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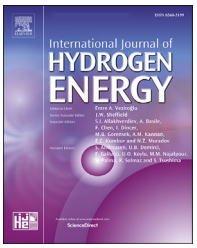

Comparative performance and thermoeconomic analyses of high temperature polymer electrolyte membrane based two hybrid systems

Sevgi Erzen [a], *Emin Açıkkalp* [b,*], *Arif Hepbasli* [c]

[a] *Department of Mechanical Engineering, Faculty of Engineering, Bilecik S.E. University, Bilecik, Turkey*
[b] *Department of Mechanical Engineering, Faculty of Engineering, Eskisehir Technical University, 26555, Tepebasi, Eskisehir, Turkey*
[c] *Department of Energy Systems Engineering, Faculty of Engineering, Yasar University, 35100, Bornova, Izmir, Turkey*

HIGHLIGHTS

- Using waste heat released from the high temperature PEM fuel cell by a bottom cycle.
- Considering thermocapacitive cycle and thermoelectric generator as bottom cycles.
- Carrying out thermoeconomic analyses and performance parameters for both systems.
- Having hybrid I more advantageous in terms of performance.

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ABSTRACT

The main objective of this study is to compare the two systems in terms of the thermoeconomic and the performance. The first one is called hybrid I and consists of high temperature polymer electrolyte membrane and thermocapacitive cycle. The second one is named hybrid II, which is composed of high temperature polymer electrolyte membrane and thermoelectric generator. Thermocapacitive cycle and thermoelectric generator have various advantages, such as generally lower cost and higher power density. So, they have good potential to utilize waste heat. The performance parameters of the considered hybrid systems include power density, energy efficiency, exergy efficiency and exergy destruction rate. The results have shown that hybrid I is more advantageous than hybrid II. The maximum power density values for hybrid I and hybrid II are obtained to be 2536.91W and 2049.62W while their energy efficiencies are 77.4% and 76.8%, respectively.

Introduction

With population growth, the world's energy demand has increased dramatically. To provide this energy demand, many different systems based on renewable energy have started to be designed. Renewable energy-based systems have attracted considerable attention owing to the solutions they present the environmental problems, such as greenhouse gas emission

* *Corresponding author.*
E-mail addresses: acikkalp@gmail.com, eacikkalp@gmail.com (E. Açıkkalp).
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and global warming. Especially, hydrogen, that can be used for energy production environmentally, has received intense interest recently. Thermocapacitives and fuel cells used in many fields are the most efficient technologies for the storage and conversion of energy [1].

Fuel cells and thermocapacitives fall into a number of the most influential technologies used to achieve electrochemical energy storage and conversion. A thermocapacitive cycle enables energy to be stored in an electrically dispersed dual tier at the electrode frontier surface and electrolyte via reversible charge desorption and adsorption [2]. Thermocapacitives convert the waste heat of a system or the low-grade heat of a renewable energy source into electrical energy while the temperature plays an important role in the realization of electrochemical reactions. Low-grade heat is quite abundant, but it is often wasted. Exhaust systems, solar irradiance, geothermal energy and waste heat from the PEM fuel cell can be defined as low grade heat. Thus, evaluation of low-grade heat is quite useful subject, combining renewable energy and energy efficiency. The widespread use of clean and efficient fuel has increased the importance of fuel cells and hydrogen fuel. The fuel cell converts the chemical energy it receives from the fuel (hydrogen) directly into electrical energy through electrochemical processes.

Fuel cells commonly generate electricity via electrochemical reactions. Additionally, they produce heat so as to convert to useful work. Main source of fuel cells is hydrogen, so the process producing electricity is an environmentally-benign operation [3]. The advantages of fuel cells can be sorted as energy efficiency, producing heat, reliability, cleaner electrical energy production technology and low noise [4].

The polymer electrolyte membrane fuel cell is the most prevalently preferred fuel cell kind owing to its low operating temperature, superordinate power density and moreover orderly design. There are generally two kinds of PEM fuel cells as high temperature (over 100 °C) and low temperature (below 100 °C) [4]. Nowadays, there are a great deal of procedures that are being benefited in the industry, which demonstrates the plenty existence of hydrogen. In terms of practical utilization, the storage capability is a notable factor for all fuels. On the other hand, it is much more complicated that storage of hydrogen gas due to its exceedingly fallen density. Nonetheless, today's technology allows its massive stacking in the shape of compressed hydrogen in cylinders. Polymer electrolyte membrane fuel cells (PEMFCs) are useful systems, that can quickly respond to such basic needs and trends where the technologic improvements of polymer electrolyte membrane fuel cell associated with its supportive substructure like hydrogen storage and production are in place. Despite to these achievements, there is a powerful requirement to further enhance the performance of present polymer electrolyte membrane fuel cells. Various technique impediments prevent their prevalent commercialisation as stationary application and transportation. These obstacles involve heat management and improper water, the intolerance to impurities such as carbon monoxide (CO), extremely high cost and inactive electrochemical cathode kinetics. For these problems, a novel approximation, which can be considered as a solution to polymer electrolyte membrane fuel cell, is needed. Operating polymer electrolyte membrane fuel cell at relatively higher temperatures is regarded as one of these approximations. High temperature-proton exchange membrane fuel cells operate approximately between 160 and 180 °C and in this approximation, the dynamic of the technologic obstacles is very different from the problems that affect low temperature-polymer electrolyte membrane fuel cell technology [5]. Polymer electrolyte membrane fuel cells are known as the chosen energy appliances for the use of electrical vehicles and fixed electric power-plants owing to high power density, easy operation, low operating temperature and uncomplicated structure. Researchers have started to work on high temperature-polymer electrolyte membrane fuel cells for enhancing their productivity. In this regard, they have used the methods increasing the working temperature and developing polymer electrolyte membrane fuel cells, which operate at elevated temperatures. In comparison to conventional low temperature-polymer electrolyte membrane fuel cells, both the reaction kinetic coefficient of high temperature polymer electrolyte membrane fuel cells working at the higher (100~200 °C) and the diffusivity of the fuel are increased. Compared with the waste heat from low temperature-polymer electrolyte membrane fuel cells, the waste produced in the high temperature-polymer electrolyte membrane fuel cell could be more easily recovered in combined heat and power systems for a number of practices like power generation, cooling and heating [6].

The thermoelectric generator is a useful appliance, which recycles the low-grade waste heat for the purpose of generating electricity. The semiconductor element connected in parallel or series is called thermoelectric module. The process of generating electricity using a thermoelectric module is predicated by the Seebeck effect. The thermoelectric generators have several advantages of requiring no maintenance, not having moving part, being low-priced, having a high power density and being silent. On the other hand, the most significant drawback of the thermoelectric generators is that they have the low material's figure-of-merit, which leads to lower energy efficiency.

In recent years, researchers have concentrated on studies related to hybrid systems containing high temperature fuel cell. Guo et al. [6] improved an original integrated system made up of a thermoelectric generator, a high-temperature proton exchange membrane fuel cell (HT-PEMFC) and a regenerator. The equivalent power density of the recommended combined system was enhanced by 21% in contrast to that of a self-contained high-temperature proton exchange membrane fuel cell. Hartel et al. [7] proposed a novel approximation that took into the temperature dependence of the electrostatic potential in a thermo-capacitive cycle so as to transform low-grade heat into electricity. Long et al. [8] proposed a new integrated system, which included a polymer exchange membrane fuel cell and a thermally regenerative electrochemical cycle so as to transform the waste heat into electricity. The total electricity efficiency was enhanced in a range of 2.74%–8.27% while the power output of the combined system was between 6.85% and 20.59% larger than that of the polymer electrolyte membrane fuel cell. Guo and Zhang [9] reported a new combined system with subsystems such as a thermally regenerative electrochemical cycle, a regenerator and a high-temperature polymer electrolyte membrane fuel

cell. The highest output power density obtained from the system was enhanced by 15.6% compared to that of a standalone high-temperature polymer electrolyte membrane fuel cell. Energy and exergy efficiency values were also increased by 8.5% and 11.7%, respectively. Açıkkalp and Caliskan [10] analyzed a hybrid system consisted of a chemical heat pump and a proton exchange membrane fuel cell. The results indicated that the higher output could be achieved at higher current densities while higher energy efficiencies were obtained from the current density values. Lucia et al. [11] introduced an unprecedented bioeconomic indicator so as to abstain from the difficulties caused by assessing the technologies and processes for sustainability. This indicator considered the irreversibility and exergy analysis while it could be utilized to analyze changes in weather and climate. Grisolia et al. [12] aimed at developing a novel indicator for the analysis of sustainability. Especially, it was applied to enhance the biofuel production achieved by microorganisms, starting from the biophysical conduct of the microorganisms themselves. The indicator considered all the requirements for the sustainability and development, ending up with an engrossing thermoeconomic quantity to be used by decision makers. Furthermore, it was used to demonstrate that mutualism could typify a novel approximation for the optimization of biofuels production. Lucia and Grisolia [13] suggested three novel indicators related to irreversibility. They put forward that these indicators would provide an opportunity to evaluate the technological level of production processes, their environmental impact and the socio-economic conditions of the countries. Three applications were summarized so as to emphasize the possible interest from particular researchers and scientists in engineering, economy, etc. to develop sustainable policies and approaches for decision makers. Lucia and Grisolia [14] proposed the percentage of unavailability as an indicator of the level of technological development regarding optimized energy use. It was thought that this amount could be used in socio-political and economic evaluations as it was related to the exergy lost during a process and therefore it could provide information about the level of optimization achieved through a technology or it could be quite useful to compare various technologies. Lucia [15] examined the connection between entropy and exergy to link ecophysics with biochemical engineering thermodynamics. The Municipality of Alessandria was studied to emphasize the application of theoretical results.

The electric double-layer capacitor or thermocapacitives have increasingly become attractive due to integrating that characteristic with batteries and their high specific power. The capacitors keep energy in the style of an electric charge. They are composed of two metal plates, divided through insulant called namely dielectric. The sum energy stocked is 0.5 CV^2, where V is the voltage value occurring between two conductive plates and C is the value of the capacitor. When any load is connected between these two plates, current flows by way of the load until V reaches zero. Additionally, thermocapacitives are called Electro-Chemical Double Layer Capacitors. Super-capacitors have a much thinner dielectric layer and a much larger surface area. Accordingly, these capacitors have the spacing thickness. When taking into consideration a much thinner insulant, both faces are covered with metals, one face acts as a ground, and the other face acts as a power. Thermocapacitives have three basic components called a dielectric separator, electrode and electrolyte. If the climatic change occurs quickly, in such a case energy can need to be stored much faster, and this fast storage necessitates low Equivalent Series Resistance. For this reason, thermocapacitive may be an ideal storage appliance owing to its fallen Equivalent Series Resistance as compared with another storage appliances known up to now. Moreover, this resistance brings about a lot fewer loss of power. Among the advantages of the thermo capacitive are that it has a short charging time, a high power density and is environmentally friendly. Supercapacitors have been found to be more cost-effective and reliable when compared to a battery [16].

These days, electrochemical energy systems, for example fuel cells, have played an essential role in the power source. Catalysts are implemented for fuel cells to develop the kinetics of the reactions that take place in anode and cathode. In the fuel cell, due to the low activation of oxygen in the course of oxygen reduction reaction (ORR) in the cathode, the kinetic of the cathode electrode is much slower than the anode electrode ode. For this reason, oxygen reduction reaction (ORR) plays a key role in the process of proton exchange membrane fuel cells. At the present time, the platinum (Pt) and Pt-essential electrocatalysts owing to the highest catalytic activity are the most practicable electrocatalyst for ORR in the fuel cell. The Pt in the duty of a catalyst has many virtues such as chemical resolution and superior electroconductivity. After all, due to its famine and high cost, the commercialisation of fuel cells has been restricted that restrains extensive application of proton exchange membrane fuel cells. Nowadays, the substantial searches are being performed for diminishing the expenditure of fuel cells by using worthless metals that are cost-effective, enduring, and remediation the electro catalytic activities of cathode catalyst. Some of these searches are the transition metal oxides, metal doped graphene derivatives, bimetallic alloy catalysts, carbon basic materials, graphene, metal essential porphyrin and chalcogenides. Meanwhile, these circumstances are still under exploratory since their functional determination and activity are still lower than Pt catalyst. The evolvement of new electrocatalysts for the replacement of Pt in cathode catalysts is crucial to provide admissible working (high-performance) and cost-effective polymer electrolyte membrane fuel cells. Amongst the alternative materials of Pt, carbon materials have gotten attention increasing interest as the most hopeful materials for proton exchange membrane fuel cells due to the fact that their high chemical resistance, remediation mass transferability and high electrical conductivity [17].

In this study, two hybrid systems are considered. The originality of this study is proposing and examining a hybrid system using non-traditional subsystem like super capacitor. The thermo capacitive is also used as a subsystem in the hybrid system for the first time to the best of the authors' knowledge while its performance and economic analysis are compared with a second hybrid system using a thermoelectric generator as a subsystem. High temperature-polymer electrolyte membrane fuels are silent, highly reliable and moreover non-emission. Their most prominent advantage is to generate electricity from the low-grade waste heat. Based on

this, a new combined system is proposed with the purpose of designing more ecological and less emission systems. The fundamental thermodynamic parameters, such as power output, energy efficiency and exergy efficiency and exergy destruction rate, are analyzed. Results are achieved numerically and evaluated.

System description

The system consisting of a high temperature-polymer electrolyte membrane fuel cell-thermocapacitive cycle system is named hybrid I while the system consisting of a high temperature-proton exchange membrane fuel cell-thermoelectric generator is called hybrid II. Hybrid I includes a high temperature-proton exchange membrane with a thermocapacitive. Schematic diagrams of the systems can be seen in Figs. 1 and 2. The basic purpose of the high temperature-polymer electrolyte membrane fuel cell is to produce electricity through electrochemical reactions. The fuel cell stack model is taken into account. The model computes the required hydrogen feed referring to the number of cells. The model altered covers the feed reformate fuel (hydrogen-rich gas) as an input. In the high temperature-polymer electrolyte membrane, hydrogen is electrochemically split into electron and proton on anode. Proton is transported with membrane to cathode. At cathode, protons are recombined with electrons. The output heat from the high temperature-polymer electrolyte membrane as a result of the cycle in the high temperature-polymer electrolyte membrane is the input heat to thermocapacitive. The considered integrated system consists of a high temperature-polymer electrolyte membrane used to produce electricity (P_{HT-PEM}) and high temperature (160 °C) waste heat ($\dot{Q}_H$). The waste heat ($\dot{Q}_H$) of the HT-PEM is dispatched to the thermocapacitive and electricity (P_{tc}) is obtained for needs.

Some assumptions made for the system are listed as follows:

a) All components operate under steady state conditions.
b) The temperature of the heat released from the HT-PEM is 160 °C.
c) The model regards solely the reaction of hydrogen with air (oxygen).
d) Heat losses from the HT-PEM are neglected in the calculations.

In this study, the heat released by way of the high temperature-proton exchange membrane fuel cell is solely taken into consideration to generate electricity. In addition to this, applications, such as refrigeration and heating, are neglected. The system, named hybrid II, consists of an integration of thermoelectric generator and high temperature-polymer electrolyte membrane. The heat produced from the high temperature-polymer electrolyte membrane is transferred to the thermoelectric generator where supplemental electricity is generated. The thermoelectric generators are devices, which have feature to convert heat into electricity. The semiconductor element connected in parallel or series is called thermoelectric module. The electricity production principle is known as the Seebeck effect.

Analysis

The equations for the HT-PEM are listed in Table 1 [18,19] while those for the thermocapacitive are given in Table 2 [20].

Using Eqs. (15), (16), (19) and (21), the amounts of the heat exchange occurring in the four-stage process, that is composed of the thermo-capacitive cycle, are written in Table 2 [20]. The equations for the thermoelectric generator are listed in Table 3 [19,21].

Consequently, the thermodynamic parameters, such as power output, energy and exergy efficiencies and exergy destruction rate, for the proposed hybrid systems are as follows [21]:

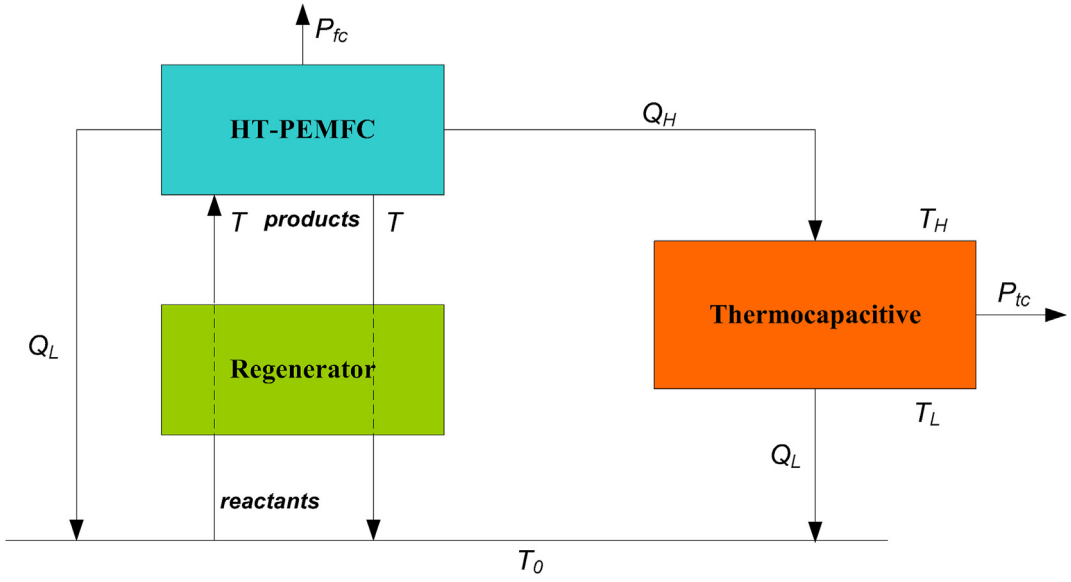

Fig. 1 – Schematic of hybrid I.

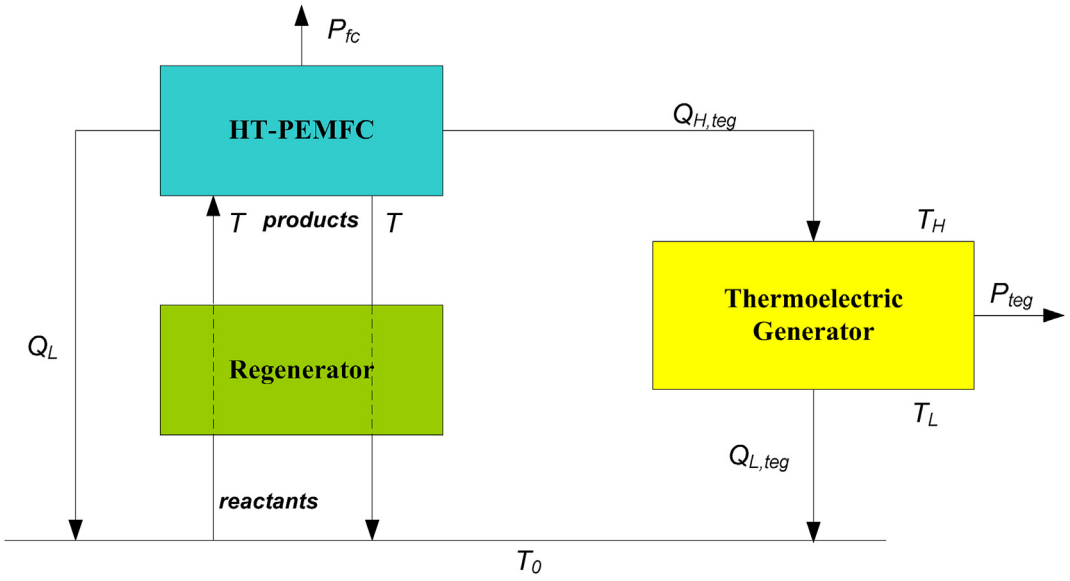

Fig. 2 – Schematic of hybrid II.

Table 1 – List of equations for the HTPEM [18,19].

Description	Unit	Equation	Equation no.
Ohmic resistance R_{ohmic}[18],	$Ohm.cm^2$	$R_{ohmic} = -0.0001667 \cdot T_{cell} + 0.2289$	(1)
Diffusion resistance R_{diff}[18],	$Ohm.cm^2$	$R_{diff} = 0.4306 - 0.0008203.T_{cell}$	(2)
Anode overpotential η_a[18],	V	$\eta_a = \frac{R.T_{cell}}{\alpha_{anode}.F} \arcsin h\left(\frac{i}{2.k_{eh}.\theta_{H_2}}\right)$	(3)
Cathode overpotential η_c[18],	V	$\eta_c = \frac{R.T_{cell}}{4.\alpha_{cathode}.F} In\left(\frac{i_o + i}{i_o}\right) + R_{diff}\left(\frac{i}{\lambda_{air} - 1}\right)$	(4)
Ohmic losses η_{ohmic}[18],	V	$\eta_{ohmic} = i.R_{ohmic}$	(5)
Total cell voltage V_{cell}[18],	V	$V_{cell} = V_0 - \eta_a - \eta_c - \eta_{ohmic}$	(6)
Power density W_{cell}[18],	W/m^2	$W_{cell} = V_{cell}.i$	(7)
Stack voltage V_{stack}[18],	V	$V_{stack} = V_{cell}.n_{cells}$	(8)
Fuel cell stack power output P_{stack}[18],	W	$P_{stack} = A_{cell}.n_{cells}.W_{cell}$	(9)
Fuel cell stack current I_{stack}[18],	A	$I_{stack} = \frac{P_{stack}}{V_{stack}}$	(10)
Energy efficiency η_{fc}[19],		$\eta_{fc} = \frac{P_{stack}}{-\Delta \dot{H}}$	(11)
Exergy destruction rate of the HT-PEM $Ex_{d,fc}$[19],	W	$Ex_{d,fc} = -\Delta \dot{G} - T\Delta \dot{S}\left(1 - \frac{T_0}{T}\right) - P_{stack}$	(12)
Exergy efficiency of the HT-PEM ϕ_{fc}[19],		$\phi_{fc} = \frac{P_{stack}}{-\Delta G - T\Delta \dot{S}\left(1 - \frac{T_0}{T}\right)}$	(13)
Heat rate transmitted from the HT-PEM to the thermocapacitive $\dot{Q}_H$[19],	W	$\dot{Q}_H = -\Delta \dot{H} - P_{stack}$	(14)

$$P_I = P_{fc} + P_{tc} \quad (34)$$

$$P_{II} = P_{fc} + P_{teg} \quad (35)$$

$$\dot{E}x_{d,I} = \dot{E}x_{d,fc} + \dot{E}x_{d,tc} \quad (36)$$

$$\dot{E}x_{d,II} = \dot{E}x_{d,fc} + \dot{E}x_{d,teg} \quad (37)$$

$$\eta_I = \frac{P_I}{\dot{m}_{H_2} LHV_{H_2}} \quad (38)$$

$$\phi_I = \frac{P_I}{\dot{m}_{H_2} \varphi LHV_{H_2}} \quad (39)$$

$$\eta_{II} = \frac{P_{II}}{\dot{m}_{H_2} LHV_{H_2}} \quad (40)$$

$$\phi_{II} = \frac{P_{II}}{\dot{m}_{H_2} \varphi LHV_{H_2}} \quad (41)$$

Firstly, the hybrid systems considered are analyzed with the help of the thermoeconomic method known as EXCEM [22]

Table 2 – List of equations for the thermocapacitive [20].

Description	Unit	Equation	Equation no.
Relativistic dielectric constant of the ultra capacitor media, ε_r	–	$\varepsilon_r = c_1 - c_2 T$ $c_1 = 58.58$and $c_2 = 0.085K^{-1}$	(15)
Capacitance, C	F	$C = \frac{q}{V} = \frac{\varepsilon_0 \varepsilon_r S_{el}}{4\pi L_{eff}}$	(16)
Effective thickness, L_{eff}	m	$L_{eff} = \frac{1}{\sqrt{8\pi\rho_0 \lambda_B}}$ $\rho_0(1/m^3)$ and $\lambda_B = e^2/(\varepsilon_0 \varepsilon_r k_B T)$	(17)
High-temperature heat reservoir at T_H(K) along the occurring at the constant temperature charging and discharging processes, Q_{34}	W	$Q_{34} = a_1 bG(T_1)h(T_1)$ $a_1 = \frac{\pi}{\varepsilon_0 S_{el}} q_H{}^2(1 - r_q{}^2)$, $b = (1/e)\sqrt{\varepsilon_0 k_B/(8\pi\rho_0)}$, $h(T) = \sqrt{T\varepsilon_r}$, $G(T) = (c_1 - c_3 T^2)/\varepsilon_r{}^2(T)$, $r_q = q_L/q_H$, $S_i(i = 1, 2, 3, 4)$	(18)
Heat transferred between the thermocapacitive and the low-grade heat sink at T_L(K), Q_{12}	W	$Q_{12} = -a_1 bG(T_2)h(T_2)$ $a_1 = \frac{\pi}{\varepsilon_0 S_{el}} q_H{}^2(1 - r_q{}^2)$, $b = (1/e)\sqrt{\varepsilon_0 k_B/(8\pi\rho_0)}$, $h(T) = \sqrt{T\varepsilon_r}$, $G(T) = (c_1 - c_3 T^2)/\varepsilon_r{}^2(T)$, $r_q = q_L/q_H$, $S_i(i = 1, 2, 3, 4)$	(19)
Thermocapacitive during two isoelectric quantity processes, Q_{23}	W	$Q_{23} = \frac{2\pi b}{\varepsilon_0 S_{el}}\left(\frac{h(T_1)}{\varepsilon_r(T_1)} - \frac{h(T_2)}{\varepsilon_r(T_2)}\right) q_H^2$ $a_1 = \frac{\pi}{\varepsilon_0 S_{el}} q_H{}^2(1 - r_q{}^2)$, $b = (1/e)\sqrt{\varepsilon_0 k_B/(8\pi\rho_0)}$, $h(T) = \sqrt{T\varepsilon_r}$, $G(T) = (c_1 - c_3 T^2)/\varepsilon_r{}^2(T)$, $r_q = q_L/q_H$, $S_i(i = 1, 2, 3, 4)$	(20)
Heat exchanges between the regenerator, Q_{41}	W	$Q_{41} = -\frac{2\pi b}{\varepsilon_0 S_{el}}\left(\frac{h(T_1)}{\varepsilon_r(T_1)} - \frac{h(T_2)}{\varepsilon_r(T_2)}\right) q_L^2$ $a_1 = \frac{\pi}{\varepsilon_0 S_{el}} q_H{}^2(1 - r_q{}^2)$, $b = (1/e)\sqrt{\varepsilon_0 k_B/(8\pi\rho_0)}$, $h(T) = \sqrt{T\varepsilon_r}$, $G(T) = (c_1 - c_3 T^2)/\varepsilon_r{}^2(T)$, $r_q = q_L/q_H$, $S_i(i = 1, 2, 3, 4)$	(21)

where the ratio of thermodynamic loss rate (in this article, exergy loss rate, described as the difference between exergy input and output rates, is considered) to capital cost [22] is used and called thermoeconomic factor:

$$R_k = \frac{(Exergydestructionrate)_k}{Z_k} \quad (42)$$

where Z refers to the capital cost of the system and it is attained by multiplying unit cost (c) for per kW. The power output value for the designed system can be calculated as [23]:

$$Z_k = P_k c_k \quad (43)$$

Table 3 – List of equations for the thermoelectric generator [19,21].

Description	Unit	Equation	Equation no.
Heat input to the thermoelectric generator $\dot{Q}_{H,teg}$[19],	W	$\dot{Q}_{H,teg} = N\left(\beta I T - I^2\frac{r}{2} + K(T - T_L)\right)$	(22)
Heat discarded from the thermoelectric generator $\dot{Q}_{L,teg}$[19],	W	$\dot{Q}_{L,teg} = N\left(\beta I T_L + I^2\frac{r}{2} + K(T - T_L)\right)$	(23)
Power acquired from the thermoelectric generator, P_{teg} [19]	W	$P_{teg} = \dot{Q}_{H,teg} - \dot{Q}_{L,teg}$	(24)
Exergy destruction rate, $Ex_{d,teg}$ [19]	W/K	$Ex_{d,teg} = \left(\frac{\dot{Q}_{L,teg}}{T_L} - \frac{\dot{Q}_{H,teg}}{T}\right)$	(25)
Energy efficiency, η_{teg} [19]	–	$\eta_{teg} = \frac{P_{teg}}{\dot{Q}_{H,teg}}$	(26)
Exergy efficiency ϕ_{teg}[19],	–	$\phi_{teg} = \frac{P_{teg}}{\dot{Q}_{L,teg}\left(1 - \frac{T_0}{T}\right)}$	(27)
Seebeck coefficient, β [21]	–	$\beta = 2x(22224 + 930.6T_m - 0.9905T_m{}^2)x10^{-9}$	(28)
Electrical resistivity $\rho_p = \rho_n$[21],	Ω	$\rho_p = \rho_n = (5112 + 163.4T_m + 0.6279T_m{}^2)x10^{-10}$	(29)
Thermal conductivity λ[23],	W/mK	$\lambda_p = \lambda_n(62605 - 277.7T_m + 0.413T_m{}^2)x10^{-4}$	(30)
Mean temperature T_m[21],	K	$T_m = \left(\frac{T + T_L}{2}\right)$	(31)
Electric resistance r[21],	Ω	$r = \left(\frac{\rho_p + \rho_n}{C}\right)$	(32)
Thermal conductivity coefficient K[21],	W/mK	$K = \left(\frac{\lambda_p + \lambda_n}{C}\right)$	(33)

Results and discussion

In this paper, the two hybrid systems for the purpose of the producing electricity using the rejected heat from the high temperature-proton exchange membrane fuel cell are considered. Thermocapacitive cycle and thermo electric generators are chosen as subsystems. Exergy destruction density, energy efficiency, power density and exergy efficiency are determined using a thermoeconomic method, which is called EXCEM.

Fig. 3 shows a variation of power outputs according to current density. Hybrid I, hybrid II and high temperature-polymer electrolyte membrane power outputs have maximum values, which are named optimum points. This means that all systems have a maximum power output in a certain point. High temperature-polymer electrolyte membrane attains its ideal value at $J = 1.03$ A/cm^2. For hybrid I and hybrid II, the optimum values are reached at $J = 1.08$ A/cm^2 and $J = 1.03$ A/cm^2, respectively. The corresponding power output values for hybrid I, hybrid II and high temperature-polymer electrolyte membrane are 792.36 W, 879.078 W and 798.341 W, respectively. Those power output values from hybrid I are higher than those from hybrid II while the power output values from the thermocapacitive cycle are higher than those of the thermoelectric generator. The lowest power output value is derived from the thermoelectric generator. The power outputs from the thermocapacitive cycle and thermoelectric generator rise with current density. This increase ranges from 3.794 to 184.469 W for the thermocapacitive cycle, and from 0.797 to 10.172 W for the thermoelectric generator.

Fig. 4 indicates variation of exergy destruction rate with current density. Exergy destruction rate is the lost power resulting from the irreversibilities while it is directly proportional to the current density. As the current density increases, the rate of exergy destruction rises significantly. The obtained consequences indicate that the exergy destruction rate value of hybrid I is much higher than that of hybrid II. When thermoelectric generator and thermocapacitive cycle are considered in terms of exergy destruction rate intensity value, that of thermocapacitive cycle is smaller. The system component with the lowest exergy destruction rate intensity value is high temperature-polymer electrolyte membrane fuel cell. Exergy destruction value of the thermoelectric generator is lower than that of the thermocapacitive cycle. It is seen that the exergy destruction value of hybrid I has a higher value compared to hybrid II. When the results are compared in terms of exergy destruction values in the working circumstances, one can say that the rate of exergy destruction at the maximum power output rises 10 times for the hybrid systems.

Fig. 5 shows a variation of energy efficiencies depending on current density. Energy efficiency is a measure of how energy source is utilized for producing electricity. The bigger values mean that the higher amount energy source can be converted to electricity. Results show that hybrid I, the thermoelectric generator and the thermocapacitive cycle have the extremum values while high temperature-proton exchange membrane with hybrid II lacks attain such an extreme value. The peak dots are attained at $J = 0.28$ A/cm^2 for the thermocapacitive cycle and $J = 0.23$ A/cm^2 for the thermoelectric generator. The energy efficiencies corresponding to these current densities are 51.6%, 6.32% and 0.2%, respectively. The energy efficiencies of hybrid II and the HT-PEM decrease with current density, indicating the highest values of 50.5% and 50.4%, respectively. The energy efficiency values of hybrid I are higher than those of hybrid II and, clearly, energy efficiency

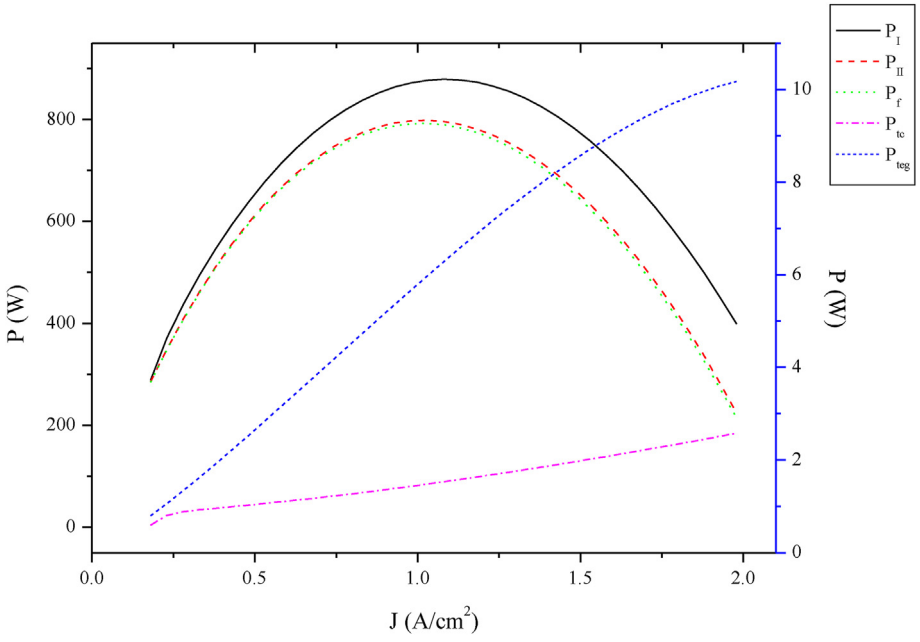

Fig. 3 – Variation of the power density by current density.

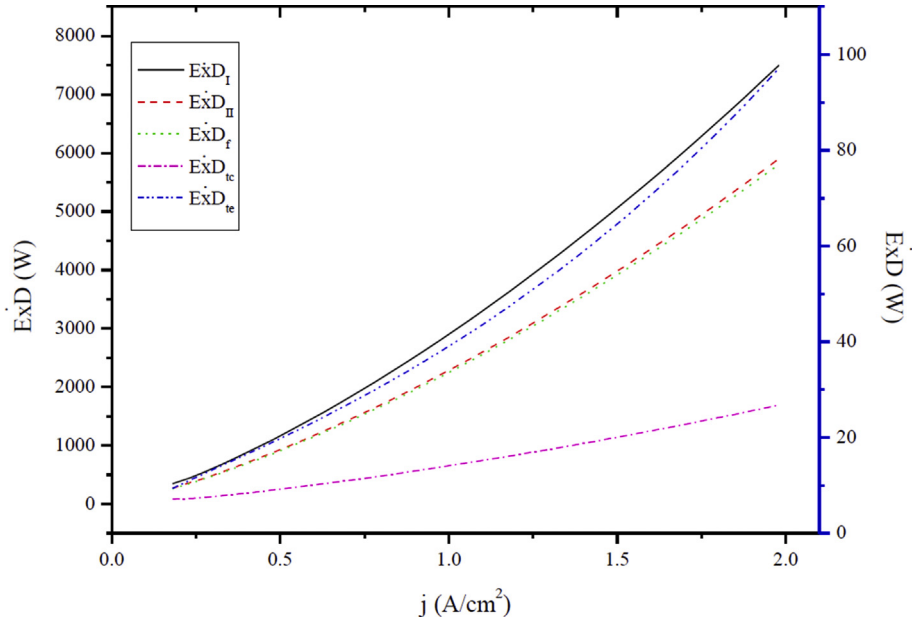

Fig. 4 – Variation of the exergy destruction rate by current density.

values of the thermocapacitive cycle are higher than those of the thermoelectric generator, which has the lowest energy efficiency compared to other components because it has a low figure of merit, which results in lower energy efficiency. These results illustrate us that the thermocapacitive cycle has a higher efficiency value than the thermoelectric generator. When the same heat input is provided for the considered hybrid systems, a higher power density than the thermocapacitive cycle is produced. It may be concluded that the contribution of the subsystems to the energy efficiencies of the hybrid system is approximately 3% for hybrid I and 0.1% for hybrid II.

Fig. 6 indicates a variation of exergy efficiencies depending on current density. Exergy efficiency values, which are a measure of the quality use of energy resources, are seen to have similar results when compared to energy efficiency values. Thermoelectric generator, thermocapacitive cycle and hybrid I have extreme dots. The corresponding exergy efficiency values are 53.1%, 20.3% and 0.9%, respectively. Hybrid I has greater exergy efficiency values than hybrid II. Extremum dots of the HT-PEM, and hybrid II amount to 52.0%, and 52.1%, respectively. As the current density increases, the extremum dots decline. Exergy efficiencies for the HT-PEM and hybrid II are almost the same with their highest values and

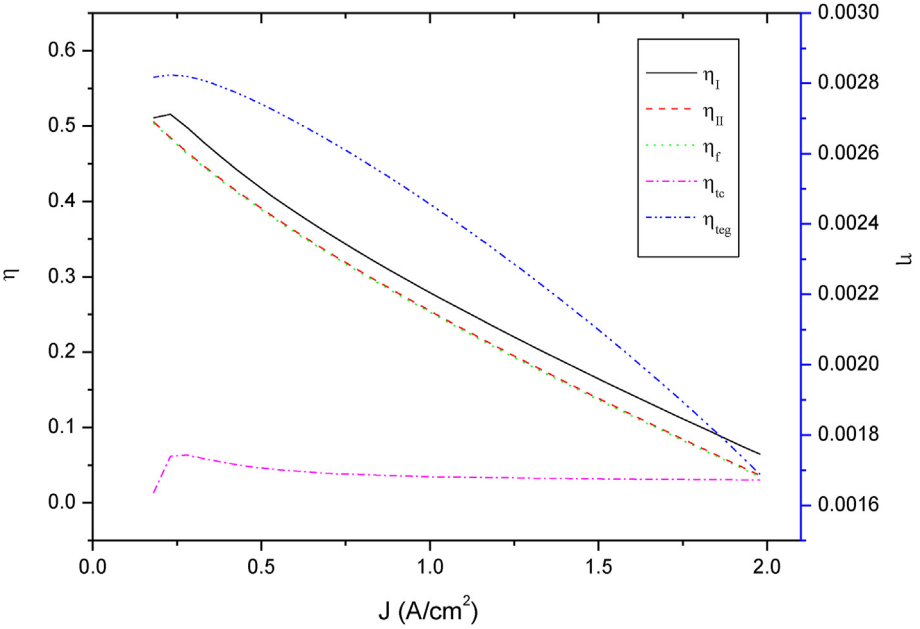

Fig. 5 – Variation of the energy efficiencies by current density.

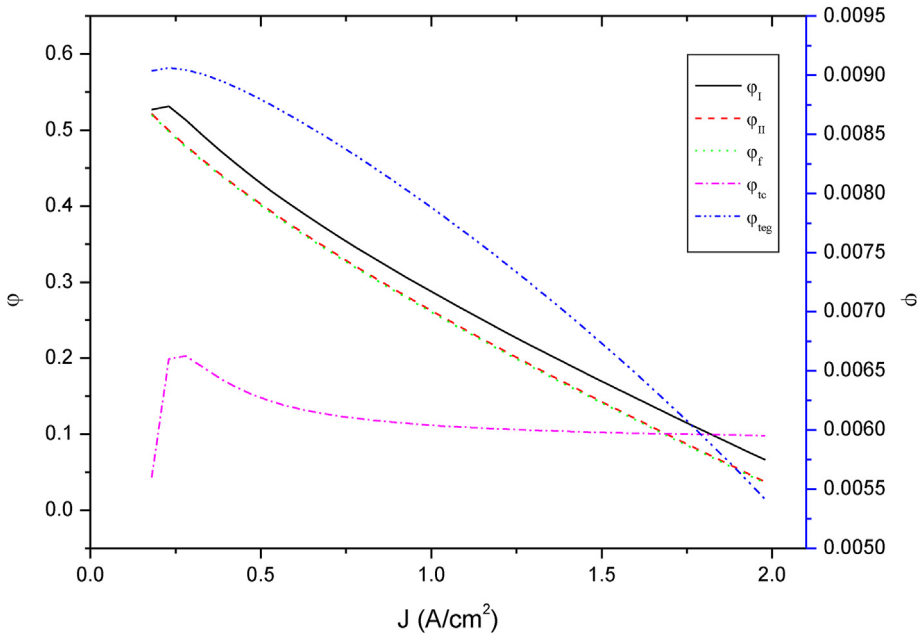

Fig. 6 – Variation of the exergy efficiencies by current density.

approximately identical with each other. Contributions of the subsystems to the exergy efficiencies are about 4% for hybrid I and 0.1% for hybrid II.

Fig. 7 illustrates the results of the EXCEM analysis. These values show the ratio of the last power to capital cost. It provides us information about the points where lost power cost is minimum. Results show that thermocapacitive cycle and thermoelectric generator have the maximum (critical) points. They reached their critical values at $J = 0.28$ A/cm^2 and $J = 0.93$ A/cm^2, which correspond to 0.082 W/$ and 1.772 W/$, respectively. All other systems have a decreasing trend with current density. Based on the results obtained, the biggest current density should be chosen for low R values.

P-η-R curves are drawn for better understanding the relations between power output, energy efficiencies and thermoeconomic costs in Figs. 8 and 9. In these figures, P_{max}, P_{η}, P_R, η_{max}, η_P, R_{min} and R_P represent the maximum power output, the power output corresponding to maximum efficiency, the power output corresponding to the thermoeconomic factor at the minimum value, the maximum efficiency, the energy efficiency at the maximum power, the minimum thermoeconomic factor, the thermoeconomic factor at the highest power. Commonly,

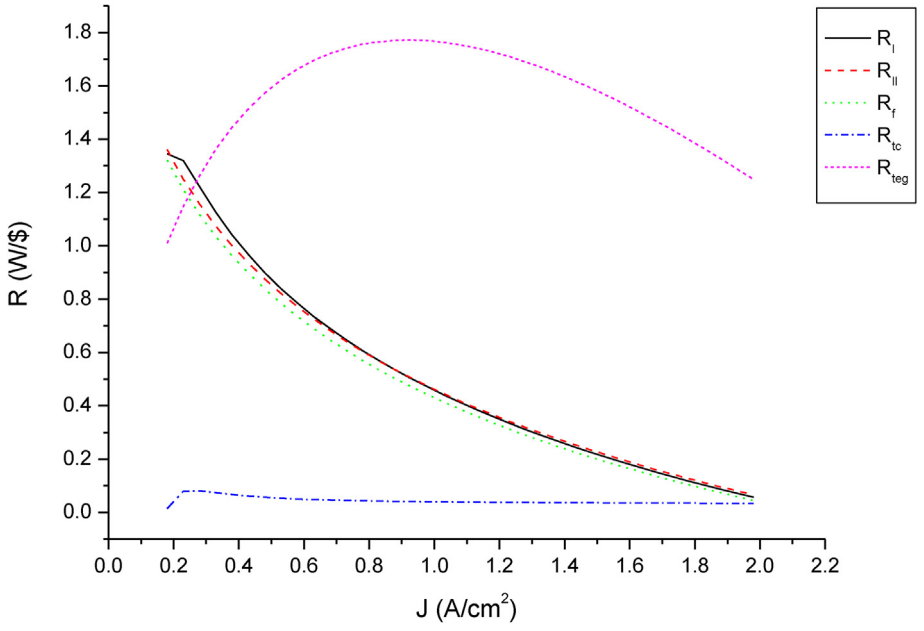

Fig. 7 – Variation of the exergy destruction cost by current density.

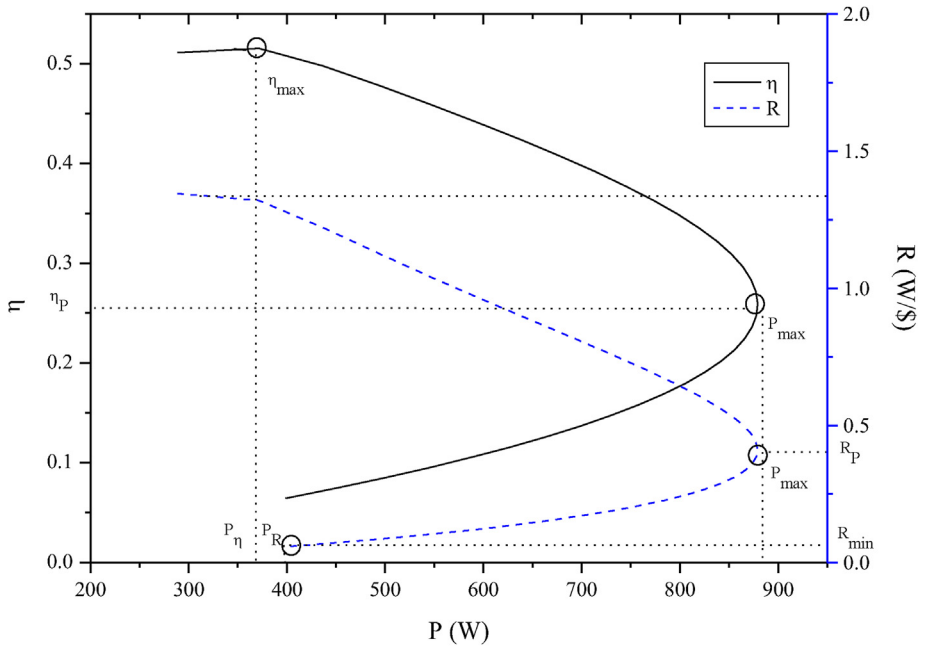

Fig. 8 – P-η-R curve of hybrid I.

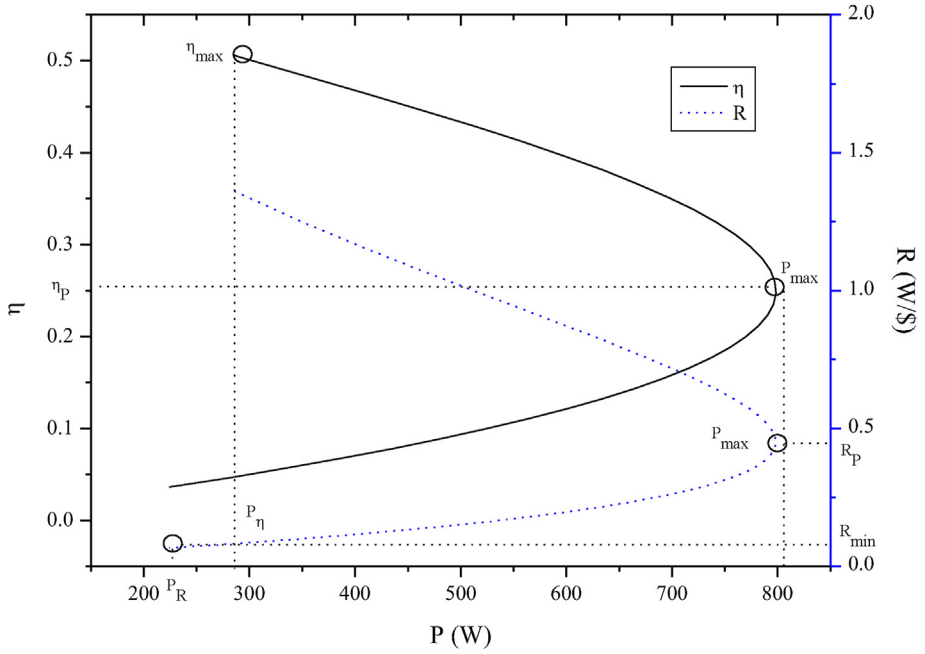

Fig. 9 – P-η-R curve of hybrid II.

the best operation area is chosen as $P_{max} \leq J \leq \eta_{max}$. However, economic issues should be included in the evaluation while the thermoeconomic factor needs to be considered. When the results are investigated, one can see that P_{η} values are 371.72 W and 278.41 W for hybrid I and hybrid II, respectively. They have the highest values with 42.3% and 35.8%. P_R values are maximum at 45.3% for hybrid I and 28.7% for hybrid II. η_P values are equal to 50.4% and 46.4% of the maximum energy efficiencies. P_R values are equal to 30.6% of the maximum thermoeconomic factor for both systems.

These results show that the optimum current density should be selected at the highest power output or close to it. To obtain higher power output and energy efficiency values between 25 and 30% while the thermoeconomic factor is less than 50%, the current density should be selected as $0.93\ A/cm^2 \leq J \leq 1.08\ A/cm^2$.

It is seen that hybrid I is more effective than hybrid II since figure of merit of the thermoelectric generators is relatively low and this affects their performance (power output and efficiency values) as extremely negative. For these reasons, the

performance of the thermocapacitive cycle is better than that of the thermoelectric generator when used as a bottom cycle. Another reason for the low efficiency values of the thermoelectric generator is relatively low temperature of the waste heat from the high temperature-proton exchange membrane and this shows that thermocapacitive cycle is much more convenient than the thermoelectric generators for utilizing low temperature heat sources.

Accuracy of the power obtained from hybrid systems was verified by comparing the power outputs available in the literature. Hybrid systems were compared with the results reported by Açıkkalp and Ahmadi [24], who investigated a phosphoric acid fuel cell thermally regenerative electrochemical cycle hybrid system by considering various parameters including ecological function at different temperatures. The results showed that the highest power output densities for hybrid I and hybrid II were 2536.91 W and 2049.62 W, respectively. Açıkkalp and Ahmadi [24] offered a phosphoric acid fuel cell-thermally regenerative electro chemical hybrid system as an alternative power generation system. The maximum power output of the hybrid system was 950 W, which indicated that the recommended system could be thermodynamically favorable. The results of the present work have a reasonable agreement with the data in the foregoing literature. In the hybrid systems, the lower the current densities, the better the agreement.

Some researchers have focused on power obtained from HT-PEMFC in recent years. The power density obtained from HT-PEMFC was validated verified by considering the power values available in the literature. In this regard, Barreras et al. [25] dealt with the design and working tests of a HT-PEMFC stack using a CHP device towards residential applications. They achieved a maximum power value of 650 W via the small 5-cell stack. A current density of 0.545 A/cm^2 was achieved, demonstrating that the 30-cell HT-PEMFC stack could deliver a nominal sum power of approximately 2300 W. Jannelli et al. [26] compared the performance of combined systems, which were made up of HT-PEMFC and LT-PEMFC. The power unit consisted of two stacks so as to supply with the changeable request of electric load with high efficiency. For dimensioning power units capable of supplying a maximum electrical power of 2.5 ± 0.2 kW, two design criteria, the so-called fixed cell voltage and fixed current density, were considered. Najafi et al. [27] proposed and applied three different strategies so as to interchange the electrical and thermal generation of an HT-PEM fuel cell based CHP plant. In the fuel partialization strategy, the supplied fuel was fractionally reduced down to 50% of its initial value. It was also indicated that the gross electrical power decreased from 30.1 kW at full load down to 17.3 kW while the thermal generation was diminished from 50.0 kW to 22.4 kW. In the second strategy, power/heat shifting, the imposed current of the stack was reduced. This resulted in an augmentation in the anodic stoichiometric ratio, which in turn decreased the net electrical power from 27.6 kW to 15.6 kW while the thermal generation, by contrast with, increased by 6 kW. In the last strategy, the first and second approximations were compounded; at each fuel partialization level, the anodic stoichiometric ratio was changed. The main purpose of Najafi et al. [28] was to evaluate the optimum long term performance of a HT-PEMFC based micro CHP plant by performing two particular multi-purpose optimization approximations. It was obtained that using optimization procedure I, the cumulative average electrical efficiency of the plant developed from 26.03% at normal operation to 27.56% at optimized condition. Moreover, it was specified that by employing the ideal points attained in optimization procedure II, the average cumulative electrical power generation was enhanced from 25.4 kW (at normal operation) to 26.8 kW. The results of the present work have a reasonable agreement with those of the previous studies.

Conclusions

This study performs a comparative performance analysis and assessment of the high temperature-polymer electrolyte membrane-thermocapacitive cycle and high temperature-polymer electrolyte membrane - thermoelectric generator hybrid systems in terms of energetic and exergetic aspects. Exergy destruction rate, thermoeconomic factor, energy efficiency, power density and exergy efficiency are also parametrically investigated. Several significant concluding remarks may be listed as follows:

- The highest power output densities for hybrid I and hybrid II are determined to be 2536.91 W and 2049.62 W, respectively.
- The maximum energy efficiencies are 51.6% for hybrid I and 50.4% for hybrid II.
- Hybrid I seems to be more reasonable and favorable than hybrid II because contribution of the thermocapacitive cycle more than the thermoelectric generator. Reason for this is the low figure of merit of the thermoelectric generator.
- When the results obtained are examined, the current density should be selected between $0.93\ A/cm^2 \leq J \leq 1.08\ A/cm^2$.

For future studies, it is recommended to perform advanced exergy analyses including environmental and economic approaches along with dynamic performance analysis.

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.

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Nomenclature

A_{cell}	Fuel cell active area (cm^2)
C	Geometry factor

c	Unit cost for per kW ($/kW)
$\dot{E}x_d$	Exergy destruction rate (W/K)
e	Elementary charge (C)
F	Faraday' s constant (C/mol)
$\dot{G}$	Total Gibbs free energy change rate (W)
$\dot{H}$	Total energy released per unit time (W)
h	Molar enthalpy (J/mol)
I	Current of the thermoelectric units (A)
I_{stack}	Fuel cell stack current (A)
i	Current density (A/cm^2)
i_0	Exchange current density (A/cm^2)
K	Thermal conductivity coefficient (W/mK)
k	Constant (J/K)
k_{eh}	H_2 electron-oxidation rate constant (A/cm^2)
L	Thickness of the electrical dual stratum in the thermo capacitive (m)
N	Quantity of the thermoelectric units
n	Number of cells in the fuel cell stack
P	Power (W)
Q	Heat (J)
$\dot{Q}$	Waste heat rate (W)
q	Charge (C)
$\dot{q}$	Hydrogen consumption (mol/s)
R	Gas constant (J/Kmol)
r	Electric resistance (Ω)
r_q	Charge ratio
S	Area of the porous surface (m^2)
$\dot{S}$	Entropy (W/K)
s	Molar entropy (J/kmol)
T	Temperature (K)
U	İnternal energy of the electrolyte in the thermo capacitive (J)
V	Voltage (V)
Z	Capital cost ($)

Subscripts

B	Boltzmann
diff	diffusion
e	electron
eff	effective
el	electrode
fc	fuel cell
H	High
H_2	Hydrogen
i	state
L	Low
m	mean
o	open circuit
tc	thermocapacitive
teg	thermoelectric generator

Greek symbols

Δ	Changes of electrochemical reaction
θ	H_2 adsorption/desorption constant
φ	Exergetic coefficient
α	Charge transfer coefficient
β	Seebeck coefficient
ε	Dielectric constant in the vacuum (C^2/Nm^2)
η	Energy efficiency
λ	Air stoichiometry, cathode side
λ_p, λ_n	Thermal conductivity ($W/m.K$)
ρ	Concentration of the electrolyte in the unfilled situation
ρ_p, ρ_n	Electrical resistivity (Ω)
ϕ	Exergy efficiency

Abbreviations

HT-PEMFC	High-temperature proton exchange membrane fuel cell
PEMFCs	Polymer electrolyte membrane fuel cells

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