuel cells (PAFCs) is available and suitable for additional power generation by means of organic Rankine cycles (ORCs). A new hybrid system model is proposed by integrating PAFC with ORC, where the ORC model is modified in absence of complex working fluid properties. The energetic, exergetic and ecological (3E) performances for the PAFC-ORC hybrid system are evaluated based on thermodynamic laws and steady-state mathematical models. Numerical results show that maximum power output density and maximum ecological objective function (EOF) density of the hybrid system are increased about 25.2 % and 57.5% by comparing to that of the single PAFC system, respectively. Optimum working regions of various performance parameters for the hybrid system are determined considering the trade-offs between multiple optimization criteria. Moreover, the effects of the operating temperature, exchange current density, electrolyte thickness and pinch temperature ratio on the hybrid system performance are analyzed. The obtained results may provide some help for understanding the 3E performance of such an actual cogeneration system.

Key Words: Phosphoric acid fuel cell; Organic Rankine cycle; Energetic; Exergetic; Ecological

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1. Introduction

The depletion of fossil fuel reserves, ongoing energy crises and increasing pollution promote development of renewable energy sources [1, 2]. The fuel cell (FC) technologies have been considered as a solution to help humankind to resist global warming and meet energy demand, and they have attracted widespread attention, especially in some developed countries including US, UK, Japan and Korea [3, 4]. According to the data from the US Department of Energy [5], the FC market increased from \$630 million in 2013 to about \$2.54 billion in 2018, highlighting the growing interest and prospect of FCs.

Among a variety of FCs, phosphoric acid fuel cells (PAFCs) are considered to be one of the most commercialized and well-established hydrogen-oxygen fuel cell technologies [6, 7]. This is because PAFCs have high durability and simple structure due to their moderate operating temperature. However, some disadvantages still limit the further development of PAFCs, such as the low power density, short lifetime and high manufacturing cost [8]. In order to solve those problems, a number of previous works were focused on materials [9, 10], electrochemical techniques [11, 12], transport processes [13, 14], stack systems [15-17] and etc. [18, 19]. These results have laid solid foundations for the performance improvement and quickly accelerating the commercialization process.

In the last decade, relevant studies about PAFC-based hybrid systems have aimed to further improve the fuel utilization [20-25]. The waste heat produced by PAFCs can be harvested to drive some energy conversion devices for the combined cooling, heating, and power (CCHP) applications. The first commercial-scale combined heating and power (CHP) system for PAFC was introduced in 1970s [4]. Since then, the heat-driven refrigerator [20, 21] and thermoelectric cooler [7, 22] were

reported for additional cooling purposes. For additional power generation, Chen et al. [23] used the thermoelectric generator (TEG) to recover the waste heat from PAFC. Açıkkalp [24] evaluated a PAFC-TEG hybrid system with the economic and thermoeconomic point of views. In addition, Açıkkalp et al. [25] also proposed a thermally regenerative electrochemical cycle to recover the PAFC waste heat [25].

Organic Rankine cycles (ORCs) are widely used to recycle various low-grade heat energies, such as solar energy [26], biomass energy [27], geothermal heat [28, 29], industrial waste heat [30, 31], etc. [32]. The ORC performance is routinely related to the detailed working fluid properties. However, Zhao et al. [33] and Perna et al. [34] found that the impacts of working fluid properties on the ORC performance were negligible under optimal conditions. Moreover, Lee et al. [35, 36] developed analytical models to optimize the ORC performance without any working fluid data. It was discovered that the thermal efficiency at the ORC maximum power mainly was dependent on the initial temperatures and pinch-temperature differences of the heating and cooling fluids.

Due to the unique merits such as simple equipment, high security and efficiency, ORCs have been widely used as waste heat recovery technologies for fuel cells [33, 34, 37-45]. For example, Angelino et al. [37] and Vatani et al. [38] proposed molten carbonate fuel cell-ORC hybrid systems, and Mamaghani et al. [39] further studied the integrated system performance based on the energetic, exergetic, economic and environmental evaluations. Akkaya et al. [40] proposed an SOFC-ORC hybrid system and revealed the impacts of some representative operating parameters on the hybrid system performance. Al-Sulaiman et al. [41, 42] performed the energetic and exergetic analyses for this system, and then Pierobon et al. [43] further investigated the system performance using thermodynamic analyses. Furthermore, Borello et al. [44] and He et al. [45] conducted evaluations

on the performances of proton exchange membrane fuel cell (PEMFC)-ORC hybrid power systems. However, so far, performance evaluation on the PAFC-ORC hybrid system is seldom researched, which may provide valuable insights for the practical operation and optimum design of such a hybrid system.

In the present work, a PAFC-ORC hybrid system is proposed to evaluate its performance based on the 3E analyses. Each component within the hybrid system will be mathematically described in detail, where the ORC will adopt an optimization model without any input of working fluid properties. Mathematical expressions for power output, energetic efficiency, exergy destruction rate, exergetic efficiency, EOF and ecological coefficient of performance (ECOP) for the PAFC, ORC and PAFC-ORC hybrid system will be derived, from which the 3E performance characteristics for PAFC-ORC hybrid system will be evaluated. Optimum working regions of various performance parameters for the hybrid system will be also determined using different optimization criteria. Furthermore, the influences of some typical parameters on the 3E performances for the PAFC-ORC hybrid system will be discussed.

2. System description

The working principle of the PAFC-ORC hybrid system is schematically presented by Fig. 1. The hybrid system consists of a PAFC, an ORC and a regenerator, where the regenerator preheats the imported air and fuel using the high-temperature gas products out of the PAFC. The ORC consists of two heat exchangers (HEA and HEB), an expander (EX), a generator (GE), a condenser (CO) and a pump (PU). The PAFC acts as the high-temperature heat source that drives the ORC. In the PAFC, the electrochemical reaction produces electric power generation P_{fc} and waste heat. The produced electricity is transported to loads by an external circuit. A part of the waste heat, \dot{Q}_L , is dissipated

into the environment inevitably, meanwhile, the second part \dot{Q}_{re} is transferred to the regenerator to compensate the regeneration losses, and the third part \dot{Q}_H is used to drive the ORC for the output power P_{orc} . \dot{Q}_C is the heat rate from the ORC to the environment.

The following hypotheses are made to simplify the hybrid system model:

- Reactants of the fuel cell are completely consumed [46];
- The working temperature and pressure for the PAFC are constants [21];
- The PAFC-ORC hybrid system works at steady-state conditions [47];
- The cold and hot junction temperatures for the ORC are equal to the environment and PAFC working temperatures, respectively [23];
- Reactants of the PAFC are ideal gases that have constant thermodynamic and electrochemical properties [21];
- Factors leading to energy dissipation in the ORC are neglected [36];
- The ORC is worked under optimization states.

2.1. Phosphoric acid fuel cell

The PAFC is composed of an anode, a cathode and an electrolyte, which works as the topping cycle of the hybrid system. The chemical energies of hydrogen and oxygen are directly converted into electrical and thermal energies in the PAFC. The overall fuel cell reaction inside the PAFC can be expressed as: $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g) + \text{electricity} + \text{heat}$. The fuel cell theoretical maximum potential, i.e., named reversible potential, can be derived by the Nernst equation [47], i.e.,

$$U_{rev} = \frac{\Delta g^0}{n_e F} + \frac{RT}{n_e F} \ln \left(\frac{a_{H_2} a_{O_2}^{0.5}}{a_{H_2O}} \right) \quad (1)$$

where Δg^0 is the change of molar Gibbs free energy of the electrochemical reaction under standard conditions, and $n_e = 2$ is the number of electrons transferred per hydrogen molecule [7]; F and

R are, respectively, the Faraday's constant and universal gas constant; a_{H_2} , a_{O_2} and a_{H_2O} are, respectively, the partial pressures of H_2 , O_2 and H_2O [23]. Due to the ohmic overpotential (U_{ohm}), concentration overpotential (U_{con}) and activation overpotential (U_{act}), the output voltage of the PAFC U_{fc} is smaller than U_{rev} , which can be explicitly given by [23]

$$U_{fc} = U_{rev} - U_{ohm} - U_{con} - U_{act} \quad (2)$$

$$U_{ohm} = \frac{t_{ele}}{\kappa} j \quad (3)$$

$$U_{con} = b \exp(cj) \quad (4)$$

$$U_{act} = \frac{RT}{\alpha n_e F} \ln \left(\frac{j}{j_0} \right) \quad (5)$$

where j is the operating current density of the PAFC; t_{ele} is the electrolyte thickness; κ is the specific conductivity for the aqueous phosphoric acid solution [25]; b and c are two constants that can be found in Ref. [7]; α and j_0 are, respectively, the charge transfer coefficient and exchange current density [25].

The power output, P_{fc} , and electric efficiency, η_{fc} , for the PAFC are, respectively, given by [23, 48]

$$P_{fc} = U_{fc} j A = \left[U_{rev} - \frac{RT}{\alpha n_e F} \ln \left(\frac{j}{j_0} \right) - b \exp(cj) - \frac{t_{ele}}{\kappa} j \right] j A \quad (6)$$

and

$$\eta_{fc} = \frac{P_{fc}}{-\dot{\Delta H}} \quad (7)$$

where $-\dot{\Delta H} = -\frac{jA\Delta h}{n_e F}$ stands for the total energy released by the reaction per unit time; A is the electrode effective surface area; and Δh is the change of the molar enthalpy [7].

The exergy destruction rate, ExD_{fc} , and exergetic efficiency, ϕ_{fc} , for the PAFC can be,

respectively, given by [47]

$$ExD_{fc} = -\Delta \dot{G} - T \Delta \dot{S} (1 - T_0/T) - P_{fc} \quad (8)$$

and

$$\varphi_{fc} = \frac{P_{fc}}{-\Delta \dot{G} - T \Delta \dot{S} (1 - T_0/T)} \quad (9)$$

where $-\Delta \dot{G} = -\frac{jA\Delta g}{n_e F}$ and $-\Delta \dot{S} = -\frac{jA\Delta s}{n_e F}$ are, respectively, the total Gibbs free energy change rate and the total entropy change rate [46]; Δg is the molar Gibbs free energy change; and Δs stands for the molar entropy change.

The entropy production rate for the PAFC, $\dot{\delta}_{fc}$, can be calculated as [49, 50]

$$\dot{\delta}_{fc} = (-\Delta \dot{H} - P_{fc}) / T \quad (10)$$

The EOF for the PAFC, E_{fc} , can be defined as [49]

$$E_{fc} = P_{fc} - T_0 \dot{\delta}_{fc} \quad (11)$$

The ECOP for the PAFC, ϕ_{fc} , can be expressed as [49]

$$\phi_{fc} = P_{fc} / (T_0 \dot{\delta}_{fc}) \quad (12)$$

2.2. Regenerator

Based on Refs. [23, 33], the regeneration loss rate is directly proportional to the temperature difference between exhaust products and inlet reactants, i.e.,

$$\dot{Q}_{re} = K_{re} A_{re} (1 - \beta) (T - T_0) \quad (13)$$

where K_{re} is the heat-transfer coefficient of the regenerator; A_{re} and β are, respectively, the heat-transfer area and effectiveness.

2.3. Organic Rankine cycle

As shown in Fig. 1, the ORC operates between the hot reservoir (i.e., PAFC) and the cold

reservoir (i.e., environment). The HEB of the ORC can increase the temperature of the subcooled liquid from the PU by a relatively high-temperature liquid from the EX. The ORC adopts a modified Rankine engine model, which is alternately connected to cooling fluid and heating fluid with finite-rate heat capacities [51]. The temperature-entropy (T - S) diagram for the modified ORC is shown in Fig. 2, and the modified ORC can be equivalently regarded as a Carnot cycle operating between temperatures T_e and T_c [36]. The ORC includes four processes: isobaric heating (4-1), adiabatic expansion (1-2), isobaric exothermic (2-3) and adiabatic compression (3-4). Due to the low efficiencies of the EX and PU, the expansion and compression processes are non-isentropic and can be described as 1-2' and 3-4', respectively. The heat source temperature initially cools from T_{H1} to T_{H2} with the heat rejection, and the heat sink temperature initially warms up from T_{L1} to T_{L2} with the heat addition. Thus, the heat input rate \dot{Q}_H and heat rejection rate \dot{Q}_L of the ORC can be, respectively, computed as [35]

$$\dot{Q}_H = C_H (T_{H1} - T_{H2}) \quad (14)$$

$$\dot{Q}_L = C_L (T_{L2} - T_{L1}) \quad (15)$$

The outlet temperatures of heating fluid at HEA and cooling fluid at HEB are, respectively, given by [36]

$$T_{H2} = T_e + T_{PH} \quad (16)$$

$$T_{L2} = T_c + T_{PL} \quad (17)$$

Combining Eqs. (14) - (17), one has

$$\dot{Q}_H = C_H (T_{He} - T_e) \quad (18)$$

$$\dot{Q}_L = C_L (T_c - T_{Le}) \quad (19)$$

where C_H and C_L are, respectively, the heat capacities for the heating fluid and cooling fluid, and

$$T_{He} = T_{H1} - T_{pH} \quad (20)$$

$$T_{Le} = T_{L1} - T_{pL} \quad (21)$$

T_{pH} and T_{pL} are the pinch temperatures for the heating fluid and cooling fluid [36].

Based on the second law of thermodynamics, the entropy generation rate of the ORC can be expressed as [51]

$$\dot{\delta}_{orc} = \dot{Q}_L / T_c - \dot{Q}_H / T_e \quad (22)$$

Based on Eqs. (18) and (19), Eq. (22) can be rewritten as

$$\dot{\delta}_{orc} = \frac{C_L(T_c - T_{Le})}{T_c} - \frac{C_H(T_{He} - T_e)}{T_e} \quad (23)$$

Thus, T_e can be given by

$$T_e = \frac{C_L T_{He} T_c}{C_L(T_c - T_{Le}) + C_H T_c - T_c \dot{\delta}_{orc}} \quad (24)$$

According to Eqs. (18), (19) and (24), the output power for the ORC, P_{orc} , can be calculated as [36]

$$P_{orc} = \dot{Q}_H - \dot{Q}_L = C_H \left[T_{He} - \frac{C_L T_{He} T_c}{C_L(T_c - T_{Le}) + C_H T_c - T_c \dot{\delta}_{orc}} \right] - C_L(T_c - T_{Le}) \quad (25)$$

Substituting Eq. (25) into the extreme condition $\partial P_{orc} / \partial T_e = 0$, one has

$$T_c = T_{Le}^{0.5} \frac{C_H T_{He}^{0.5} + C_L T_{Le}^{0.5}}{C_H + C_L - \dot{\delta}_{orc}} \quad (26)$$

Thus, P_{orc} can be rewritten as

$$P_{orc} = \frac{x(1-x)C_T^2(T_{He}^{0.5} - T_{Le}^{0.5})^2 - C_T(xT_{He} - (1-x)T_{Le})\dot{\delta}_{orc}}{C_T - \dot{\delta}_{orc}} \quad (27)$$

where $x = C_H / C_T$ and $C_T = C_H + C_L$.

Substituting Eq. (27) into the extreme condition $\partial P_{orc} / \partial x = 0$, one has

$$x_{opt} = 0.5 - 0.5 \frac{(T_{He}^{0.5} + T_{Le}^{0.5}) \dot{\delta}_{orc}}{(T_{He}^{0.5} - T_{Le}^{0.5}) C_T} \quad (28)$$

The output power of the ORC can be rewritten as

$$P_{orc} = \frac{x_{opt} (1 - x_{opt}) C_T^2 (T_{He}^{0.5} - T_{Le}^{0.5})^2 - C_T (x_{opt} T_{He} - (1 - x_{opt}) T_{Le}) \dot{\delta}_{orc}}{C_T - \dot{\delta}_{orc}} \quad (29)$$

The energy efficiency for the ORC, η_{orc} , can be defined as [23]

$$\eta_{orc} = P_{orc} / \dot{Q}_H \quad (30)$$

The exergy destruction rate for the ORC, ExD_{orc} , can be given by [47]

$$ExD_{orc} = \dot{Q}_H (1 - T_0/T_H) - \dot{Q}_L (1 - T_0/T_L) + P_{orc} \quad (31)$$

The exergetic efficiency of the ORC, ϕ_{orc} , can be written as [49]

$$\phi_{orc} = \frac{P_{orc}}{\dot{Q}_H (1 - T_0/T_H)} \quad (32)$$

The EOF for the ORC, E_{orc} , can be given by [49]

$$E_{orc} = P_{orc} - T_0 \dot{\delta}_{orc} \quad (33)$$

The ECOP for the ORC, ϕ_{orc} , can be expressed as [49]

$$\phi_{orc} = P_{orc} / (T_0 \dot{\delta}_{orc}) \quad (34)$$

2.4. Performance of the hybrid system

According to the Newton's heat-transfer law and the first law of thermodynamics, \dot{Q}_L and \dot{Q}_H can be, respectively, given by [47, 52]

$$\dot{Q}_L = \alpha_L A_L (T - T_0) \quad (35)$$

and

$$\dot{Q}_H = -\Delta \dot{H} - P_{fc} - \dot{Q}_{re} - \dot{Q}_L = A \left[(1 - \eta_{FC}) \frac{-\Delta h}{n_e F} j - (c_1 + c_2)(T - T_0) \right] \quad (36)$$

where α_L and A_L are the heat-leak coefficient and the heat-leak area, respectively; $c_1 = [K_{re} A_{re} (1 - \beta)] / A$ and $c_2 = (\alpha_L A_L) / A$ are two temperature independent constants related to the heat transfer irreversibilities, effectiveness of the regenerator, geometric size of the regenerator and the PAFC and polar plate area of the PAFC [20]. Combining Eqs. (18) and (36), the heat capacity of the heating fluid for the ORC can be further expressed as

$$C_H = \frac{A}{T_{He} - T_e} \left[(1 - \eta_{FC}) j \frac{-\Delta h}{n_e F} - (c_1 + c_2)(T - T_0) \right] \quad (37)$$

The power output, P_{hy} , and energy efficiency, η_{hy} , of the hybrid system can be, respectively, written as

$$P_{hy} = P_{fc} + P_{orc} \quad (38)$$

and

$$\eta_{hy} = P_{hy} / (-\Delta \dot{H}) \quad (39)$$

The output power for the ORC P_{orc} can be equivalently described by an output voltage $U_{orc,eq}$ with respect to the PAFC operating electric current [36], and thus one has

$$U_{orc,eq} = P_{orc} / Aj \quad (40)$$

Therefore, the equivalent output voltage for the hybrid system $U_{hy,eq}$ can be given by [36]

$$U_{hy,eq} = P_{hy} / Aj = U_{fc} + U_{orc,eq} \quad (41)$$

The exergy destruction rate, ExD_{hy} , and exergetic efficiency, ϕ_{hy} , for the hybrid system can be, respectively, expressed as [41]

$$ExD_{hy} = -\Delta \dot{G} - T \Delta \dot{S} (1 - T_0 / T) - P_{hy} \quad (42)$$

and

$$\phi_{hy} = \frac{P_{hy}}{-\Delta \dot{G} - T \Delta \dot{S} (1 - T_0 / T)} \quad (43)$$

The entropy production rate for the hybrid system, $\dot{\delta}_{hy}$, can be given by

$$\dot{\delta}_{hy} = (-\Delta \dot{H} - P_{hy}) / T \quad (44)$$

The EOF for the hybrid system, E_{hy} , can be calculated by [49]

$$E_{hy} = P_{hy} - T_0 \dot{\delta}_{hy} \quad (45)$$

The ECOP for the hybrid system, ϕ_{hy} , can be given by [49]

$$\phi_{hy} = \frac{P_{hy}}{T_0 \dot{\delta}_{hy}} \quad (46)$$

The energy efficiency for the ORC, $\eta_{orc,eq}$, can be determined as [36]

$$\eta_{orc,eq} = \frac{P_{orc}}{-\Delta \dot{H}} \quad (47)$$

The equivalent exergetic efficiency, $\phi_{orc,eq}$, and the equivalent ECOP, $\phi_{orc,eq}$, for the ORC in term of the hybrid system can be, respectively, described as [36]

$$\phi_{orc,eq} = \frac{P_{orc}}{-\Delta \dot{G} - T \Delta \dot{S} (1 - T_0 / T)} \quad (48)$$

and

$$\phi_{orc,eq} = P_{orc} / (T_0 \dot{\delta}) \quad (49)$$

3. Results and discussion

On the basis of default parameters in Table 1, the 3E performance characteristics for the PAFC-ORC hybrid system can be evaluated. These parameters are considered as unchanged ones unless specified elsewhere.

3.1. Generic performance characteristics

The current-voltage curves for the PAFC, ORC and hybrid system are shown in Fig. 3. The operating voltage for the PAFC, U_{fc} , decreases with j due to the increases of U_{ohm} , U_{act} and U_{con} as j increases. The equivalent voltage for the ORC, $U_{orc,eq}$, monotonically increases with j

because the heat rate from the PAFC to the ORC increases with j . However, the total equivalent voltage of the hybrid system, $U_{hy,eq}$, is a monotonically decreasing function of j , because the reduction of U_{fc} is larger than the increment of $U_{orc,eq}$ as j increases.

Figs. 4~6 compare the 3E performances between the PAFC system, ORC and hybrid system, respectively, where $P_{fc}^* = P_{fc} / A$, $P_{orc}^* = P_{orc} / A$ and $P_{hy}^* = P_{hy} / A$ are the power densities for the single PAFC system, ORC and hybrid system, respectively; $ExD_{fc}^* = ExD_{fc} / A$ ($E_{fc}^* = E_{fc} / A$), $ExD_{orc}^* = ExD_{orc} / A$ ($E_{orc}^* = E_{orc} / A$) and $ExD_{hy}^* = ExD_{hy} / A$ ($E_{hy}^* = E_{hy} / A$) are the corresponding exergy destruction rate densities (EOF densities), respectively; P_{orc}^* , $\eta_{orc,eq}$, ExD_{fc}^* , ExD_{orc}^* , ExD_{hy}^* , $\phi_{orc,eq}$, E_{orc}^* and $\phi_{orc,eq}$ are monotonically increasing functions of j , while η_{fc} , η_{hy} , ϕ_{fc} , ϕ_{hy} , ϕ_{fc} and ϕ_{hy} are monotonically decreasing functions of j . P_{fc}^* , P_{hy}^* , E_{fc}^* and E_{hy}^* first ascend and then descend with j , while they attain maximum values at different j . Through numerical calculation, a maximum power density of $P_{hy,max}^* = 6036.7 \text{ W m}^{-2}$ and a corresponding optimal current density of $j_{hy,P} = 9470.8 \text{ A m}^{-2}$ of the hybrid system can be achieved. Comparing to the maximum power density $P_{fc,max}^* = 4822.4 \text{ W m}^{-2}$ and the corresponding optimal current density $j_{fc,P} = 8760.8 \text{ A m}^{-2}$ of the single PAFC system, it is found that the maximum power density and optimal current density of hybrid system are larger than those of the single PAFC system. E_{hy}^* attains its maximum $E_{hy,max}^*$, 2913.1 W m^{-2} , at $j = j_{hy,E} = 7050.8 \text{ A m}^{-2}$, while E_{fc}^* reaches its maximum $E_{fc,max}^*$, 1850.0 W m^{-2} , at $j = j_{fc,E} = 5270.8 \text{ A m}^{-2}$. $E_{hy,max}^*$ is approximately 57.5% higher than $E_{fc,max}^*$. $\eta_{hy,P}$ ($\eta_{fc,P}$), $ExD_{hy,P}^*$ ($ExD_{fc,P}^*$), $\phi_{hy,P}$ ($\phi_{fc,P}$), $E_{hy,P}^*$ ($E_{fc,P}^*$) and $\phi_{hy,P}$ ($\phi_{fc,P}$) are the energy efficiency, exergy destruction rate density, exergetic efficiency, EOF density and ECOP for the hybrid system (single PAFC system) at $j = j_{hy,P}$ ($j = j_{fc,P}$). $P_{hy,E}^*$ ($P_{fc,E}^*$), $\eta_{hy,E}$ ($\eta_{fc,E}$), $ExD_{hy,E}^*$ ($ExD_{fc,E}^*$), $\phi_{hy,E}$ ($\phi_{fc,E}$) and $\phi_{hy,E}$ ($\phi_{fc,E}$) are the output power density, energy

efficiency, exergy destruction rate density, exergetic efficiency and ECOP for the hybrid system (single PAFC system) at $j = j_{hy,E}$ ($j = j_{fc,E}$). For the typical parameters given in Table 1, the above key performance parameters are compared in Table 2. It can be seen from Table 2 that the 3E performances of the hybrid system are significantly better than those of a single PAFC system in terms of either output power optimization criterion or EOF optimization criterion. From the above analyses, coupling an ORC to a PAFC is an effective way for performance improvement.

To obtain the optimal working regions, the variations of the exergetic efficiency (curves 1 and 2) and EOF density (curves 3, 4 and 5) for the hybrid system with power density are illustrated in Fig. 7, where $\varphi_{hy,max}$ is the maximum of φ_{hy} . φ_{hy} increases at the expense of P_{hy}^* in the curve 1, while it decreases as P_{hy}^* reduces in the curve 2. By considering the balance between energetic and exergetic performances, the optimal regions for the PAFC-ORC hybrid system should be $0 \leq j \leq j_{hy,P}$, $0 \leq P_{hy}^* \leq P_{hy,max}^*$, $\varphi_{hy,max} \leq \varphi_{hy} \leq \varphi_{hy,P}$ and $0 \leq E_{hy}^* \leq E_{hy,P}^*$. On the other hand, E_{hy}^* improves as P_{hy}^* arises in curves 3 and 5, while it increases at the expense of P_{hy}^* in the curve 4. By considering the trade-off between energetic and ecological performances, the optimal regions for the PAFC-ORC hybrid system should be located in $j_{hy,E} \leq j \leq j_{hy,P}$, $P_{hy,E}^* \leq P_{hy}^* \leq P_{hy,max}^*$, $\varphi_{hy,P} \leq \varphi_{hy} \leq \varphi_{hy,E}$ and $E_{hy,P}^* \leq E_{hy}^* \leq E_{hy,max}^*$.

4. Parametric study

To further understand the thermodynamic performance of the PAFC-ORC hybrid system, in this section, the effects of some key parameters (including the operating temperature, exchange current density, electrolyte thickness and pinch temperature ratio) on 3E performances for the hybrid system are discussed through parametric studies.

4.1. Effects of operating temperature

Fig. 8 shows the 3E performances under different operating temperatures T . An increasing T can simultaneously enhance the gas effective diffusion, electrochemical reactivity and ionic conductivity of the PAFC as well as the power output and energy efficiency of the ORC. Thus, the performance of the PAFC-ORC hybrid system is improved with the increasing T . Fig. 8 also illustrates that P_{hy}^* , η_{hy} , ϕ_{hy} , E_{hy}^* and ϕ_{hy} increase while ExD_{hy}^* diminishes as T increases. $P_{hy,max}^*$ is equal to 5640.9, 6036.7 and 6300.9 W m⁻² and $E_{hy,max}^*$ is equal to 2509.0, 2913.1 and 3242.0 W m⁻² when T is set as 433, 453 and 473 K, respectively. In Fig. 9, $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$, $E_{hy,P}^*$, $j_{hy,E}$, $P_{hy,E}^*$ and $E_{hy,max}^*$ are improved with the increase of T , while $\phi_{hy,E}$ is reduced as T raises. Although a larger T is beneficial for improving the hybrid system performance, it may also cause some problems such as worse stability, longer start-up time and shut-down time.

4.2. Effects of electrolyte thickness

Fig. 10 shows the 3E performances for the hybrid system under different electrolyte thicknesses t_{ele} . It can be seen from Eq. (3) that t_{ele} has a positive influence on the ohmic overpotential U_{ohm} . Therefore, the performances of the PAFC system and the hybrid system can be turned by adjusting the thicknesses t_{ele} . As verified in Fig. 10, the 3E performances of the hybrid system are improved while P_{hy}^* , η_{hy} , ϕ_{hy} , E_{hy}^* and ϕ_{hy} are decreased as t_{ele} is decreased. For the typical parameters in Table 1, when t_{ele} is equal to 0.001, 0.002 and 0.003 m, $P_{hy,max}^*$ are 7325.9, 6036.7 and 4905.5 W m⁻² and $E_{hy,max}^*$ are 4323.6, 2913.1 and 2066.1 W m⁻², respectively. Furthermore, $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$, $E_{hy,P}^*$, $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ are reduced as t_{ele} increases. As a result, decreasing the electrolyte thickness can improve the hybrid system performances. Simultaneously, the mechanical properties of the electrolyte are somewhat reduced as the electrolyte thickness descends [53].

4.3. Effects of exchange current density

The exchange current density j_0 is the rate for both oxidation and reduction per unit of electrode area at equilibrium states. It is a measure of the ability for the electrode to perform an electrochemical reaction [54, 55]. A higher j_0 means that the surface of the electrode is more active. Thus the activation overpotential U_{act} is a monotonically decreasing function of j_0 as shown in Eq. (5), and a larger j_0 is beneficial for exergetic and ecological performances of the PAFC-ORC hybrid system. As shown in Fig. 11, $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$, $E_{hy,P}^*$, $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ are increased with an increase in j_0 . Moreover, P_{hy}^* , η_{hy} , ϕ_{hy} , E_{hy}^* and ϕ_{hy} are improved while ExD_{hy}^* is diminished as j_0 increases. When j_0 is 0.02, 0.06 and 0.1 A m⁻², $P_{hy,max}^*$ equals 5801.2, 6036.7 and 6146.7 W m⁻² and $E_{hy,max}^*$ is 2626.6, 2913.1 and 3049.9 W m⁻², respectively. So far, researchers are trying to increase the phosphoric acid concentration, operating temperature, electrode catalyst loading, catalyst specific surface area and so on to improve the exchange current density of the fuel cell [55].

4.4. Effects of pinch temperature ratio

$\gamma = T_{pL} / T_{pH}$ is defined as the pinch temperature ratio which affects the ORC performance.

Based on Eqs. (18)-(21), the output power for the ORC can be given by

$$\begin{aligned} P_{orc} &= C_H (T_{H1} - T_{pH} - T_e) - C_L (T_c - T_{L1} + T_{pL}) \\ &= C_H \left[(T_{H1} - T_e) - \left(\frac{1}{x_{opt}} - 1 \right) (T_c - T_{L1} + T_M) + \left(\frac{1}{x_{opt}} - 2 \right) \frac{T_M}{1 + \gamma} \right] \end{aligned} \quad (50)$$

where $T_M = T_{pL} + T_{pH}$. Based on Eq. (28), one has $x_{opt} < 0.5$, i.e., $(x_{opt}^{-1} - 2) > 0$, and thus P_{orc} decreases as γ increases. Thus, the PAFC-ORC hybrid system performances are degraded with γ , as displayed in Fig. 12. P_{hy}^* , η_{hy} , ϕ_{hy} , E_{hy}^* and ϕ_{hy} are diminished while ExD_{hy}^* is improved as γ increases. $P_{hy,max}^*$ is equal to 6138.7, 6036.7 and 5989.0 W m⁻² and $E_{hy,max}^*$ is equal to 3015.6,

2913.1 and 2866.8 W m⁻² when γ is fixed as 1/3, 1, 3, respectively. In Fig. 13, $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$, $E_{hy,P}^*$, $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ are decreased as γ increases.

5. Conclusions

A theoretical model of PAFC-ORC hybrid system has been established with the aim to harvest the waste heat from the PAFC for additional electricity generation via ORC. Mathematical expressions for the power, energy efficiency, exergy destruction rate, exergetic efficiency, EOF and ECOP for the stand-alone PAFC, ORC and PAFC-ORC hybrid system are derived, from which the 3E performances for PAFC-ORC hybrid system are revealed. The maximum power density for the hybrid system ($P_{hy,max}^* = 6036.7 \text{ W m}^{-2}$) allows approximately 25.2% higher than that of the single PAFC system ($P_{fc,max}^* = 4822.4 \text{ W m}^{-2}$). The maximum EOF density for the hybrid system ($E_{hy}^* = 2913.1 \text{ W m}^{-2}$) allows approximately 57.5% higher than that of the single PAFC system ($E_{fc,max}^* = 1850.0 \text{ W m}^{-2}$). ORCs are found to be effective for waste heat recovery for PAFCs. The optimal working regions for various performance parameters are determined using different optimization criteria. Furthermore, the effects for various parameters on the 3E performances of the PAFC-ORC hybrid system are revealed. The obtained research results may provide some new insights and valuable guidance for PAFC performance improvement via cogeneration approaches.

Acknowledgments

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Nomenclature

A	Effective polar plate area of PAFC (m^2)
A_L	Heat-transfer area between the fuel cell and the environment (m^2)
a	Partial pressures (atm)
b	Constant in Eq. (4)
C	Heat capacity rate (W)
c	Constant in Eq. (4)
c_1 and c_2	Constants in Eq. (36) ($\text{W m}^{-2} \text{K}^{-1}$)
E	Ecological objective function (W)
ExD	Exergy destruction rate (W)
F	Faraday's constant (C mol^{-1})
$-\Delta G$	Gibbs free energy change (J)
$-\Delta H$	Total energies released (J)
j	Operating current density of the PAFC (A m^{-2})
j_0	Exchange current density of the PAFC (A m^{-2})
K_L	Heat-leak coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
n_e	Number of electrons exchanged per hydrogen molecule
U	Voltage (V)
U_{act}	Activation overpotential (V)
U_{con}	Concentration overpotential (V)
U_{ohm}	Ohmic overpotential (V)
U_{rev}	Reversible potential (V)

P	Power output (W)
Q	Heat (J)
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
$-\Delta S$	Entropy change (J K^{-1})
T	Operating temperature of PAFC (K)
t_{ele}	Thickness of the electrolyte (cm)
x	Heat capacity rate
<i>Greek symbols</i>	
α	Charge transfer coefficient
β	Regenerator effectiveness
δ	Entropy production (J K^{-1})
ϕ	Ecological coefficient of performance
φ	Exergetic efficiency
η	Electric efficiency
σ_{ele}	Proton conductivity of the electrolyte ($\Omega \text{ m}^{-1}$)
ε	Irreversibility ratio of the ORC
γ	Pinch temperature ratio
<i>Subscripts</i>	
0	Ideal standard
eq	Equivalent
fc	Phosphoric acid fuel cell
H	High

hy	PAFC-ORC hybrid system
L	Low
max	Maximum
orc	Organic Rankine cycle
p	Pinch
re	Regenerative
*	Unit area
Δ	Difference
•	Unit time

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Table captions

Table 1. Parameters used in the modeling.

Table 2. Performance parameter comparisons between the single PAFC system and the PAFC-ORC hybrid system.

Figure captions

Fig. 1. The schematic diagram of the PAFC-ORC hybrid system, where the ORC consists of two heat exchangers (HEA and HEB), an expander (EX), a generator (GE), a condenser (CO) and a pump (PU).

Fig. 2. Temperature-entropy diagram for the modified ORC.

Fig. 3. Current-voltage curves for the single PAFC system, ORC and PAFC-ORC hybrid system.

Fig. 4. Energetic performance comparisons between the single PAFC system, ORC and PAFC-ORC hybrid system: (a) power density; (b) energy efficiency, where $P_{fc}^* = P_{fc} / A$, $P_{orc}^* = P_{orc} / A$ and $P_{hy}^* = P_{hy} / A$ are the corresponding power densities; $P_{hy,max}^*$ (at $j = j_{hy,P}$) and $P_{fc,amx}^*$ (at $j = j_{fc,P}$) are the maximum values for P_{hy}^* and P_{fc}^* , respectively; the maximum EOF densities for the hybrid system and the single PAFC system are obtained at $j = j_{hy,E}$ and $j = j_{fc,E}$; $P_{hy,E}^*$ ($P_{fc,E}^*$) is the value for P_{hy}^* (P_{fc}^*) at $j = j_{hy,E}$ ($j = j_{fc,E}$). $\eta_{fc,P}$ and $\eta_{fc,E}$ are, respectively, values of η_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, and $\eta_{hy,P}$ and $\eta_{hy,E}$ are values of η_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$, respectively.

Fig. 5. Exergetic performance comparisons between the single PAFC system, ORC and PAFC-ORC hybrid system: (a) exergy destruction rate density; (b) exergetic efficiency, where $ExD_{fc}^* = ExD_{fc} / A$, $ExD_{orc}^* = ExD_{orc} / A$ and $ExD_{hy}^* = ExD_{hy} / A$ are the corresponding exergy destruction rate densities; $ExD_{hy,P}^*$ and $ExD_{hy,E}^*$ are, respectively, values for ExD_{hy}^* at $j = j_{hy,P}$ and at $j = j_{hy,E}$, $ExD_{fc,P}^*$ and $ExD_{fc,E}^*$ are, respectively, values for ExD_{fc}^* at

$j = j_{fc,P}$ and at $j = j_{fc,E}$; $\phi_{hy,P}$ and $\phi_{hy,E}$ are, respectively, values of ϕ_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$; and $\phi_{fc,P}$ and $\phi_{fc,E}$ are values of ϕ_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, respectively.

Fig. 6. Ecological performance comparisons between the single PAFC system, the ORC and the PAFC-ORC hybrid system: (a) EOF density; (b) ECOP, where $E_{fc}^* = E_{fc} / A$, $E_{orc}^* = E_{orc} / A$ and $E_{hy}^* = E_{hy} / A$ are the corresponding EOF densities; $E_{hy,max}^*$ and $E_{fc,amx}^*$ are, respectively, the maximum values for E_{hy}^* and E_{fc}^* ; $E_{hy,P}^*$ and $E_{hy,E}^*$ are, respectively, values for E_{hy}^* at $j = j_{hy,P}$ and at $j = j_{hy,E}$, $E_{fc,P}^*$ and $E_{fc,E}^*$ are, respectively, values for E_{fc}^* at $j = j_{fc,P}$ and at $j = j_{fc,E}$; $\phi_{hy,P}$ and $\phi_{hy,E}$ are, respectively, values of ϕ_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$; and $\phi_{fc,P}$ and $\phi_{fc,E}$ are values of ϕ_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, respectively.

Fig. 7. Variations of ϕ_{hy} (curves 1 and 2) and E_{hy}^* (curves 3, 4 and 5) versus P_{hy}^* .

Fig. 8. Effects of the operating temperature T on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 9. (a) Variations of $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$ and $E_{hy,P}^*$ versus T ; and (b) Curves of $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ versus the operating temperature T .

Fig. 10. Effects of the electrolyte thickness t_{ele} on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 11. Effects of the exchange current density j_0 on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 12. Effects of the pinch temperature ratio γ on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 13. (a) Variations of $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$ and $E_{hy,P}^*$ versus the pinch temperature ratio γ ; and (b) Curves of $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ versus the pinch temperature ratio γ .

Table 1. Parameters used in the modeling.

Parameter	Value
Faraday constant, F (C mol ⁻¹)	96,485
Universal gas constant, R (J mol ⁻¹ K ⁻¹)	8.314
Number of electrons, n_e	2 [7]
Operating pressure, p (atm)	1.0 [25]
Operating temperature, T (K)	453 [7]
Ambient temperature, T_0 (K)	298 [20]
Constant b	0.00003 [7]
Constant c	0.0008 [7]
Partial pressure of H ₂ , a_{H_2} (atm)	1.0 [23]
Partial pressure of O ₂ , a_{O_2} (atm)	0.105 [23]
Partial pressure of H ₂ O, a_{H_2O} (atm)	0.5 [23]
Charge transfer coefficient, α	0.5 [25]
Exchange current density, j_0 (A m ⁻²)	0.06 [25]
Thickness of the electrolyte, t_{ele} (m)	0.002 [25]
Polar plate area of the cell, A (m ²)	0.0015 [7]
Constant, c_1 (W K ⁻¹ m ⁻²)	0.2 [20]
Constant, c_2 (W K ⁻¹ m ⁻²)	0.2 [20]
Pinch temperatures, T_{pH} , T_{pL} (K)	10, 10 [36]
Irreversibility ratio, ε	0.0075 [36]

Table 2. Performance parameter comparisons between the single PAFC system and the PAFC-ORC hybrid system.

	$\eta_{i,P}$	$ExD_{i,P}^*$	$\phi_{i,P}$	$E_{i,P}^*$	$\phi_{i,P}$	$P_{i,E}^*$	$\eta_{i,E}$	$ExD_{i,E}^*$	$\phi_{i,E}$	$\phi_{i,E}$
	(%)	(W m ⁻²)	(%)	(W m ⁻²)	(%)	(W m ⁻²)	(%)	(W m ⁻²)	(%)	(%)
$i = fc$	43.7	7645.2	44.2	727.1	1.2	3758.3	56.5	3435.0	57.3	2.0
$i = hy$	50.5	5196.0	51.4	2151.3	1.5	5285.3	59.4	3077.1	60.3	2.2
Increase rate (%)	15.6	32.0	16.3	195.9	25	40.6	5.1	10.4	5.1	10

Fig. 1.

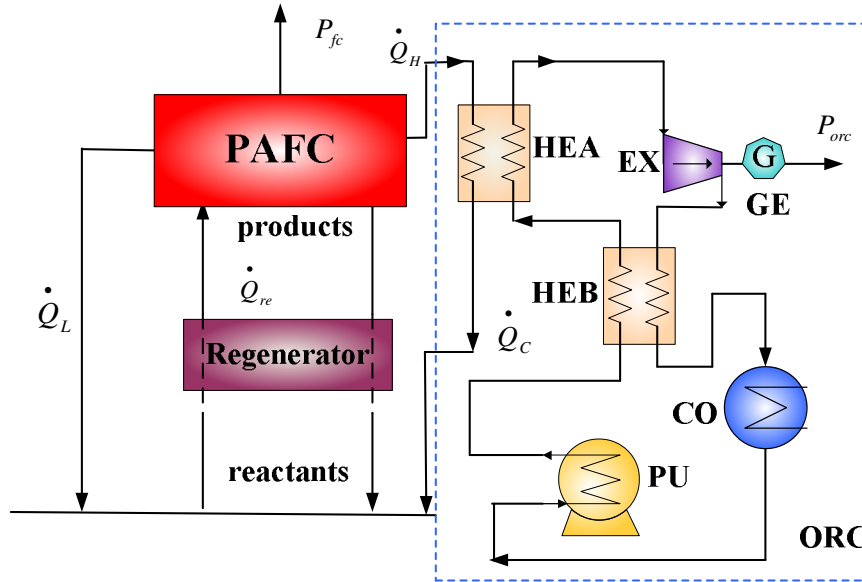


Fig. 1. The schematic diagram of the PAFC-ORC hybrid system, where the ORC consists of two heat exchangers (HEA and HEB), an expander (EX), a generator (GE), a condenser (CO) and a pump (PU).

Fig. 2.

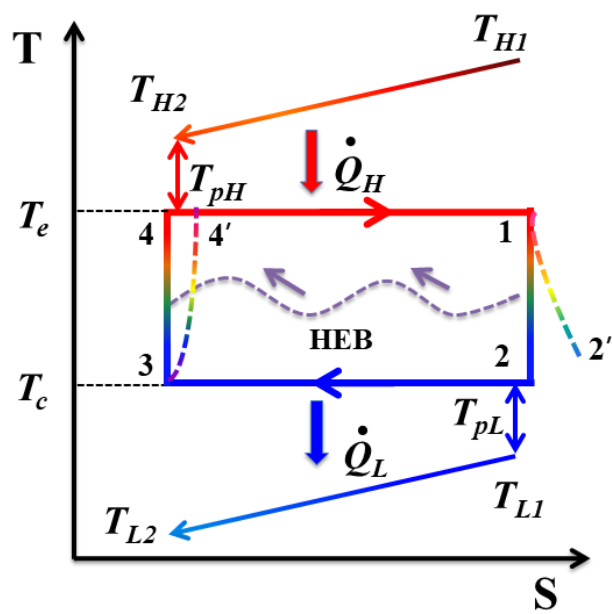


Fig. 2. Temperature-entropy diagram for the modified ORC.

Fig. 3.

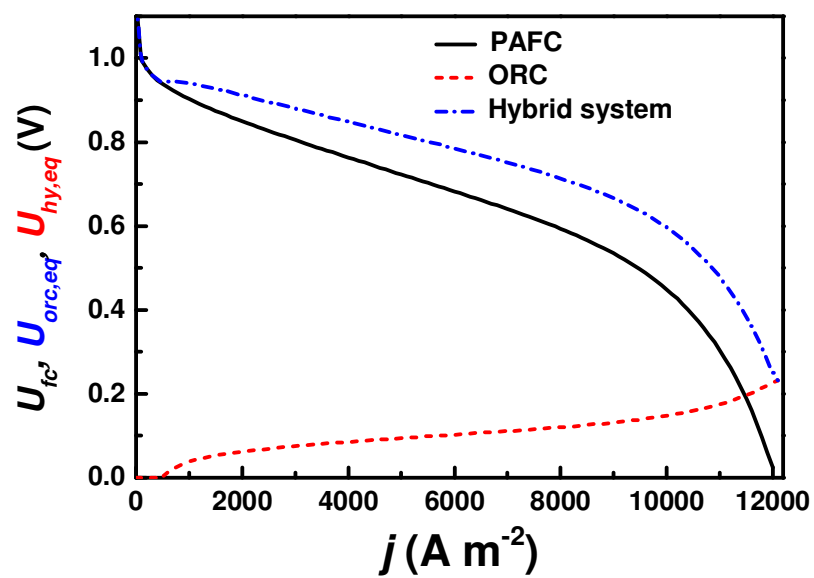


Fig. 3. Current-voltage curves for the single PAFC system, ORC and PAFC-ORC hybrid system.

Fig. 4.

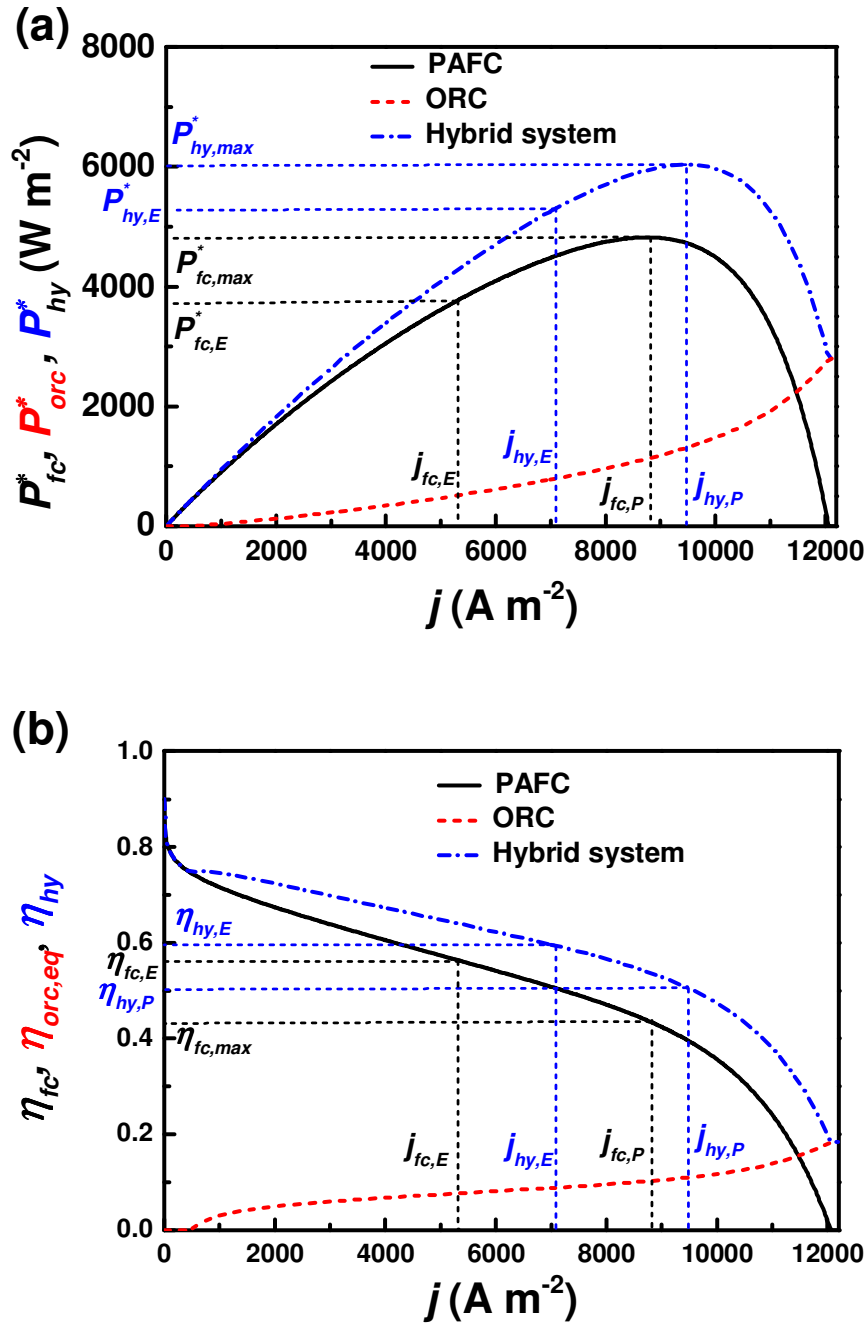


Fig. 4. Energetic performance comparisons between the single PAFC system, ORC and PAFC-ORC

hybrid system: (a) power density; (b) energy efficiency, where $P_{fc}^* = P_{fc} / A$, $P_{orc}^* = P_{orc} / A$

and $P_{hy}^* = P_{hy} / A$ are the corresponding power densities; $P_{hy,max}^*$ (at $j = j_{hy,P}$) and $P_{fc,max}^*$

(at $j = j_{fc,P}$) are the maximum values for P_{hy}^* and P_{fc}^* , respectively; the maximum EOF densities for the hybrid system and the single PAFC system are obtained at $j = j_{hy,E}$ and $j = j_{fc,E}$; $P_{hy,E}^*$ ($P_{fc,E}^*$) is the value for P_{hy}^* (P_{fc}^*) at $j = j_{hy,E}$ ($j = j_{fc,E}$). $\eta_{fc,P}$ and $\eta_{fc,E}$ are, respectively, values of η_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, and $\eta_{hy,P}$ and $\eta_{hy,E}$ are values of η_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$, respectively.

Fig. 5.

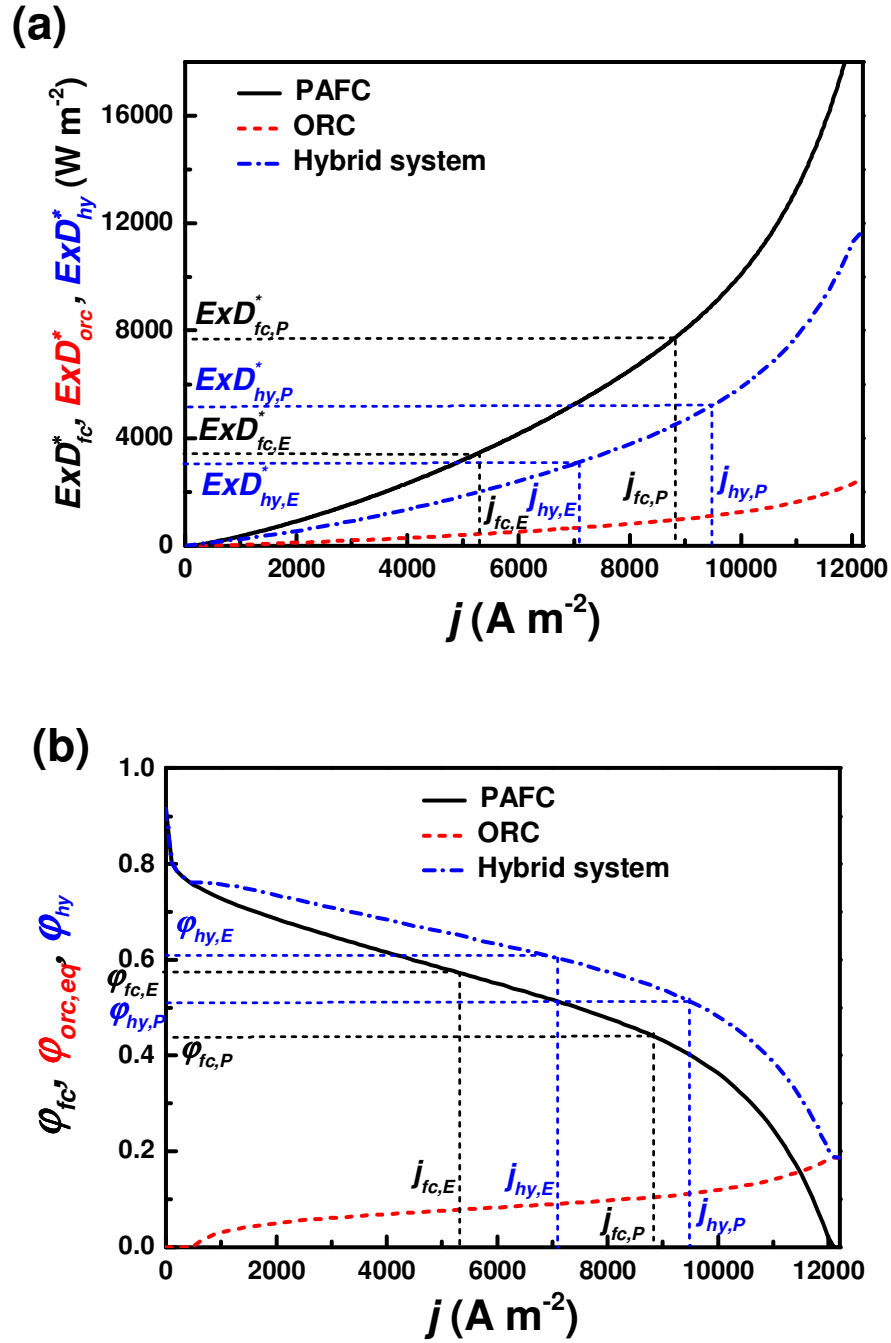


Fig. 5. Exergetic performance comparisons between the single PAFC system, ORC and PAFC-ORC hybrid system: (a) exergy destruction rate density; (b) exergetic efficiency, where $ExD_{fc}^* = ExD_{fc} / A$, $ExD_{orc}^* = ExD_{orc} / A$ and $ExD_{hy}^* = ExD_{hy} / A$ are the corresponding

exergy destruction rate densities; $ExD_{hy,P}^*$ and $ExD_{hy,E}^*$ are, respectively, values for ExD_{hy}^* at $j = j_{hy,P}$ and at $j = j_{hy,E}$, $ExD_{fc,P}^*$ and $ExD_{fc,E}^*$ are, respectively, values for ExD_{fc}^* at $j = j_{fc,P}$ and at $j = j_{fc,E}$; $\varphi_{hy,P}$ and $\varphi_{hy,E}$ are, respectively, values of φ_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$; and $\varphi_{fc,P}$ and $\varphi_{fc,E}$ are values of φ_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, respectively.

Fig. 6.

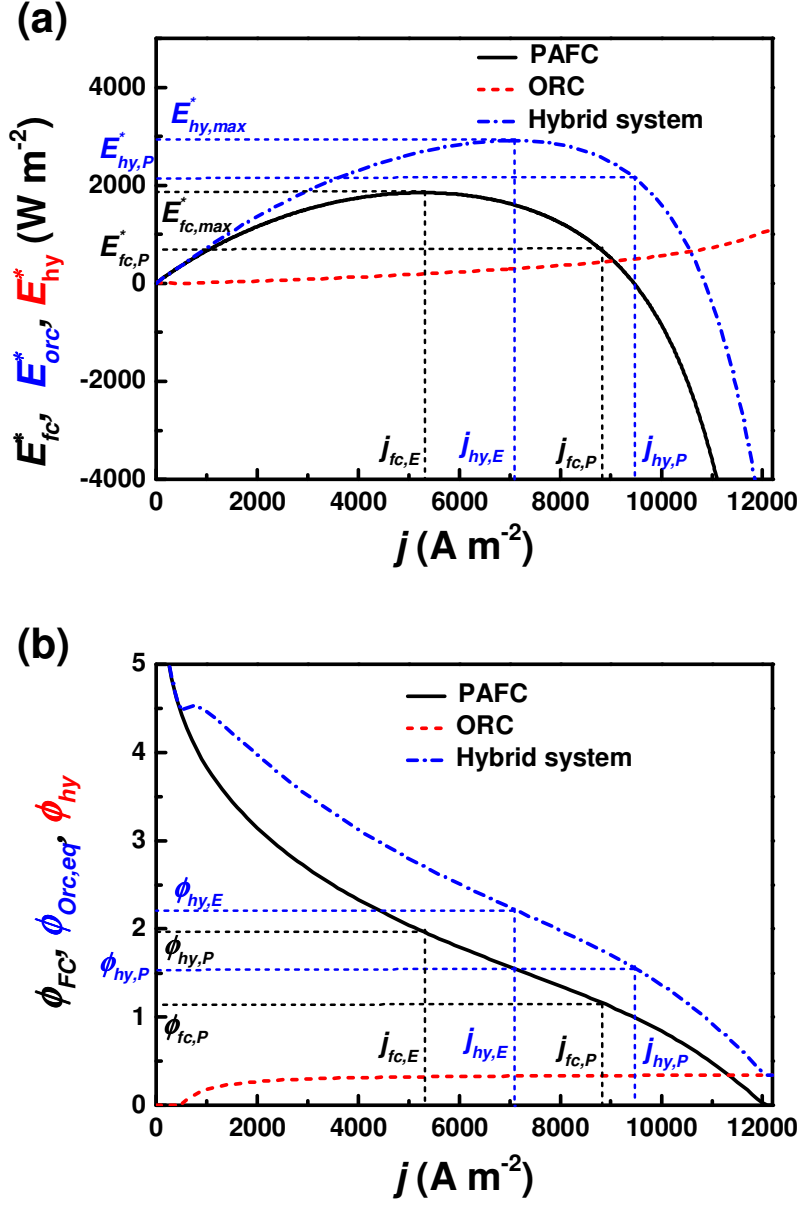


Fig. 6. Ecological performance comparisons between the single PAFC system, the ORC and the

PAFC-ORC hybrid system: (a) EOF density; (b) ECOP, where $E_{fc}^* = E_{fc} / A$, $E_{orc}^* = E_{orc} / A$ and $E_{hy}^* = E_{hy} / A$ are the corresponding EOF densities; $E_{hy,max}^*$ and $E_{fc,max}^*$ are, respectively, the maximum values for E_{hy}^* and E_{fc}^* ; $E_{hy,P}^*$ and $E_{hy,E}^*$ are, respectively, values for E_{hy}^* at $j = j_{hy,P}$ and at $j = j_{hy,E}$, $E_{fc,P}^*$ and $E_{fc,E}^*$ are, respectively, values for

E_{fc}^* at $j = j_{fc,P}$ and at $j = j_{fc,E}$; $\phi_{hy,P}$ and $\phi_{hy,E}$ are, respectively, values of ϕ_{hy} at $j = j_{hy,P}$ and $j = j_{hy,E}$; and $\phi_{fc,P}$ and $\phi_{fc,E}$ are values of ϕ_{fc} at $j = j_{fc,P}$ and $j = j_{fc,E}$, respectively.

Fig. 7.

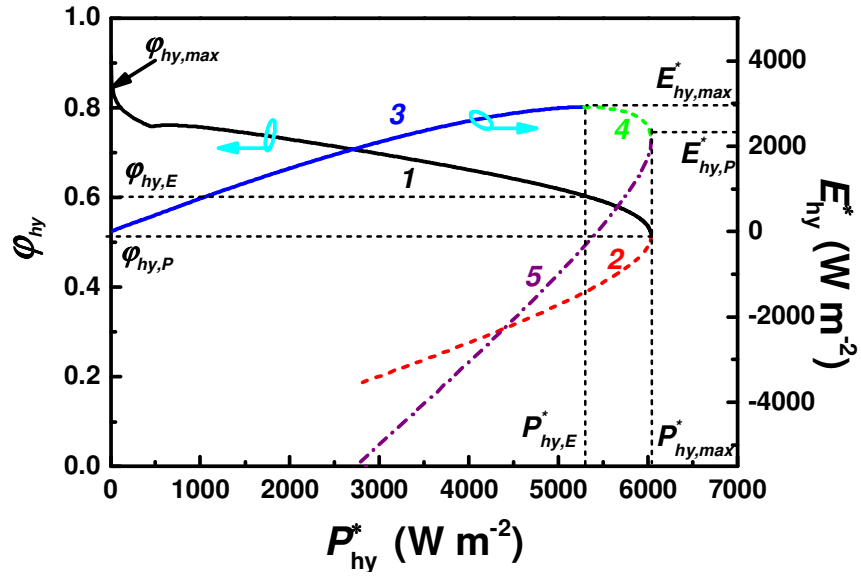
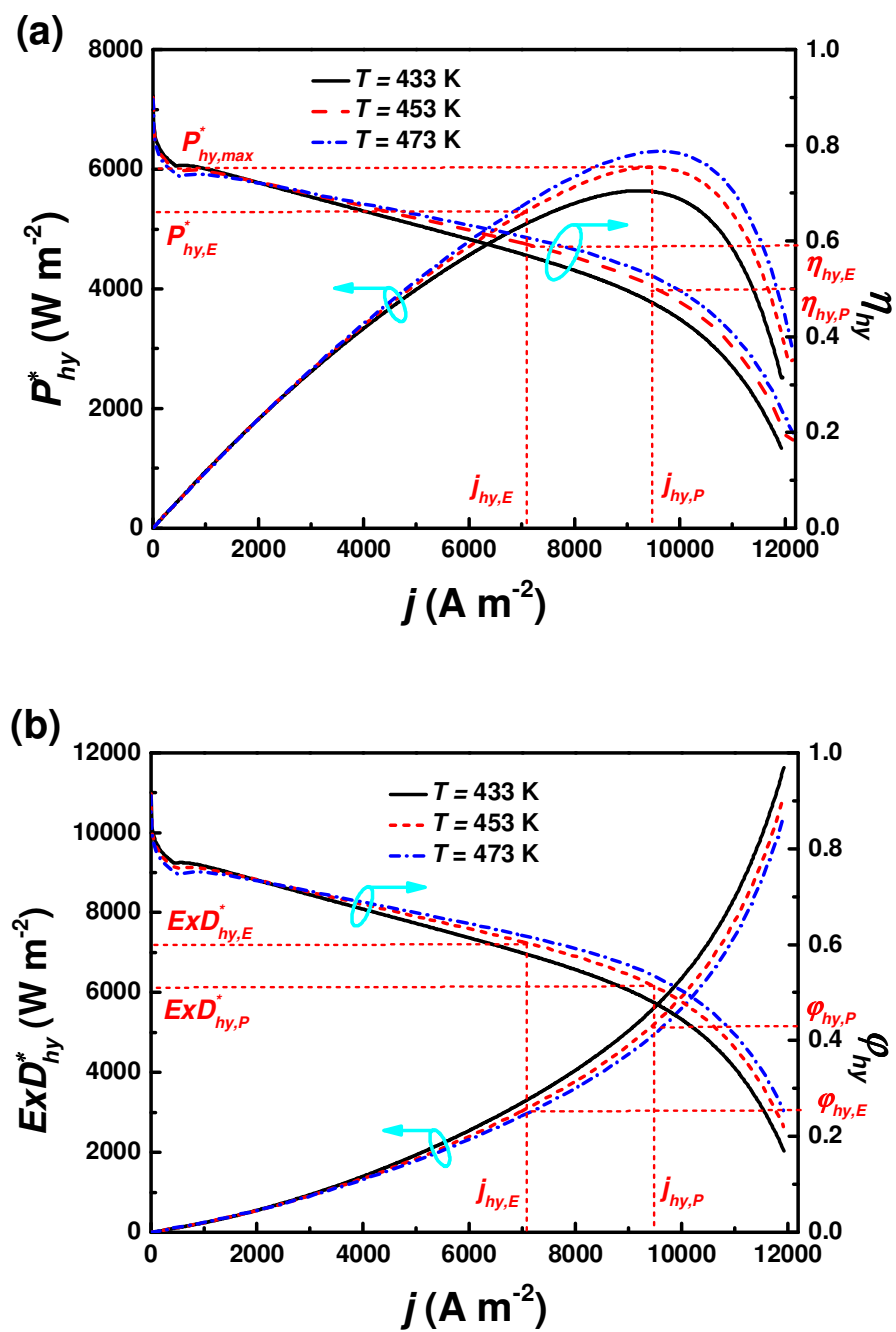


Fig. 7. Variations of ϕ_{hy} (curves 1 and 2) and E_{hy}^* (curves 3, 4 and 5) versus P_{hy}^* .

Fig. 8.



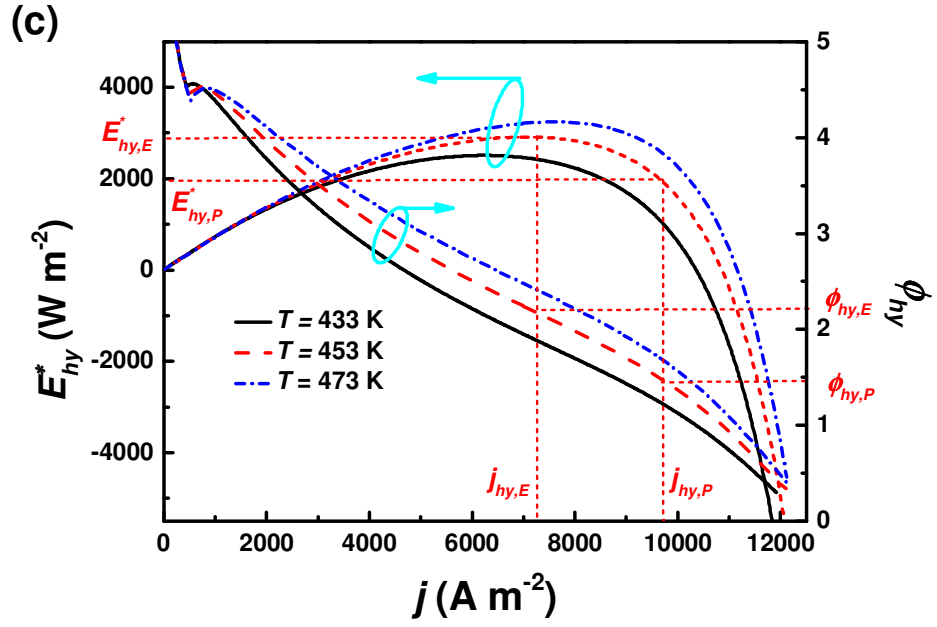


Fig. 8. Effects of the operating temperature T on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 9.

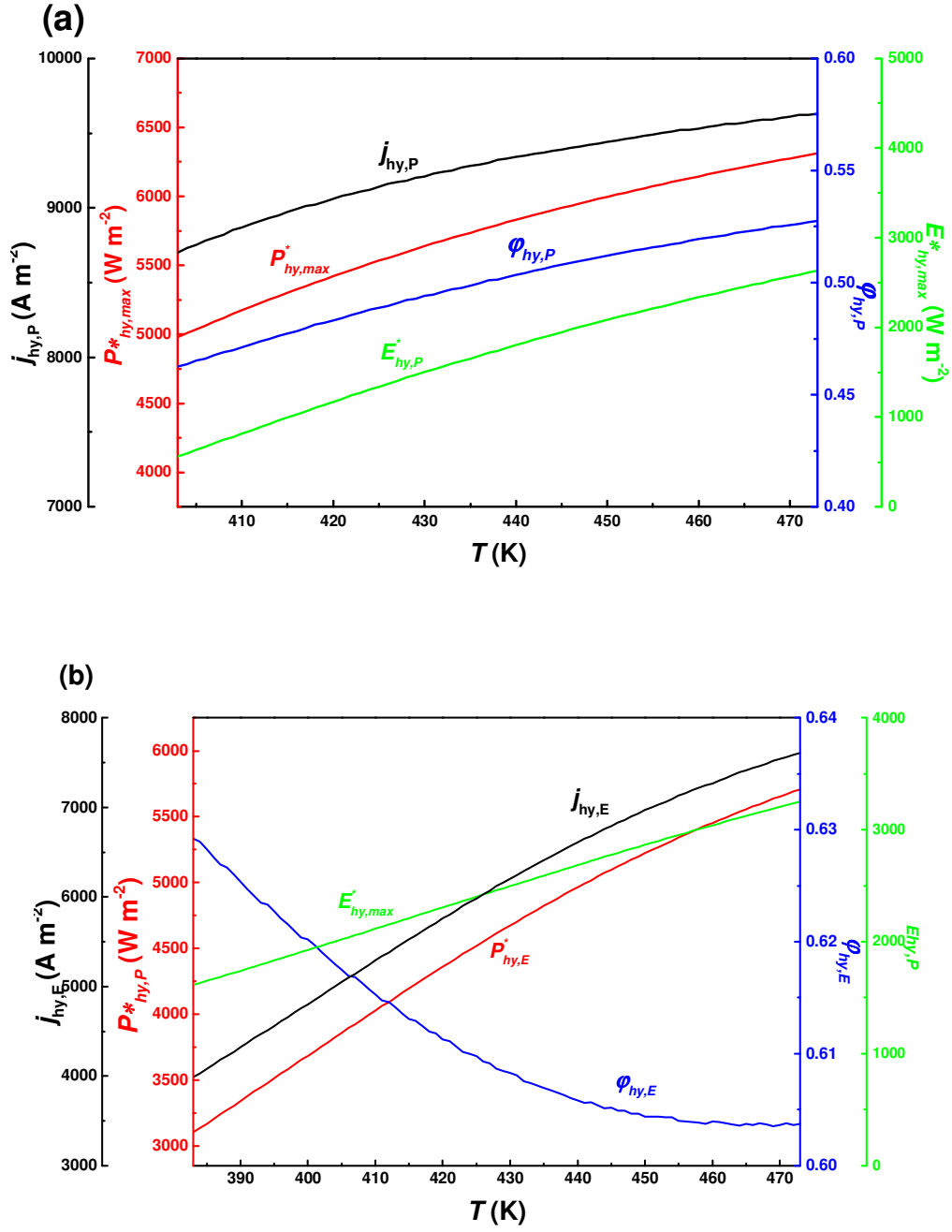
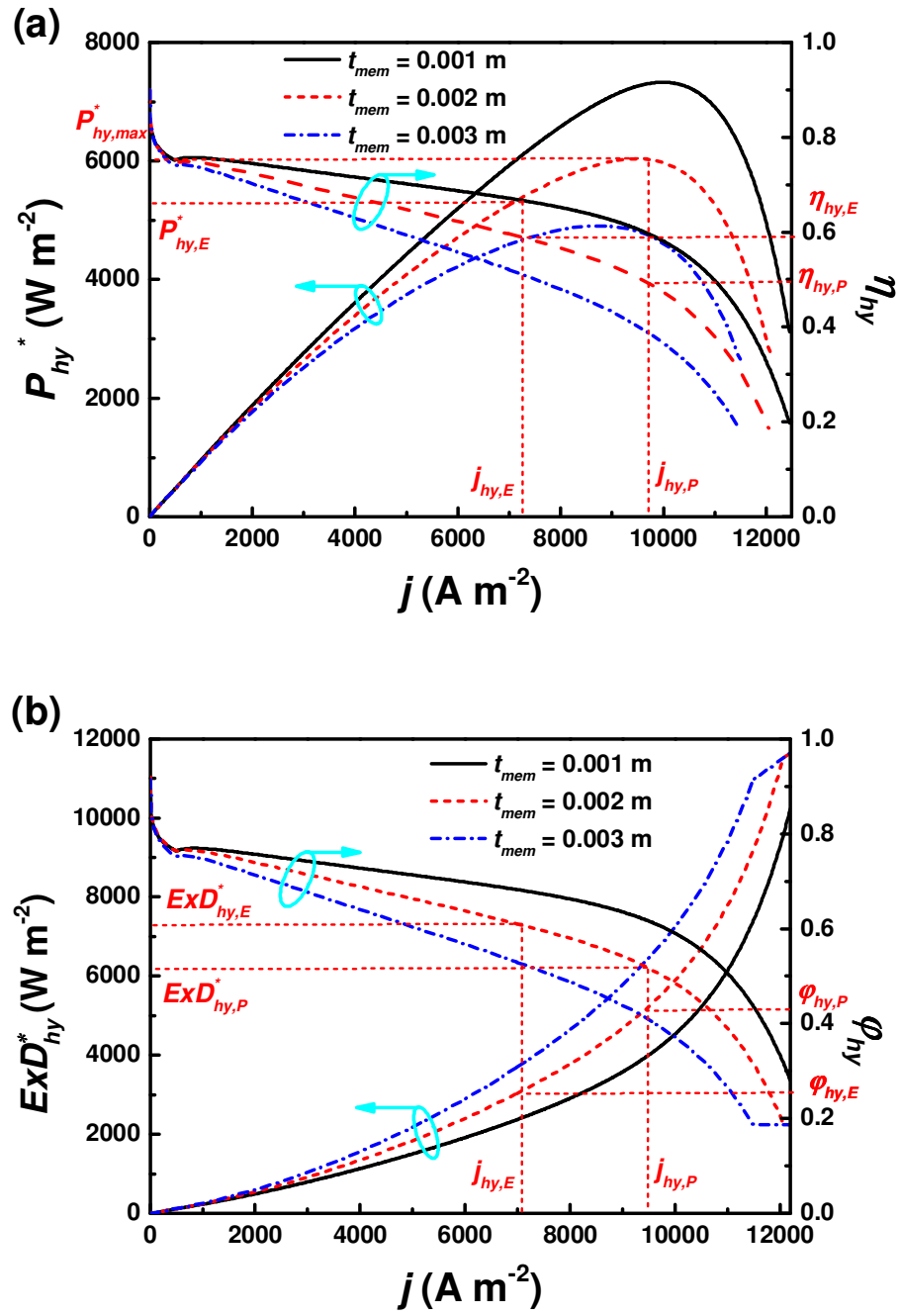


Fig. 9. (a) Variations of $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$ and $E_{hy,P}^*$ versus T ; and (b) Curves of $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ versus the operating temperature T .

Fig. 10.



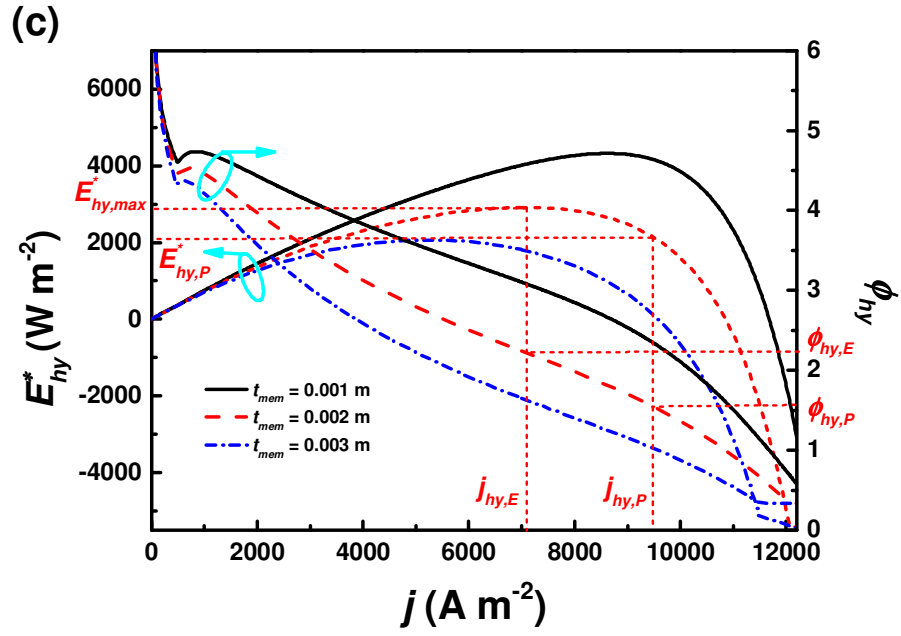
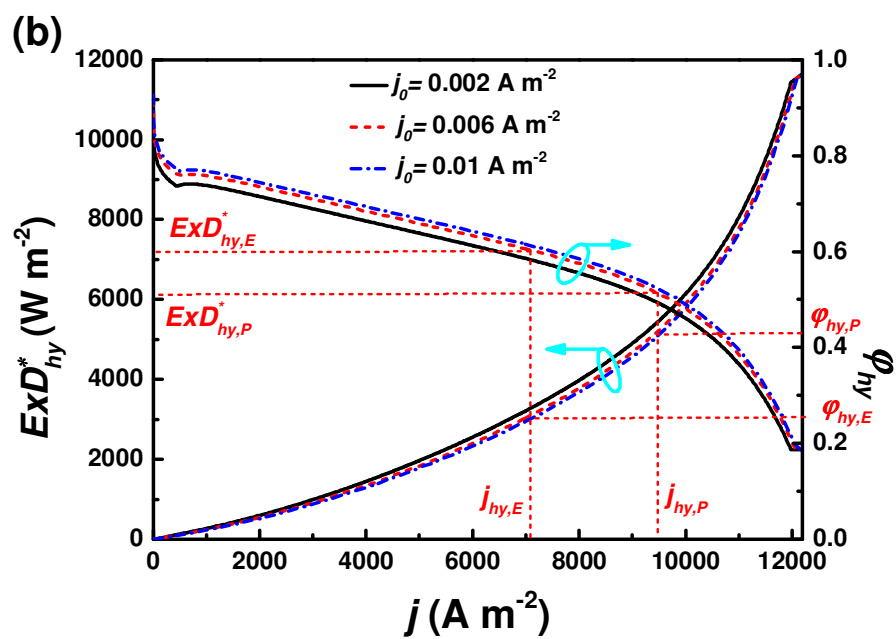
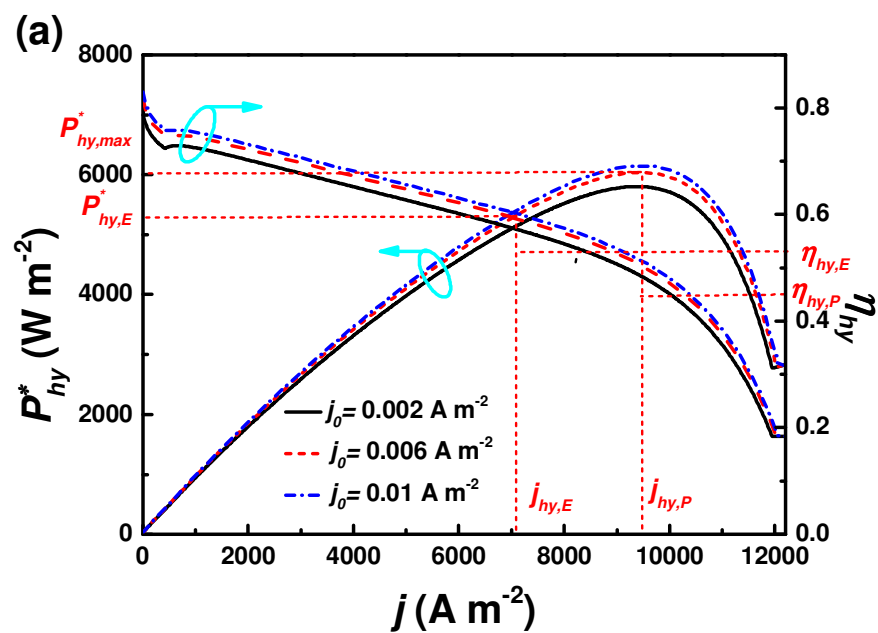


Fig. 10. Effects of the electrolyte thickness t_{ele} on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig 11.



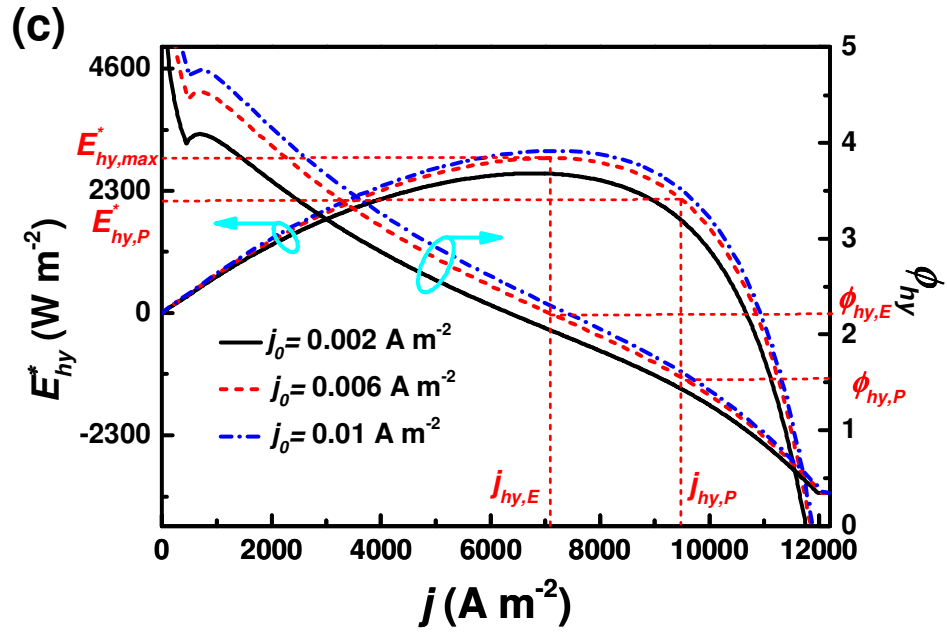
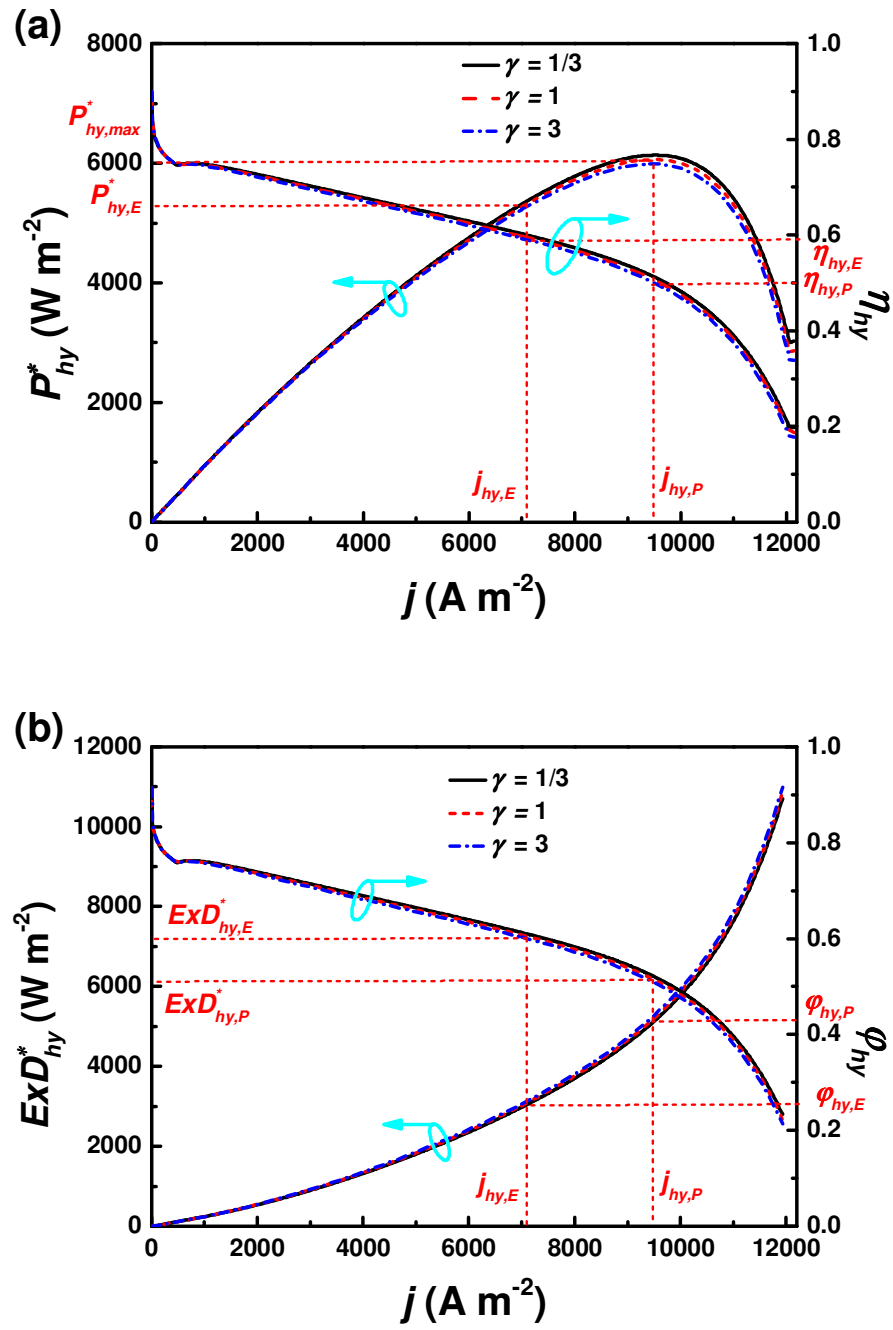


Fig. 11. Effects of the exchange current density j_0 on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 12.



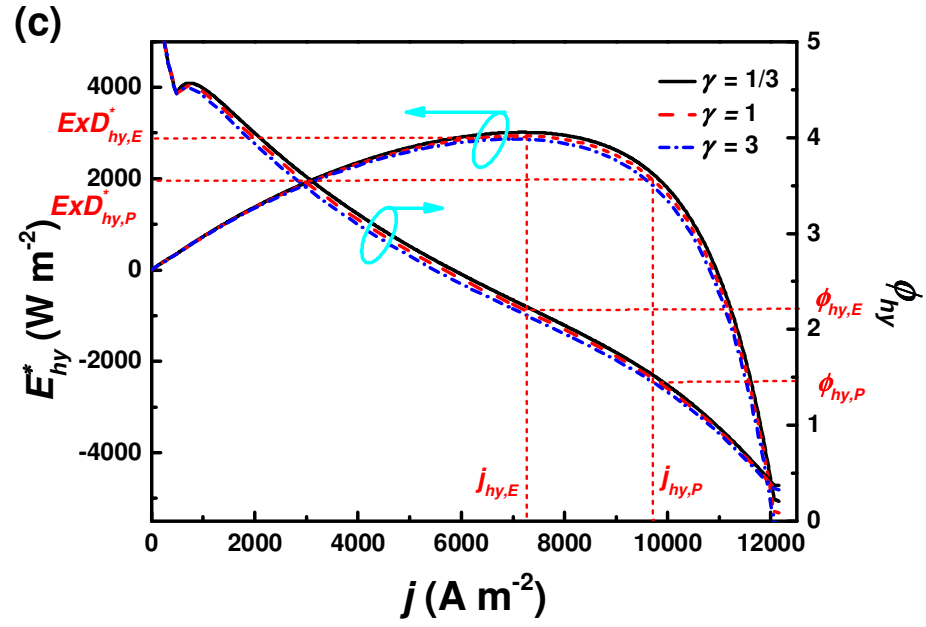


Fig. 12. Effects of the pinch temperature ratio γ on (a) energetic, (b) exergetic and (c) ecological performances for the PAFC-ORC hybrid system.

Fig. 13.

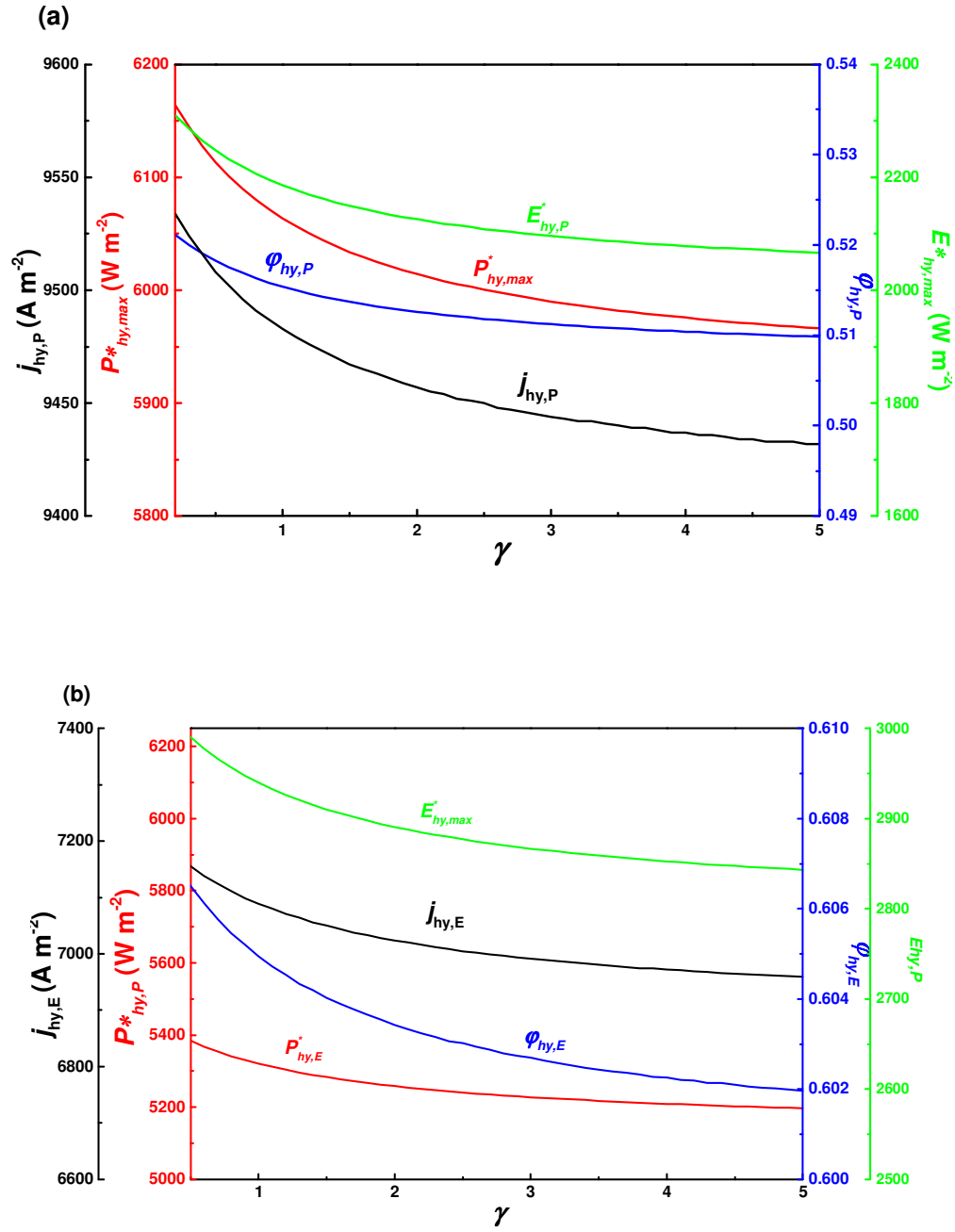


Fig. 13. (a) Variations of $j_{hy,P}$, $P_{hy,max}^*$, $\phi_{hy,P}$ and $E_{hy,P}^*$ versus the pinch temperature ratio γ ; and
 (b) Curves of $j_{hy,E}$, $P_{hy,E}^*$, $\phi_{hy,E}$ and $E_{hy,max}^*$ versus the pinch temperature ratio γ .