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Thermodynamic analysis of the performance of an irreversible ammonia-fed solid oxide fuel cell

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Abstract

To investigate the performance of an irreversible direct ammonia-fed solid oxide fuel cell, the direct ammonia-fed solid oxide fuel cell based on oxygen ion conductivity was modeled using finite time thermodynamic theory. First, mathematical expressions for the output power, output efficiency, ecological objective function and ecological coefficient of performance of the direct ammonia-fed solid oxide fuel cell were derived. Further, the effects of parameters such as operating temperature, operating pressure, fuel utilization, and electrolyte thickness on the performance of direct ammonia-fed solid oxide fuel cell were numerically investigated. The results show that as the operating temperature of direct ammonia-fed solid oxide fuel cell increases, the performance of direct ammonia-fed solid oxide fuel cell including output power, output efficiency, ecological objective function and ecological coefficient of performance will be improved. Under certain conditions, increasing fuel utilization can improve output power, output efficiency and ecological performance. Increasing the electrolyte thickness will decrease the finite time thermodynamic performance of direct ammonia-fed solid oxide fuel cell. Moreover, the microstructure of the electrode also affects the performance of direct ammonia-fed solid oxide fuel cell, and the ecological objective function is increased by 16.9% when the electrode porosity is increased from 0.4 to 0.8.

Keywords: Direct ammonia-fed solid oxide fuel cell; FTT; Parametric study; Ecological coefficient of performance

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1. Introduction

There is an urgent need to find new clean and renewable sources of energy for normal socio-economic development, so solar, wind, nuclear, tidal, hydrogen have become new options [1, 2]. Solar, wind and geothermal energy (tidal energy) have the advantages of being renewable and non-polluting. However, the climate, geographical location, time intermittency and other limitations make the large-scale popularization of the use of large-scale is hindered while solid oxide fuel cell (SOFC) is not lim-

ited by the above factors. The chemical energy of the fuel itself may be transformed into electricity at any moment as long as it is electrified. Fuel options include hydrogen, methanol, natural gas, and biomass gas [3]. Thus, it is characterized by fuel flexibility. But it is difficult to storage and transportation hydrogen for the case of requiring high pressure vessels and good tanks for storage of compressed hydrogen [4].

At present, ammonia is proposed to be used as a sustainable fuel [5–7]. Ammonia is less expensive per unit volume of stored energy than hydrogen, making it simpler to generate, store, and

Nomenclature

A_{cell} – active cell area, m^2
 E_r – cell reversible voltage, V
 E^0 – voltage at standard pressure, V
 F – Faraday's constant, C/mol
 G – Gibbs free energy, J
 J_0 – exchange current density, A/m^2
 J – current density, A/m^2
 J_t – total battery current, A/m^2
 LHV_{NH_3} – lower heating value of the ammonia fuel, kJ/mol
 m_{NH_3} – mass flow rate, kg/h
 N – number of single cells
 $n_{H_2, equ}$ – equivalent molar flow rate of H_2 , mol/s
 $n_{H_2, consumed}$ – actual molar flow rate consumed of, mol/s
 n_{fuel} – amount of fuel required, mol
 p_i – partial pressures of i , atm
 p_i^{TB} – partial pressures of at the three-phase boundary, atm
 P – power density, W/m^2
 R – gas constant, $J/(mol \cdot K)$
 R_Ω – electrolyte resistivity, $\Omega \cdot m$
 S_g – cyclic entropy increase
 T – operating temperature, K
 T_0 – ambient temperature, K
 T_L – temperature of the low-temperature heat source, K
 U_f – fuel utilization, %
 $V_{act, an}$ – anodic activation overpotential, V
 $V_{act, ca}$ – cathodic activation overpotential, V
 V_{ohm} – ohmic overpotential, V
 $V_{con, an}$ – anodic concentration overpotential, V

$V_{con, ca}$ – cathodic concentration overpotential, V
 W – output power, W
 z – number of electrons

Greek symbols

α – charge transfer coefficient
 λ_{H_2} – mole fraction of hydrogen, %
 σ – entropy production rate, $W/(K \cdot m^2)$
 σ_m – electrolyte thickness, mm
 τ – cycle period
 φ – output exergy, kJ/mol

Subscripts and Superscripts

0 – standard conditions
 act – activation
 an – anode
 ca – cathode
 con – concentration
 H_2 – hydrogen H_2
 H_2O – water
 O_2 – oxygen
 ohm – Ohmic

Abbreviations and Acronyms

DA-SOFC – direct ammonia-fed solid oxide fuel cell
 ECOP – ecological coefficient of performance
 FTT – finite time thermodynamics
 PEMFC – proton exchange membrane fuel cell
 SOFC – solid oxide fuel cell

transport. Besides, Ammonia is relatively safe to use because its pungent odor is easily detected. Most importantly, liquid ammonia is not released when used as fuel cell fuel, which is cost effective [8]. As a result, there has been increasing research into the use of ammonia as a sustainable fuel in fuel cells, especially in SOFCs. Ammonia fuel and solid oxide fuel cells are an ideal combination to address decarbonization issues in transportation sectors such as shipping, heavy vehicles, and aviation [9]. For instance, Toyota's Mirai and Hyundai's Nexa have successfully passed testing using the direct ammonia-fed solid oxide fuel cell (DA-SOFC) system in Australia. In addition, Japanese company IHI has partnered with Toyota to commercialize small cogeneration systems based on DA-SOFC, which can be used for power generation in homes, factories, and other places to reduce fossil energy [10]. Therefore, it is of great significance to study DA-SOFC in order to achieve carbon-free transportation and other fields.

For now, researches on DA-SOFC mainly includes electrolyte types [11–13], electrolyte materials [14,15], electrode materials and parameter research [16]. Ni et al. [17] tested direct ammonia fuel cells with different electrolytes. Specifically SOFC based on proton conductivity (SOFC-H) and SOFC based on oxygen ion conductivity (SOFC-O) were tested separately. The large ohmic overpotential of the SOFC-H electrolyte results in a much lower practical performance of the proton conduction direct ammonia fuel cell than the oxygen ion conduction direct

ammonia fuel cell. The electrolyte is an important structure of DA-SOFC, it transports oxygen ions or protons between the anode and cathode to complete the electrochemical reaction of DA-SOFC [18]. At the relevant working temperature of the fuel cell, an ideal electrolyte should be stable. Because it is highly conductive and stable in a variety of conditions, yttria-stabilized zirconia (YSZ) is the most often utilized electrolyte for direct ammonia fuel cells with oxygen ion conducting electrolyte (SOFC-O). Kaur and Singh [19] studied the influence of cathode materials on the operating temperature of fuel cells. The findings indicate that the cathode material significantly impedes the reduction of the fuel cell's operating temperature. This is primarily due to the dominance of cathode activation polarization when the fuel cell's operating temperature lowers. Jiang and Chan [20] analyzed the specific requirements of SOFC anode materials. The results show that the anode material must have sufficient electrical conductivity, chemical and mechanical stability and activity for electrochemical reactions. Li et al. [21] conducted a study to investigate the impact of operating temperature on the performance of DA-SOFCs. The findings indicate that the efficiency of the DA-SOFC is significantly influenced by the level of breakdown of the entering NH_3 . Siddiqui and Dincer [8] conducted a study to examine the impact of electrolyte thickness and operating temperature on the performance of a DA-SOFC. According to the findings, the peak power density of the fuel cell and the performance of the battery are both able to be greatly

enhanced by reducing the electrolyte thickness and increasing the operating temperature, respectively. Yin et al. [22] showed through research that increasing the temperature can increase the reaction rate inside the fuel cell and then significantly improve the performance of the fuel cell.

Finite time thermodynamics is an extension and promotion of classical thermodynamics, a new branch of modern thermodynamic theory, mainly studying the laws of energy flow and entropy flow of non-equilibrium systems in finite time. In the development process of finite time thermodynamics, the research on internal reversible Carnot cycle model, efficiency at maximum power output, basic optimization relations, unified theory of internal reversible cycles, irreversible cycle theory and other aspects play an extremely important role. Traditional methods of studying fuel cells are usually based on idealized assumptions, such as equilibrium conditions under infinite time. Finite time thermodynamics (FTT) takes into account the irreversibility and actual operating conditions in the actual system, thus providing a more realistic model which reflects the actual Fuel cell performance accurately. The goal of finite time thermodynamics is to achieve the best performance in a given time, which is different from the traditional approach that focuses on the equilibrium state. This means finite time thermodynamics can optimize the power output and efficiency of the fuel cell in a specific time period, which is very important to many practical applications. The purpose of FTT is to minimize the irreversibility of a thermal system in a finite time constraint by seeking performance boundaries for thermodynamic processes. The use of finite time thermodynamics theory is to determine the best thermodynamic efficiency of a DA-SOFC under limited time limitations, with the objective of enhancing the actual output performance of the fuel cell [23–25].

Sieniutycz and Poświata [26] used finite time thermodynamic optimization method to study the ultimate output performance of fuel cells. Ye et al. [27] used exergy analysis theory to study the performance of two fuel cell systems under different operating conditions. The findings indicate that raising the operational temperature of the fuel cell leads to a corresponding enhancement in both the power output and efficiency of the system. Conversely, the influence of relative humidity and operating pressure on the performance of the system is found to be negligible. Ishak et al. [28] conducted their investigation of the ammonia fuel cell system using energy and exergy analysis methodologies. The findings indicate that there is a negative correlation between the amount of fuel use and the system's energy and exergy efficiency. By raising the temperature of the fuel cell, one may improve both its energy efficiency and its exergy efficiency. You et al. [29] analyzed the energy, energy efficiency, economic, and environmental aspects of the SOFC polygeneration system. They then used the NSGA-II technique to carry out two sets of multi-objective optimizations, with the goal of optimizing the system's performance in various situations. Xu et al. [30] developed a thermodynamic model for irreversible proton exchange membrane fuel cells (PEMFCs) and investigated the impact of several factors, including operating temperature, film thickness, and operating pressure, on the performance of the fuel cell. Enhancing the operating temperature and

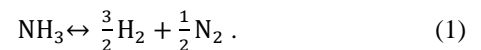
pressure of a PEMFC has been shown to have a positive impact on its performance. Similarly, it has been noted that the degree of phosphoric acid doping may greatly enhance the fuel cell's performance. This is mostly attributed to the influence of phosphoric acid doping on the proton exchange membrane's conductivity.

The main contribution of applying the FTT method in this paper is to establish various thermodynamic evaluation index models for performance analysis and optimization, as well as to study the irreversible process of DA-SOFC. Firstly, the irreversibility of DA-SOFC was analyzed from the perspective of finite-time thermodynamics, and a voltage model considering the irreversibility was established. From this, the finite time thermodynamic indexes such as power, efficiency, entropy production rate, ecological objective function and ecological coefficient of performance (ECOP) of DA-SOFC were derived. Then, the performance of DA-SOFC is analyzed, and the effects of operating temperature, operating pressure, fuel utilization, electrolyte thickness and electrode porosity on various finite time thermodynamic indexes of DA-SOFC are studied. We believe that this finite time thermodynamic model can provide new ideas for future fuel cell research. The irreversibility analysis of fuel cells can better identify the source of polarization loss in fuel cells and provide direction for future improvements in fuel cell performance. Evaluate the performance of DA-SOFC under different operating parameters, and the results obtained can provide theoretical guidance for the optimization design and practical application of fuel cells.

2. Finite time thermodynamic model of irreversible DA-SOFC

2.1. Working mechanisms

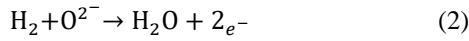
The operation of solid oxide fuel cells, which rely on oxygen ion conducting electrolytes, need the transportation of ions through the electrolyte. Introduce either pure oxygen gas or air to the cathode compartment of the fuel cell. At the boundary between the cathode and electrolyte, the process of oxygen reduction occurs, resulting in the formation of oxygen ions. The aforementioned ions traverse the electrolyte and engage in an electrochemical process with hydrogen gas at the boundary between the anode and electrolyte, resulting in the generation of water vapor. Ammonia fuel decomposes at the anode of an ammonia fuel cell. This decomposition process results in the formation of two distinct products, referred to as H_2 and N_2 . The reaction equation is as follows:



The hydrogen gas produced by decomposition reacts with oxygen ions at the anode-electrolyte interface to produce water vapor. The fuel cell releases hydrogen, nitrogen, unreacted ammonia fuel, and produced water vapor. The hydrogen concentration is diluted as a result of the creation of nitrogen during the thermal breakdown of ammonia, which lowers the fuel cell's reversible cell potential. At low temperatures and without a catalyst, the decomposition rate is slower, but at high temperatures

and with a catalyst, the decomposition rate is faster. Figure 1 describes the working principle of the ammonia-fed. The electrochemical reactions on the anode and cathode of SOFC are as follows:

– anode reaction:



– cathode reaction:

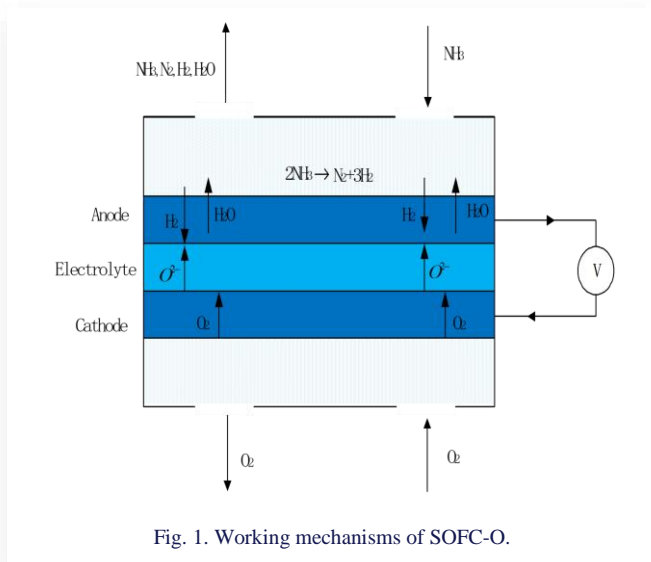


Fig. 1. Working mechanisms of SOFC-O.

2.2. Reversible potential of DA-SOFC

In order to calculate the maximum output power, efficiency of DA-SOFC, the voltage of the fuel cell consists of irreversible factors such as activation polarization, ohmic polarization, concentration polarization, and thermal irreversibility, which are not considered in the ideal model. Under situations when the circuit is open, the potential (voltage) may be characterized as:

$$E_r = E^0 + \frac{RT}{2F} \ln \left[\frac{p_{\text{H}_2} p_{\text{O}_2}^{1/2}}{p_{\text{H}_2\text{O}}} \right], \quad (4)$$

$$E^0 = \frac{-\Delta G}{zF}, \quad (5)$$

where E_r is the cell reversible voltage; E^0 is the voltage at standard pressure, R is the gas constant; T is the operating temperature; F is Faraday's constant; p_{H_2} , p_{O_2} and $p_{\text{H}_2\text{O}}$ are the partial pressures of hydrogen, oxygen, and water on the anode side, respectively; G is the Gibbs free energy; and z is the number of electrons involved in the chemical reaction, set to a value of 2.

The irreversibility within the cell leads to energy loss, which is represented by the overpotential. Thus, the single DA-SOFC voltage can be expressed as:

$$V = E_r - V_{act,an} - V_{act,ca} - V_{ohm} - V_{con,an} - V_{act,ca}, \quad (6)$$

where $V_{act,an}$ and $V_{act,ca}$ are the anodic and cathodic activation overpotentials, respectively; V_{ohm} is the ohmic overpotential at

the electrolyte; $V_{con,an}$ and $V_{act,ca}$ are the anodic and cathodic concentration overpotentials, respectively.

2.3. Overpotential of DA-SOFC

Due to the irreversibility of electrode dynamics, the losses occurring in fuel cells are referred to as activation overpotentials. The correlation between the activation overpotential and the current density of a fuel cell is mathematically represented by the Butler-Volmer equation:

$$J = J_0 \left[\exp \left(\frac{\alpha z F V_{act}}{RT} \right) - \exp \left(-\frac{(1-\alpha) z F V_{act}}{RT} \right) \right], \quad (7)$$

where J_0 is the exchange current density, z is the number of electrons involved per reaction.

This depends on the material and structure of the electrode used [31]. This effect is described by the charge transfer coefficient (α), which is numerically between 0 and 1. It is usually taken as 0.5. Thus, the activation overpotential can be expressed as:

$$V_{act,i} = \frac{RT}{F} \sinh^{-1} \left(\frac{J}{z J_{0,i}} \right), \quad i = \text{cathode or anode}. \quad (8)$$

The ohmic overpotential (V_{ohm}) illustrates the ionic resistance of the electrolyte. The ohmic overpotential can be evaluated according to Ohm's law [32]. The ohmic overpotential of DA-SOFC electrolyte is expressed as:

$$V_{ohm} = J \sigma_m R_\Omega, \quad (9)$$

where σ_m is the current density, R_Ω is the electrolyte thickness; is the electrolyte resistivity.

Water vapor is produced at the SOFC-O anode and the concentration at the electrode is related to the partial pressure of the gas. Thus the anode concentration overpotential and cathode concentration overpotential are expressed as:

$$V_{con,an} = \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}^{TB} p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{H}_2\text{O}}^{TB}} \right), \quad (10)$$

$$V_{con,ca} = \frac{RT}{4F} \ln \left(\frac{p_{\text{O}_2}}{p_{\text{O}_2}^{TB}} \right), \quad (11)$$

where $p_{\text{H}_2}^{TB}$, $p_{\text{O}_2}^{TB}$ and $p_{\text{H}_2\text{O}}^{TB}$ are the partial pressures of H_2 , O_2 and H_2O at the three-phase boundary, respectively.

The current density J is defined by [33]:

$$J = \frac{J_t}{N A_{cell}} = \frac{n U_f F x n_{\text{H}_2, equ}}{N A_{cell}}, \quad (12)$$

$$n_{\text{H}_2, equ} = n_{fuel}, \quad (13)$$

$$U_f = \frac{n_{\text{H}_2, consumed}}{n_{\text{H}_2, equ}}, \quad (14)$$

where J_t is the total battery current, N and A_{cell} are the number of single cells and the active cell area, respectively, U_f is the fuel utilization, $n_{\text{H}_2, equ}$ is the equivalent molar flow rate of H_2 , n_{fuel} and λ_{H_2} are the amount of fuel required and the mole fraction of hydrogen, respectively, $n_{\text{H}_2, consumed}$ is the actual molar flow rate consumed.

2.4. Finite-time thermodynamic performance analysis of DA-SOFC

The output power density of DA-SOFC can be expressed as follows [34]:

$$\begin{aligned}
 P &= JV = J(E_r - V_{act,an} - V_{act,ca} - V_{ohm} - V_{con,an} - V_{con,ca}) \\
 &= J \left[E^0 + \frac{RT}{2F} \ln \left(\frac{p_{H_2}(p_{O_2})^{\frac{1}{2}}}{p_{H_2O}} \right) - \frac{RT}{F} \sinh^{-1} \left(\frac{J}{zJ_{ca}} \right) + \right. \\
 &\quad \left. - \frac{RT}{F} \sinh^{-1} \left(\frac{J}{zJ_{an}} \right) - J\sigma_m R_\Omega - \frac{RT}{2F} \ln \left(\frac{p_{H_2}^{TB} p_{H_2O}}{p_{H_2} p_{H_2O}^{TB}} \right) - \frac{RT}{4F} \ln \left(\frac{p_{O_2}}{p_{O_2}^{TB}} \right) \right].
 \end{aligned} \quad (15)$$

The output efficiency of an energy conversion device may be determined by dividing the energy output by the total energy intake. Therefore, the expression for the output efficiency of DA-SOFC may be represented by the following equation [35]:

$$\begin{aligned}
 n(\%) &= \frac{P}{m_{NH_3} \cdot LHV_{NH_3}} = \\
 &= \frac{J(E_r - V_{act,an} - V_{act,ca} - V_{ohm} - V_{con,an} - V_{con,ca})}{m_{NH_3} \cdot LHV_{NH_3}}, \quad (16)
 \end{aligned}$$

where m_{NH_3} is the mass flow rate; is the lower heating value of the ammonia fuel.

Angulo-Brown [36] proposed an ecological objective function $E = P - T_L \sigma$ as an objective to discuss the performance of finite time Carnot engines (where T_L is the temperature of the low-temperature heat source, P is the output power of the finite time heat engine, and σ is the entropy production rate). By substituting T_L with T_0 in the mathematical model, the ecological objective function may be represented as [37]:

$$E = P - T_L \sigma, \quad (17)$$

$$\sigma = \frac{-\Delta H^0 - P}{T_0}, \quad (18)$$

where T_0 a represents the ambient temperature. Based on the analysis of FTT theory, references [38,39] provide unified ecological optimization indicators for thermodynamic cycles:

$$E = \frac{\varphi}{\tau} - \frac{T_e \Delta S}{\tau} = \frac{\varphi}{\tau} - T_0, \quad (19)$$

where φ represents the cycle output exergy, τ is the cycle period, T_0 is the ambient temperature, and ΔS is the entropy production of the entire cycle.

Chen et al. [37] proposed that the actual power dissipation is formulated as $T_0 \sigma$. When seen from the perspective of exergy analysis, the ecological criteria function is defined as the difference between the rate at which exergy is produced and the amount of power that is lost in the process. The following is an expression that may be used to describe the ecological goal function of DA-SOFC:

$$\begin{aligned}
 E &= p - T_0 \sigma = (E_r - V_{act,an} - V_{act,ca} + \\
 &\quad - V_{ohm} - V_{con,an} - V_{con,ca}) J - T_0 \sigma. \quad (20)
 \end{aligned}$$

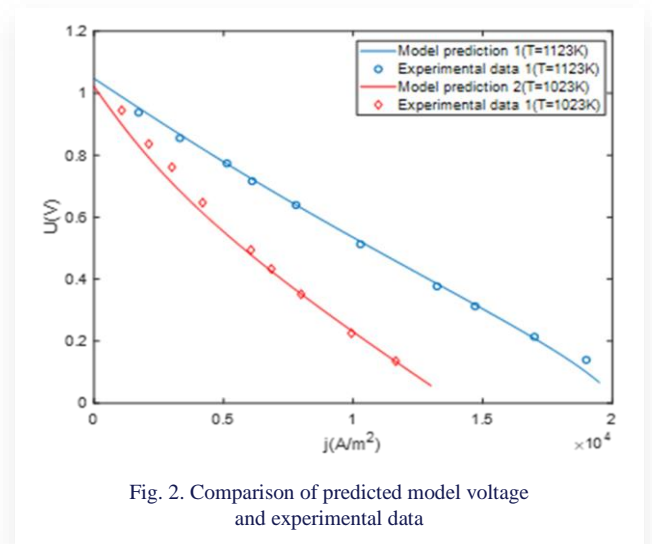


Fig. 2. Comparison of predicted model voltage and experimental data

Ust et al. [40] introduced the concept of the ECOP as a means to evaluate and enhance the efficiency of limited time irreversible dual cycles. The ecological coefficient of performance is a metric that quantifies the efficiency of a system by measuring the ratio of power production to the loss of availability. It may be mathematically represented as:

$$ECOP = \frac{W}{T_0 S_g}. \quad (21)$$

Based on previous research, Ust et al. [40] proposed a new ecological objective function, called ECOP. In the context of DA-SOFC, the ecological performance coefficient refers to the proportion between the actual output power and power dissipation, which can be expressed as:

$$ECOP = \frac{P}{T_0 \sigma} = \frac{J(E_r - V_{act,an} - V_{act,ca} - V_{ohm} - V_{con,an} - V_{con,ca})}{T_0 \sigma}. \quad (22)$$

The new ecological coefficient of performance optimizes the relationship between output power and power dissipation, and is an important evaluation index for DA-SOFC.

2.5. Model verification

Among various types of fuel cells, SOFC has obvious advantages in power generation efficiency, environmentally friendly power generation and fuel flexibility [41]. This characteristic makes SOFC technology attract much attention in practice. It can not only effectively reduce environmental pollution, but also have more flexible fuel options. While hydrogen is considered an ideal fuel, its production, storage and transportation present problems. Moreover, under different experimental conditions, the power difference between solid oxide fuel cells using ammonia fuel and hydrogen is less than 4%, so ammonia fuel is the best choice [42].

Figure 2 shows the comparison results of the voltage predicted by the established DA-SOFC model and experimental data at 1023 K and 1123 K [42]. The operating pressure is 1atm and the electrolyte thickness is 30 μ m. The results show that the established model agrees well with the experimental data with a maximum error of 5%.

3. Results and discussion

For SOFC to be widely commercialized, a suitable fuel should be selected. Among all fuels, ammonia has the best volume density and better hydrogen storage weight density. It has lower liquefaction requirements and is easier to store and transport. Ammonia is therefore especially suited for tiny, portable systems and applications in automobiles. A finite time thermodynamic evaluation index and the known model of irreversible DA-SOFC are used to study the influence of various parameters on the performance of DA-SOFC. Table 1 lists the fundamental characteristics of the cell that will be used in the ensuing computational investigation. The remaining parameters stay the same while one is altered to examine its impact.

Table 1. Relevant parameters involved in DA-SOFC single cell [42–48].

Parameters	Value
Fuel utilization (%)	85
Exchange current density of anode, J_{an} (A/m^2)	$7 \times 10^9 \frac{P_{H_2}}{P_0} \frac{P_{H_2O}}{P_0} \exp(-\frac{100000}{RT})$
Exchange current density of cathode, J_{ca} (A/m^2)	$7 \times 10^9 (\frac{P_{O_2}}{P_0})^{0.25} \exp(-\frac{130000}{RT})$
Operating temperature, T (K)	1073
Operating pressure, p (atm)	1
Electrode porosity, ϵ	0.4
Electrode tortuosity, τ	4.25
Average pore radius of electrode, r_p (μm)	0.5
Resistivity of electrolyte, R_e (Ωm)	$2.94 \times 10^{-5} \exp(-\frac{10350}{T})$
Anode thickness (μm)	500
Electrolyte thickness (μm)	30
Cathode thickness (μm)	30

3.1. Effect of operating temperature on DA-SOFC performance

Figure 3 shows the effect of current density and temperature on the finite time thermodynamic index of DA-SOFC. Figure 3a illustrates the substantial impact of temperature escalation on the power output of the fuel cell. The output power exhibits an initial rise followed by a subsequent decline as the current density rises, given a certain operating temperature. The output power has a positive correlation with the operating temperature while the current density is constant. This phenomenon occurs due to the positive correlation between temperature and exchange current density, as well as the negative correlation between temperature and activation overpotential. Additionally, a rise in temperature leads to an enhanced rate of oxygen ion passage, resulting in a reduction of the irreversible effects caused by the ohmic overpotential. When the magnitude of power consumption is low, there will be a corresponding drop in the lowest entropy production, leading to a rise in the output power. Hence, it can be shown that the ideal output power density of a DA-SOFC may be efficiently enhanced by raising its operating temperature within a certain range. Figure 3b shows that the output efficiency

of the fuel cell will become lower as the current density increases at a certain temperature. Because the increase in current density leads to an increase in irreversible losses within DA-SOFC, resulting in lower efficiency. In addition, under a certain current density, the battery energy efficiency increases with the increase of operating temperature.

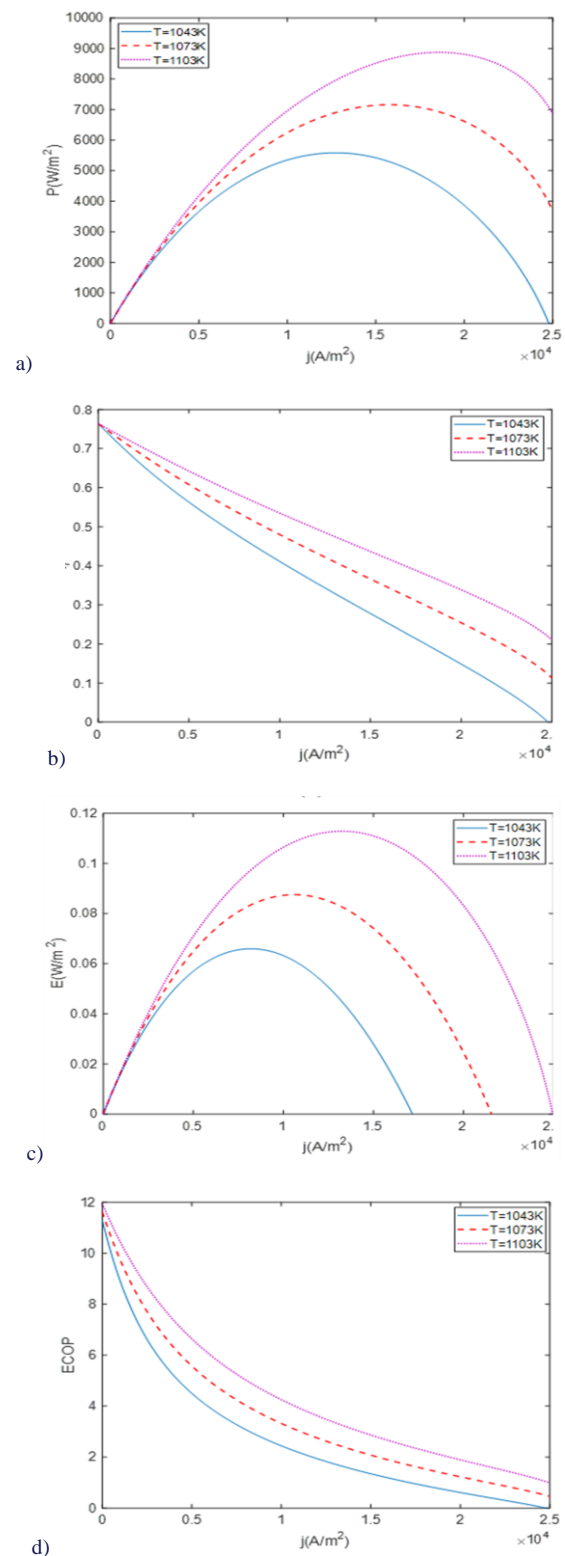


Fig. 3. Variation of P with operating temperature (a), variation of η with operating temperature (b), variation of E with operating temperature (c), variation of $ECOP$ with operating temperature (d).

It can be seen from Fig. 3c that when the operating temperature is kept constant, the ecological objective function first increases and then decreases as the current density increases. It can be explained that as the DA-SOFC reaction continues to proceed, the electrochemical reaction rate continues to increase, and the output power of DA-SOFC continues to increase. At this time, power dissipation is also increasing, but its amplitude is much smaller than the increase in output power, so the ecological objective function is increasing. As the current density continues to increase, power dissipation has been increasing, and the output power is decreasing, so the ecological objective function is gradually decreasing. An increase in the operating temperature leads to an increase in the ecological objective function. The main reason is that an increase in the operating temperature increases the output power of the irreversible DA-SOFC and reduces the power loss due to entropy formation. Therefore, when the operating temperature increases, the ecological objective function of DA-SOFC also increases.

The decrease in the ecological coefficient of performance is seen in Fig. 3d. The phenomenon of power dissipation is seen to be on the rise, while the output power is concurrently experiencing a decline. Furthermore, the ratio between the output power and power dissipation is also observed to be falling. Hence, the ecological coefficient of performance is seen to be diminishing as the operation of the DA-SOFC progresses. Raising the operational temperature has the ability to enhance the exchange current density, diminish the activation overpotential, and augment the rate of oxygen ion passage. Consequently, this mitigate the irreversible consequences associated with the ohmic overpotential. Consequently, increasing the operational temperature has the potential to enhance the ecological coefficient of performance.

3.2. Effect of operating pressure on DA-SOFC performance

Figure 4 shows the effect of operating pressure on the FTT index of DA-SOFC when the current density is 15 000 A/cm². It is clear from looking at Fig. 4a that when the operating pressure of the DA-SOFC is raised, the power density will also rise. This is due to the fact that if the operating pressure is increased, the exchange current density will keep growing, as will the reversible potential, and the irreversibility of the DA-SOFC will decrease. As a consequence of this, the power density of DA-SOFC continues becoming better. When the operating temperature is 1 073 K and the operating pressure is increased to 3 atm, the corresponding power density is 9 395.4 W/m². When the current density is 15 000 A/cm², the operating temperature is 1 073 K, and the DA-SOFC operating pressure is increased from 1 atm to 3 atm, the DA-SOFC power density increases by 33.8%. This observation demonstrates that the performance of DA-SOFC is significantly influenced by the operating pressure.

Figures 4b–4d illustrates how the DA-SOFC's output efficiency, ecological objective function, and ECOP will all improve with an increase in operating pressure. When the operating pressure of DA-SOFC with an operating temperature of 1 073 K and a current density of 15 000 A/cm² was increased from 1 atm to 3 atm (101.33 – 303.98 kPa), the output effi-

ciency, ecological objective function, and the ecological coefficient of performance of DA-SOFC increased by 33.9%, 85.5%, and 65.3%, respectively.

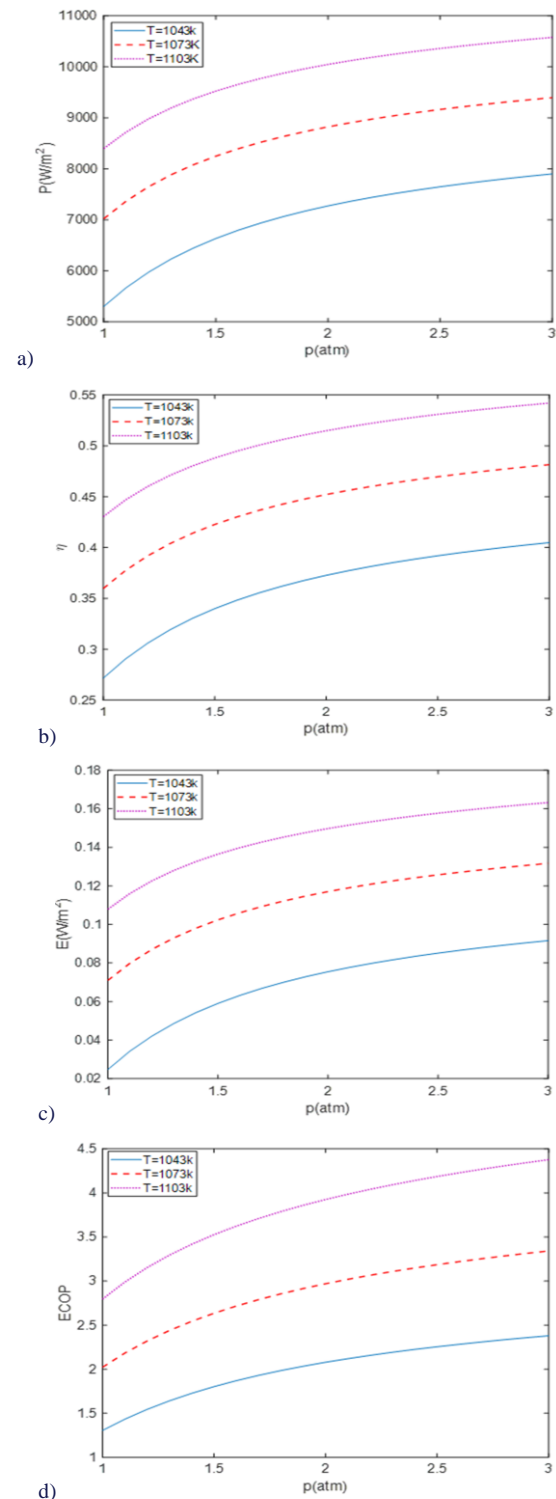


Fig. 4. Variation of P with operating pressure (a), variation of η with operating pressure (b), variation of E with operating pressure (c), variation of ECOP with operating pressure (d).

The ecological objective function increases with increased operating pressure. This is primarily because increasing operating pressure lowers power loss from entropy creation and boosts

the irreversible DA-SOFC's output power. As a result, as operating pressure increases, the ecological goal function of the DA-SOFC also increases. Increasing operating pressure can also mitigate the irreversible consequences associated with ohmic overpotentials, thereby improving ECOP.

Based on the numerical analysis, increasing the operating pressure significantly improves the finite time thermodynamic performance of the DA-SOFC. First, increasing operating pressure helps increase gas diffusion rates, making it easier for reactants to transport inside the cell. By enhancing gas transfer, cells can use fuel and oxygen more efficiently, increasing overall efficiency. Secondly, higher operating pressure helps reduce the resistance of the gas flow channel, thereby reducing internal resistance. This is critical to improving the battery's power output and response speed. However, it is important to note that excessive operating pressures may result in increased system engineering complexity as stronger materials and construction are required to withstand the greater pressures. In addition, increasing the operating pressure consumes the power of ancillary equipment such as compressor, which requires higher cost, and the cost of manufacturing and maintaining the system may also increase. Therefore, when considering increasing operating pressure, multiple factors such as performance improvement, system cost, and material strength must be comprehensively considered to find optimal operating parameters to meet the needs of specific application scenarios. Overall, optimizing operating pressure is one of the important strategies to improve fuel cell system performance, but requires a careful balance of various factors.

3.3. Effect of fuel utilization on DA-SOFC performance

Figure 5 illustrates the impact of fuel utilization on the finite time thermodynamic index of a DA-SOFC under the conditions of a current density of 15 000 A/cm² and an operating temperature of 1 073 K. The observed variations in power density exhibit distinct patterns at varying pressures, as seen in Fig 5a. The power density exhibits an upward trend as the fuel utilization ranges from 0.65 to 0.95, while maintaining a pressure of 1.5 atm (151.99 kPa) and 2 atm (202.65 kPa). As fuel utilization rises, it is seen that the output voltage lowers while the current density increases. The rise in current density surpasses the drop in voltage, resulting in an overall gain in power density. When the operating pressure is set at 1, a rise in fuel utilization from 0.65 to 0.95 results in a non-linear relationship with power density. Initially, the power density experiences an increase, followed by a subsequent reduction. The power density attains its greatest value when the fuel utilization is around 0.88. The primary factor contributing to this occurrence is the substantial drop in fuel mass flow into the fuel compressor under specified circumstances, resulting from the rise in fuel utilization. When the fuel mass flow reaches a certain value, the increase in polarization loss dominates the change in battery voltage and causes the battery output power to decrease.

Figures 5b–5d shows the corresponding output efficiency, ecological objective function and ECOP of DA-SOFC with fuel utilization at different pressures. The results indicate that the performance index of the DA-SOFC has a positive correlation

with the fuel utilization, seen at both 1.5 atm and 2 atm pressures. When $U_f = 0.65$ and $p = 1.5$ atm, the output efficiency, ecological objective function and ecological coefficient of performance are 0.37, 0.15 and 2.14, respectively. When $U_f = 0.95$ and $p = 1.5$ atm, they are 0.43, 0.21 and 2.69, respectively, and the three finite time thermodynamic indexes are improved by 14.7%, 35.3% and 25.7%.

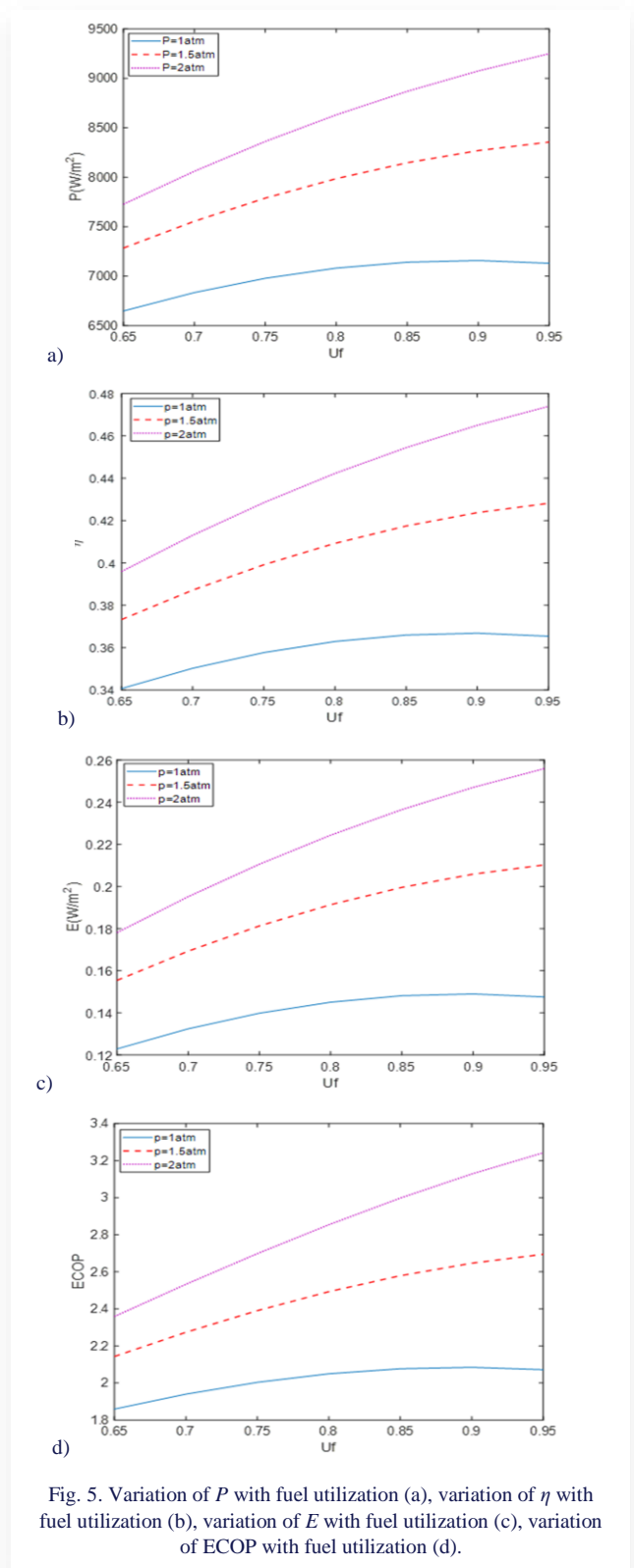


Fig. 5. Variation of P with fuel utilization (a), variation of η with fuel utilization (b), variation of E with fuel utilization (c), variation of ECOP with fuel utilization (d).

The ecological objective function increases with the increase in fuel utilization. This is mainly because an increase in fuel utilization increases the overall energy conversion efficiency of the fuel cell. Higher utilization means that more energy is efficiently converted from fuel to electricity, reducing energy waste, reducing entropy-generated power loss, and increasing the output power of the irreversible DA-SOFC. Therefore, the eco-objective function of the DA-SOFC increases as the operating pressure increases. In summary, under certain conditions, increasing the fuel utilization can improve the finite time thermodynamic performance of DA-SOFC.

Fuel utilization has an important impact on fuel cell performance. Higher fuel utilization means more efficient conversion of fuel into electricity, increasing the overall efficiency of the battery. By maximizing the use of available energy in the fuel, unnecessary waste of resources can be reduced, thereby improving the economy and sustainability of the system. High fuel utilization also helps reduce fuel costs, driving wider adoption of fuel cell technology in commercial and industrial applications. However, multiple aspects such as fuel supply, reaction kinetics, and system design need to be considered comprehensively to achieve optimal fuel utilization and maintain the long-term stability of the battery while improving efficiency. Therefore, in the development and optimization of fuel cell technology, maximizing fuel utilization is one of the key considerations to achieve efficient, economical and sustainable energy conversion.

3.4. Effect of electrolyte thickness on DA-SOFC performance

Figure 6 shows the effect of electrolyte thickness (σ_m) on the finite time thermodynamic index of DA-SOFC when the current density is 15000A/m^2 and the operating temperature is 1073K . As can be seen from Fig. 6(a), the power density and fuel cell performance significantly increase as the pressure increases and the electrolyte thickness decreases. When $P=1\text{atm}$ and the electrolyte thickness is $30\mu\text{m}$, the power density of DA-SOFC is 7141.4W/m^2 . When the electrolyte thickness is $90\mu\text{m}$, it is 1006.34W/m^2 , which is reduced 7 times. This is mainly because an electrolyte layer that is too thick will produce a large ohmic resistance, and the number and speed of ions in the electrolyte passing through the electrolyte will be reduced. The ohmic loss increases, and the internal resistance generated by the ohmic overpotential increases. Since the entropy production rate caused by ohmic resistance becomes larger, the power dissipation becomes larger, so the output power density becomes smaller.

Figures 6b-6d shows the output efficiency, ecological objective function and ECOP corresponding to DA-SOFC with electrolyte thickness at different pressures. When the electrolyte thickness increases, the three finite time thermodynamic indexes decrease significantly. As the electrolyte thickness increases, the power dissipation due to ohmic resistance becomes larger, the output efficiency becomes smaller, and the irreversible DA-SOFC ecological objective function becomes smaller. Increasing the thickness of the electrolyte, the irreversible losses become larger and thus the ecological coefficient of performance

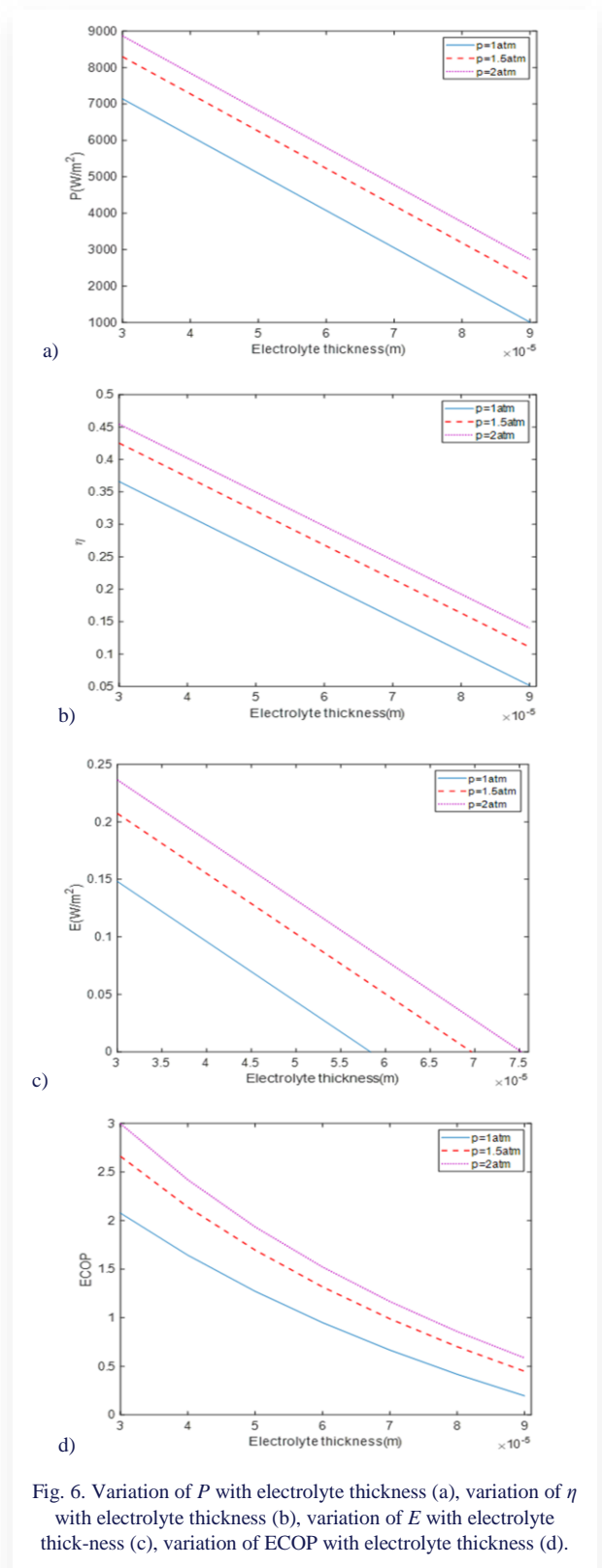


Fig. 6. Variation of P with electrolyte thickness (a), variation of η with electrolyte thickness (b), variation of E with electrolyte thickness (c), variation of ECOP with electrolyte thickness (d).

of the DA-SOFC decreases with increasing the thickness of the electrolyte.

Electrolyte thickness is a key design parameter in fuel cells and has a significant impact on cell performance. When the thickness of the electrolyte is too large, firstly, the resistance inside the battery also increases due to the increased ion transmission path. This will increase the resistance of current transmission in the electrolyte, reduce the overall conductivity of the bat-

tery, and thus affect the output power of the battery. Excessive electrolyte thickness may also lead to an increase in voltage drop between electrodes, thereby affecting battery efficiency. Secondly, an electrolyte that is too thick increases the path for gas diffusion, hindering the efficient transport of fuel and oxygen in the battery. This affects the battery's utilization efficiency of reactants and reduces the rate at which electrochemical reactions occur. As a result, the battery's response speed is slower, affecting its dynamic performance, which may be limited especially in applications that require fast response. Therefore, when designing fuel cells, the effects of electrolyte thickness on resistance and reaction rate need to be carefully balanced while considering improved stability and loss resistance to achieve optimal cell performance. This requires system engineers to make precise adjustments and optimizations based on specific application requirements when weighing these factors.

3.5. Effect of porosity on the performance of DA-SOFC

In addition to the operating parameters, the microstructure of the electrode also affects the performance of DA-SOFC. Figure 7 illustrates the impact of electrode porosity on the finite time thermodynamic index of DA-SOFC when the current density is 15 000 A/m² and the operating temperature is 1 073 K. As can be seen from Fig. 7a, the output power of DA-SOFC increases with the increase of porosity.

When the DA-SOFC operates in the low-current region, there is basically little change in the output power of the DA-SOFC as the porosity increases. Because the electrochemical reaction rate is slow at the beginning, the number of ions in the electrolyte is low and the operation speed is slow, so the impact of porosity on power density is minimal. As the electrochemical reaction proceeds, the effect on power density gradually becomes larger. The reason for this phenomenon is that the rise in porosity results in a corresponding rise in the diffusion coefficient. This increase in diffusion coefficient facilitates the movement of reactants towards the triple-phase boundary (TPB) located at the interface between the electrode and electrolyte. Additionally, it facilitates the outward transport of products from the TPB interface.

Figures 7b–7d shows the corresponding finite time thermodynamic indexes of the DA-SOFC with the change of current density at different porosities. When the current density is 15 000 A/m², the operating temperature is 1 073 K, and the porosity is increased from 0.4 to 0.8, the corresponding output efficiencies, ecological objective functions, and ecological coefficient of performance are increased by 8.3%, 16.9%, and 11.1%, respectively. Therefore, modifying the microstructure of the electrode may boost the efficiency of an irreversible DA-SOFC.

The porosity of fuel cell electrodes has an important impact on performance. Moderate porosity can improve gas diffusion and electron conduction, promote the effective transport of reactants in the electrode, and thus enhance the cell performance. Higher porosity helps to increase the passage of gases in the electrodes, providing more active surfaces and facilitating the catalytic reaction. However, too high a porosity may also lead to a loose electrode structure and reduce the effective electrode surface area, thereby affecting the rate of the reaction. In addition,

an increase in porosity may lead to a prolongation of the gas flow path and an increase in the gas diffusion resistance.

Therefore, when optimizing the fuel cell electrode porosity, factors such as gas diffusion, electron conduction and reaction rate need to be considered comprehensively to achieve the best cell performance.

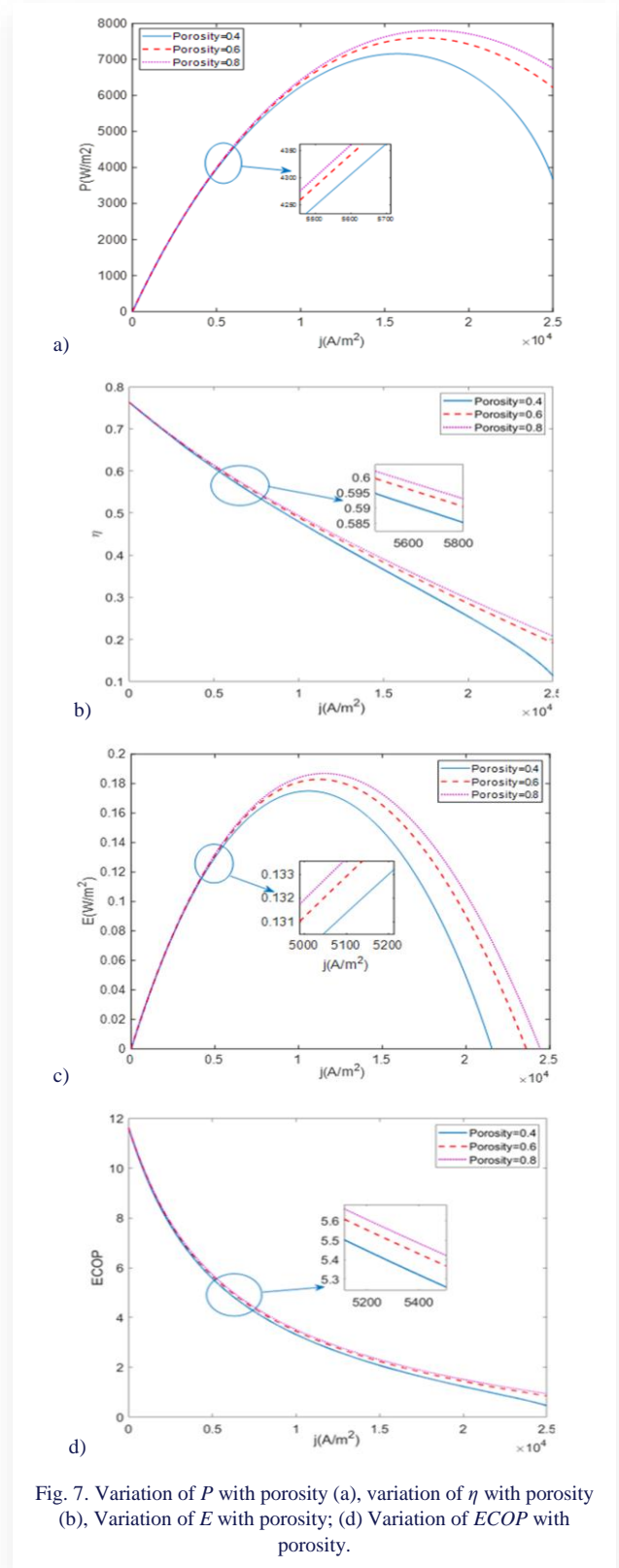


Fig. 7. Variation of P with porosity (a), variation of η with porosity (b), Variation of E with porosity; (d) Variation of $ECOP$ with porosity.

4. Conclusions

In this paper, a finite time thermodynamic model of DA-SOFC is developed after considering the effect of polarization loss. The effects of parameters such as operating temperature, operating pressure, fuel utilization, electrolyte thickness and electrode porosity on the finite time thermodynamic performance of DA-SOFC are investigated in detail.

When the current density of the irreversible DA-SOFC is 15 000 A/m², the output power density, output efficiency, ecological objective function and ECOP rise by 57.1%, 57.4%, 311% and 113%, respectively with the increase of operating temperature from 1 043 K to 1 103 K. When $p = 1$ atm (101.33 kPa), the power density first goes up and then decreases in the wake of fuel utilization. When the fuel utilization rate is about 0.88, the power density reaches the maximum value. Under certain conditions, improving fuel utilization can improve the finite time thermodynamic performance of DA-SOFC. When the electrolyte thickness increases from 30 μm to 90 μm , the power density decreases by nearly 7 times and it found that increasing the electrolyte thickness will reduce the finite time thermodynamic performance of DA-SOFC. The microstructure of the electrode also affects the performance of DA-SOFC. When the electrode porosity increases from 0.4 to 0.8, the corresponding output efficiency, ecological objective function and ecological coefficient of performance increase by 8.3%, 16.9% and 11.1% respectively.

Based on the finite time thermodynamic theory analysis, the finite time thermodynamic performance of DA-SOFC can be further improved when the operating temperature, operating pressure, the electrode porosity and fuel utilization increase and the thickness of the electrolyte decrease.

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