Model Analysis on Hydrogen Production by Hybrid system of SOEC and Solar Energy

Yuzheng Lu, Junjiao Li, Loembe Souamy, Jun Wang, Yaoming Zhang and Bin Zhu

***Abstract*— We investigate the Solid Oxide Electrolysis Cell (SOEC) can convert high temperature steam into H_2 and O_2 with high efficiency. The SOEC operating temperature is very close to the temperature of solar dish engine system which heats up the water to high temperature steam. We design an advanced the hydrogen production system utilizes solar energy as the only prime energy source in which the thermal energy is provided by solar dish thermal engine subsystem while the electrical energy is supplied by photovoltaic subsystem.**

Energy and exergy analysis have been conducted to investigate the thermodynamic–electrochemical characteristics of the hydrogen production by hybrid system of SOEC and solar energy. The effects of some important operating parameters, such as temperature, flow rate of H_2O and current density have been studied. It is found that an increase in temperature and decrease in operating voltage can reduce the exergy loss in the hybrid system.

The findings show that the difference between energy and exergy efficiency is small for the high temperature thermal energy input is only a small fraction of the total energy input. Numerical simulations are implemented for illustration and verification of the effectiveness of the solar energy.

***Index Terms*—hydrogen production, SOEC, solar energy, hybrid system, exergy analysis**

I. INTRODUCTION

Photovoltaic system directly converters sunlight into electricity. The basic of solar energy is the PV cell. The voltage and currents available at the terminals of a solar energy system may directly feed small loads such as lighting systems and DC motor. More sophisticated applications require electronic device converters to process the electricity from the solar energy. These converters perhaps used to regulate the voltage and current at the load, etc.

In order to study hydrogen production for solar energy, one first needs to know how to model of solar energy that is attached to the hybrid system, solid oxide electrolysis cell (SOEC) and exergy analysis. The mathematical model can be used in dynamic analysis of solar energy and hydrogen production system from solar energy, which can stimulate development of solar energy and related technologies.

One of these novel technologies is the solid oxide electrolysis cell (SOEC), which can convert H_2O into H_2 and O_2 in an environmentally friendly way with high efficiency [1]. According to the thermodynamics, energy demanded from electrolysis of water can be divided into electrical energy and thermal energy. It can be expressed as[2]:

$$\Delta H(T) = \Delta G(T) + T\Delta S(T) \qquad (1)$$

Where $\Delta H(T)$ is the enthalpy change of the reaction, $\Delta G(T)$ is the electrical energy demand and $T\Delta S(T)$ is the thermal energy demand [3]. The total energy demand for water and steam electrolysis is shown in Fig.1. It can be concluded that the electrical energy demand decreases with the increase of operating temperature.

To advance the knowledge and understanding of my research area, the high temperature contributes to the activity improvement of electrode. Hence, to justify my research solid oxide electrolysis cell (SOEC) generate further solar energy with the low-temperature electrolyze, high or intermediate temperature solid oxide steam electrolyze has more advantages for the fast electrochemical reactions.

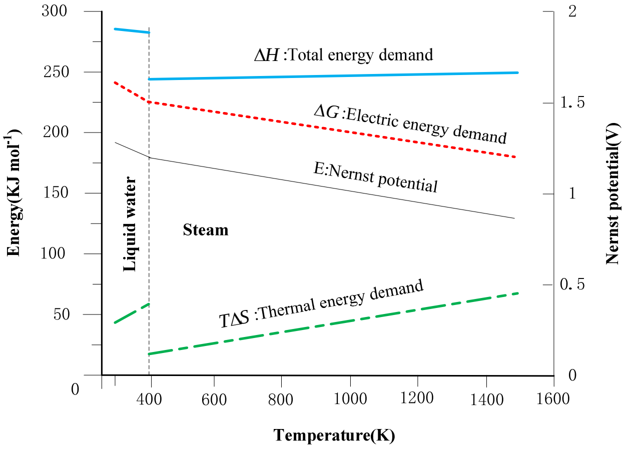

Fig.1 Energy demand for water and steam electrolysis

Electronic converter designers are usually interested in modeling PV cell, which are the main purpose, solar energy with the solid oxide electrolyze has been proposed for some years.

Arashi et al have shown the performance of the SOEC heated to 1000 ℃ by concentrating the solar energy. Electrochemical efficiency of the device was found up to 71% and the hydrogen production efficiency was also up to

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20-28% which is twice higher than that of electrolysis by photovoltaic [4]. In another approach, solar tower was used to heat the electrolyze to 700℃ by A.Houaijia[5].

The total solar energy was 4kW and the thermal efficiency of solar tower system was up to 40%. The efficiency from thermal energy to hydrogen can reach 26% which could go up to 38%. Rachid and Sofiane[6] took more attention to solid oxide electrolysis cell in which the electrical energy was taken from solar photovoltaic while the thermal energy from solar concentrating technology.J.padin and T.N.Veziroglu[7] introduced a new high-temperature steam hydrogen production system with hybrid receiver.

The hybrid (chaotic) receiver transformed solar energy into electricity and thermal energy simultaneously. According to their research results, its efficiency is higher than that of electrolysis at low temperature using photovoltaic technology. The efficiency of hybrid hydrogen production reached to 27% at 200℃, increase to 45% at 600℃, and 64% at 1000℃.

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II. Hybrid Hydrogen Production System Integrating Solar Thermal Engine and SOEC

Ni et al have given a detailed energy and exergy analysis of solid oxide electrolysis cell (SOEC) [8]. Our work in this area demonstrates that such that processes are under strict basic structure of SOEC comprises of solid oxide electrolysis cell, two heat exchangers and some other auxiliary equipments. In the present work, solar energy is utilized to provide the electrical and thermal energy. The hybrid system for hydrogen production is formed by integrating the solar dish engine, photovoltaic cell and solid oxide electrolysis cell, which is shown in Fig. 2. In our case, the total energy from solar radiation can be calculated as ignoring the inevitable losses;

$$Q_{solar} = Q_{pv} + Q_{dish} \tag{2}$$

Where Q_{solar} is the total solar radiation energy including all the energy received by photovoltaic cells Q_{pv} and solar dish engine Q_{dish} .

In this paper, the hydrogen production was achieved only using solar energy, which demonstrates a feasible approach method, the global energy crisis.

III. Thermodynamic Modeling for Hybrid Hydrogen Production

A. *Thermodynamic mode of solar energy*

The total energy from solar radiation Q_{solar} can be expressed in the form of Q_{dish} and Q_{pv}, given in Eq 2. Furthermore, Q_{dish} can be express as:

$$Q_{dish} \times \eta_t = Q_t = Q_{heat,SOEC} + Q_{heat,H_2O} \tag{3}$$

Where η_t is the conversion efficiency of solar dish thermal engine, which is related to the concentrator, receiver and heat transfer characteristics [9]; Q_t is the heat output of solar dish thermal engine, which can provide thermal energy for heating the solid oxide electrolysis cell($Q_{heat,SOEC}$) and the heat exchanger Ⅱ(Q_{heat,H_2O}) The electrical energy required for solid oxide electrolysis cell was offered by photovoltaic. The electricity obtained from photovoltaic cell can be calculated as:

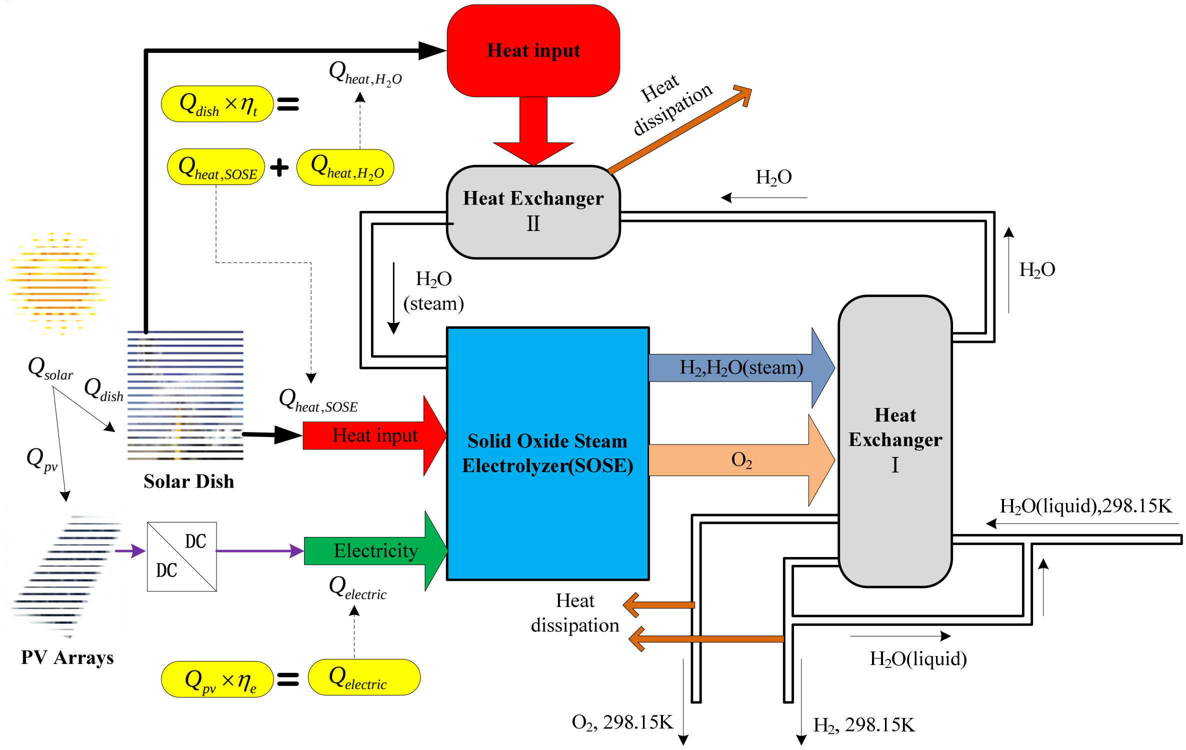

Fig.2 Solar hydrogen production via solid oxide electrolysis cell

$$P_e = \eta_e \times Q_{pv} \tag{4}$$

Where η_e is the photoelectric conversion efficiency of the photovoltaic cell which depends on the material used [10].

Exergy of solar radiation energy can be expressed as:

$$E_{X,solar} = \left[1 + \frac{1}{3}\left(\frac{T_0}{T_S}\right)^4 - \frac{4}{3}\frac{T_0}{T_S}\right] P_{solar} \tag{5}$$

Generated exergy after transforming photo to electricity/heat can be illustrated as:

$$E_{X,cs} = P_e + (1 - \frac{T_0}{T})Q_t \tag{6}$$

Where the T_0、T_S、T stand for the temperature of the reference environment, solar, and the solid oxide electrolysis cell, separately.

B. Thermodynamic mode of solid oxide electrolysis cell

According to the Nernst formula, equilibrium voltage of solid oxide electrolysis cell can be expressed as[11]:

$$E = E_0 + \frac{RT}{2F}\ln\left[\frac{P_{H_2}(P_{O_2})^{0.5}}{P_{H_2O}}\right] \tag{7}$$

Where R the ideal is gas constant; F is the Faraday constant; P_{H_2O} , P_{H_2} and P_{O_2} represent the partial pressures of respective gases at the electrode surface. E_0 is the standard potential which can be calculated in temperature range from 773K to 1773K using Eq 8; [12]:

$$E_0 = 1.253 - 2.4516 \times 10^{-4} T \tag{8}$$

However, practically speaking, the cell potential of SOEC is always higher. Than the SOEC of transition hydrogen production has been the main focus of many investigations. This is the equilibrium potential E_0 due to the central, role that hydrogen production play in various reactions (diffusion of reactants/products towards/from the electrode surface and bulk) ohmic resistance and charge transport.

Thus, the required voltage U in SOEC can be written:

$$U = E + \eta_{con,c} + \eta_{con,a} + \eta_{act,c} + \eta_{act,a} + \eta_{ohm} \tag{9}$$

Where $\eta_{con,c}$ and $\eta_{con,a}$ denote the concentration over potential of the cathode and the anode, respectively; $\eta_{act,a}$ and $\eta_{act,c}$ show the activation over potential of the anode and the cathode while η_{ohm} gives the contribution of the ohmic over potential of the electrolyte.

These over potentials cause entropy generation, which in turn results in heat production.

$$\sigma = 2F(\eta_{act,a} + \eta_{act,c} + \eta_{con,a} + \eta_{con,c} + \eta_{ohm}) \tag{10}$$

If $\sigma \geq T\Delta S$, then the heat generation due to over potentials is equaled or exceeds to the heat required for water electrolysis. Hence, the external heat is not needed for the reaction. Thus the following equation is established

$$Q_{heat,SOEC} = E_{heat,SOEC} = 0 \tag{11}$$

If $\sigma < T\Delta S$, the heat production is less than the heat requirement, then the external heat is required. The heat input to the cell can be expressed as:

$$Q_{heat,SOEC} = [T\Delta S(T) - \sigma]\dot{N}_{H_2O,reacted} = \frac{J}{2F}[T\Delta S(T) - \sigma] \tag{12}$$

$$\dot{N}_{H_2O,reacted} = \frac{J}{2F} \tag{13}$$

Where J the current density and F is the Faraday's constant.

The corresponding rate of exergy of heat input $E_{heat,SOEC}$ can be expressed as:

$$E_{heat,SOEC} = Q_{heat,SOEC}(1 - \frac{T_0}{T}) \tag{14}$$

Two counter-flow heat exchangers have been used in the solar-SOEC hybrid hydrogen production system. The heat exchanger Ⅰ is used to recycle the heat generated from the solid oxide electrolysis cell while the heat exchanger Ⅱ is employed to heat up water to the same temperature as of the SOEC cell. According to effective number of transfer units ($\varepsilon - NTU$) method the actual heat exchanger rate between two fluid streams can be calculated in [13]:

$$Q = \varepsilon Q_{\max} \tag{15}$$

Where ε is the effectiveness factor and $Q_{\max}$ is the theoretical maximum heat exchange rate between two fluids streams. The effective factor lies in the range of 0.8-0.9 for a counter-flow heat exchanger. Considering a conservative analysis, 0.8 is selected in this study. $Q_{\max}$ can be calculated according to the specific heat capacity of two fluid steams[5,14].

Neglecting contributions of the kinetic and potential exergies, the exergy of a substance can be gained by:

$$EX = E_{X,chem} + E_{X,phy} \tag{16}$$

Where $E_{X,chem}$ and $E_{X,phy}$ denote the chemical and the physical exergies, respectively. In addition, $E_{X,phy}$ can be calculated by[15]:

$$E_{X,phy} = (H - H_0) - T_0(S - S_0) \tag{17}$$

Where subscript 0 is the reference environment condition.

In a real system, losses are inevitable and the performance of the classical solid oxide electrolysis cell can be evaluated in terms of energy efficiency and exergy efficiency which are often termed as η_{en} and η_{ex} respectively. They can be defined as[8]:

$$\eta_{en} = \frac{LHV_{H_2} \times \dot{N}_{H_2,out}}{Q_{electric} + Q_{heat,SOEC} + Q_{heat,H_2O}} \tag{18}$$

$$\eta_{ex} = \frac{E_{H_2} \times \dot{N}_{H_2,out}}{E_{electric} + E_{heat,SOEC} + E_{heat,H_2O}} \tag{19}$$

where LHV_{H_2} is the lower heating value of H$_2$; $Q_{electric}$ is the rate of electrical energy input to the solid oxide electrolysis cell; $Q_{heat,SOEC}$ represents the rate of thermal energy input for solid oxide electrolysis cell;

Q_{heat,H_2O} stands for the rate of thermal energy input into the heat exchanger II for heating up the water; E_{H_2} is the exergy content of H_2; $E_{electric}$, $E_{heat,SOEC}$ and E_{heat,H_2O} are the corresponding rates of exergy input for the $Q_{electric}$, $Q_{heat,SOEC}$ and Q_{heat,H_2O}.

$\dot{N}_{H_2,out}$ is the outlet flow rate of H_2, which can be calculated as follow:

$$\dot{N}_{H_2,out} = \frac{J}{2F} = \dot{N}_{H_2O,reacted} \qquad (20)$$

Based on the above study, a new evaluation method for estimating hybrid hydrogen production system by integrating solar energy and SOEC is introduced [8,16]:

$$\eta'_{en} = \frac{LHV_{H_2} \times \dot{N}_{H_2,out}}{Q_{solar}} \qquad (21)$$

$$\eta'_{ex} = \frac{E_{X,H_2} \times \dot{N}_{H_2,out}}{E_{solar}} \qquad (22)$$

IV. MODEL ANALYSIS ON THE HYBRID HYDROGEN PRODUCTION SYSTEM

A. *Effects of temperature on SOEC system efficiencies*

Temperature is a key issue in the process of SOEC hydrogen production. The detail effects of temperature on the SOEC cell are shown in Fig. 3 to Fig.8. The concentration over potentials increase with the raise of temperature (Fig.5 and Fig.6). In contrast, the ohmic and activation overpertentials decrease with increasing temperature (Fig.7, Fig.3 and Fig.4). We find that the overdetail is mainly from the ohmic over potential as observed from Fig.3 to Fig.7. Although the effective diffusion coefficient increases while the temperature increases and the density of gas decreases. It is due to the ionic conductivity and electrode reactivity increase with a higher temperature. As the reductions in ohmic and activation over potentials are more significant than the increase in concentration over potential at high temperature, the over potentials are reduced when the temperature rises. Therefore, the SOEC cell potential decreased with an increasing temperature as shown in Fig.8.

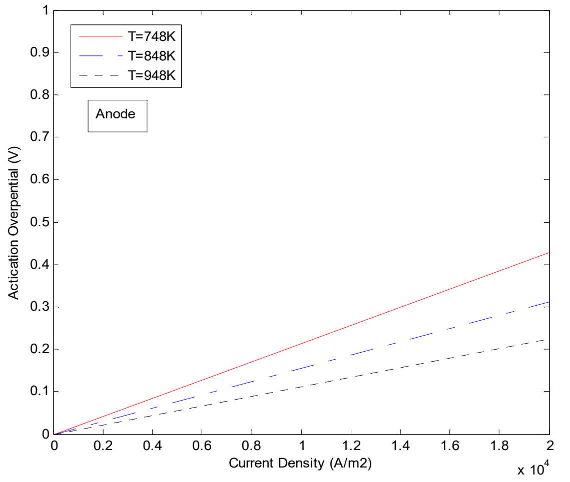

Fig.3 Effect of temperature on SOEC cell electrical performance: anode activation overpotential

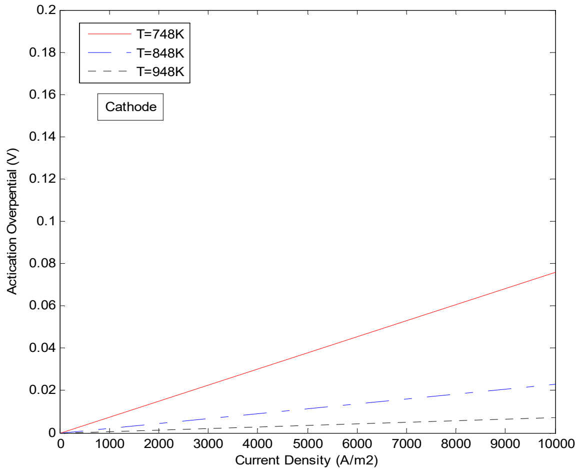

Fig.4 Effect of temperature on SOEC cell electrical performance: cathode activation over potential

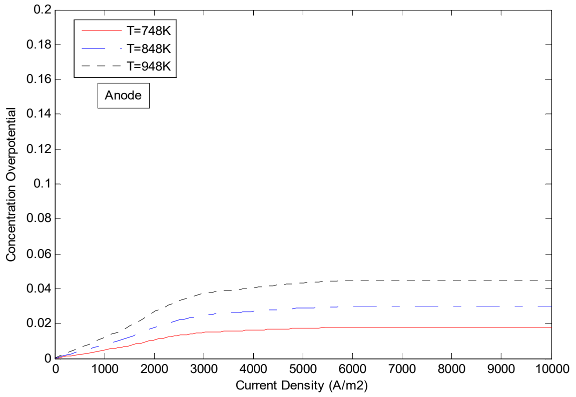

Fig.5 Effect of temperature on SOEC cell electrical performance: anode concentration overpotential

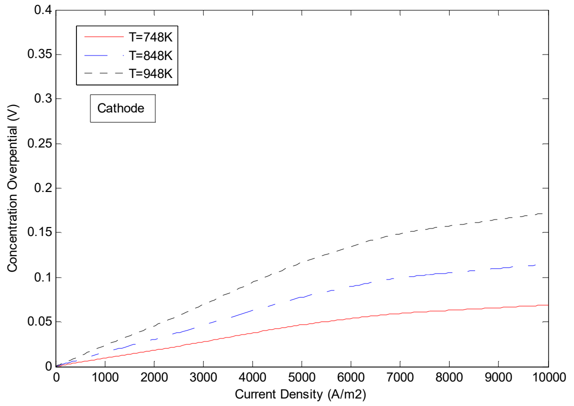

Fig.6 Effect of temperature on SOEC cell electrical performance: cathode concentration overpotential

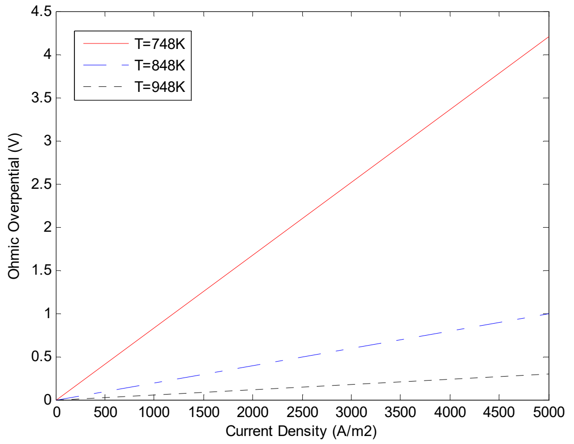

Fig.7 Effect of temperature on SOEC cell electrical performance: ohmic overpotential

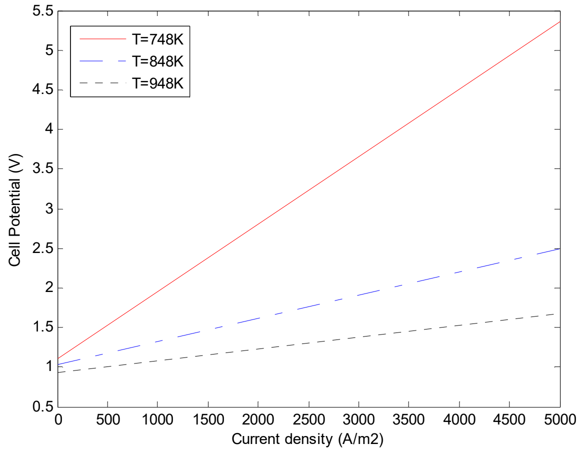

Fig.8 Effect of temperature on SOEC cell electrical performance: cell potential

The effect of cell temperature on the energy and exergy efficiency as a function of current density is graphically shown in Fig.9 and Fig. 10, respectively. Higher energy efficiency and exergy efficiency can be gained at high temperature than that at low temperature. Optimal energy efficiency and exergy efficiency occur when the current density is equal to about 1200A/m^2 at 773K. In the case of 873K, both energy efficiency and exergy efficiency increases slightly. At 973K, both energy efficiency and exergy efficiency increase significantly for low current density and increase steadily when the current density exceeds 1500A/m^2. From the Fig.3 and Fig. 4, it can be concluded that temperature has little effect on the energy and exergy efficiencies. This situation arises due to the fact that the thermal energy input is relatively more important than the electrical energy input. Moreover, the cells over potentials are small for low current density and do not differ appreciably for different temperatures of electrolysis. However, for high current density, the electrical energy input becomes more important, thus, the electrical over potentials are the dominating factors governing the energy and exergy efficiencies. As the overall over potentials decrease with increasing operation temperature, the energy and exergy efficiencies increase with increasing operation temperature for high current density. Consequently, a higher operating temperature is more effective to achieve high energy and exergy efficiencies at high current density [17].The differences between energy and exergy efficiencies are small for the reason that the high quality thermal energy contains much more exergy at high temperature. In addition, thermal energy is only a small fraction of the total energy involved. This result is same with Ni's study [11]. The present study indicates that the high quality waste heat from the SOSE cell is very valuable and should be recovered to achieve high efficiency.

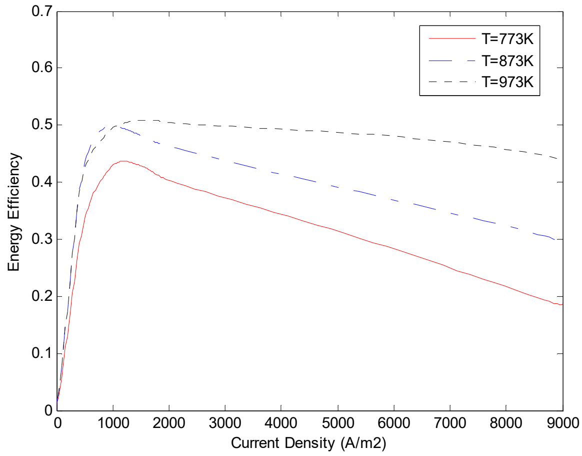

Fig.9 Energy efficiency as functions of temperature and current density

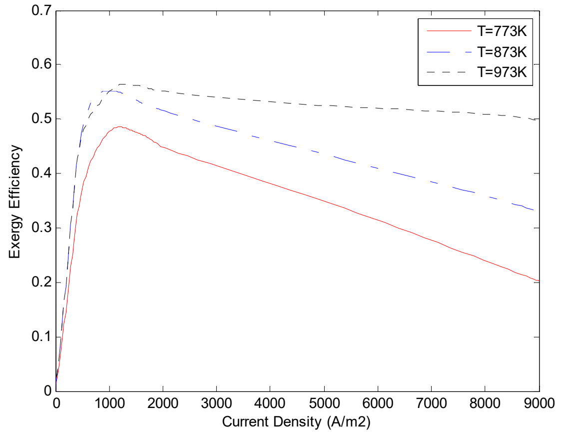

Fig. 10 Exergy efficiency as functions of temperature and current density

B. *Effects of H_2O flow rate on SOEC system efficiencies*

According to the experiment from Hino[18] and simulation study from Ni[8], the H_2O flow rate value of 0.5 mol/s is adopted as typical value in this simulation. Additionally, the value of 0.1 and 0.01 are also investigated to observe the effects of water flow rate on SOEC system efficiencies.

The effects of flow rate of H_2O on the efficiencies of the SOEC system are shown in Fig. 11 and 12. It can be seen that both energy and exergy efficiencies are decreasing while flow rate of H_2O increases. In the case of the low H_2O flow rate of 0.01 mol/s, both energy and exergy efficiencies are very sensitive to current density. This is due to the conversion molar fraction of H_2O reaches 100% at a low current density. From Fig. 11, it can be concluded that further increase in current density cannot be reached due to water is depleted. Different from the case of the low value, optimal current density are found at high value of 0.05 and 0.1mol/s. Therefore, the maximum of energy and exergy efficiencies are also appeared here.

Although both energy and exergy efficiencies are higher in high value than low value of H_2O flow rate, from the view of practical applications, low flow rate is not recommended in SOEC plant. With increasing in the flow rate of water and the range of current density, the thermal energy is the dominant energy input. As a result; the optimal current density has a positive relationship with the flow rate of water. Due to the occurrence of limiting current density at the cathode, the 100% conversion of water cannot be achieved at the flow rate of 0.1mol/s. Both of the water flow rate and current density are important parameters which should be regulated properly to achieve the optimal efficiency in practical applications.

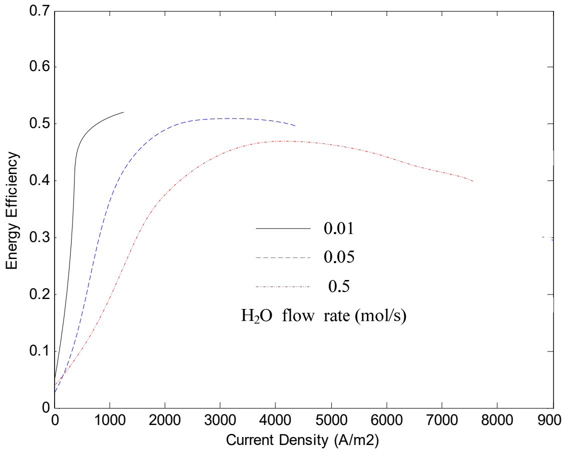

Fig.11 Energy efficiency as functions of flow rate of H_2O and current density

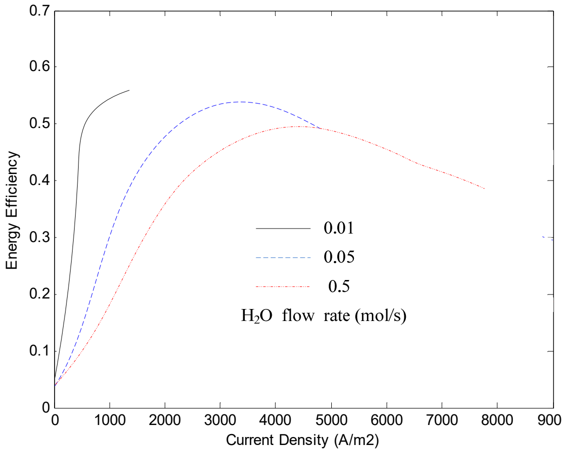

Fig.12 Exergy efficiency as functions of flow rate of H_2O and current density

C. *Case study on the hybrid hydrogen production system*

Assuming the reference spectra of solar radiation, AM1.5; the sunlight intensity is 1000W/m^2, the total solar radiation energy is 694.6kW; the photovoltaic efficiency is 15% while the solar dish engine collector efficiency is 55% and the operating temperature of solid oxide electrolysis cell is 948K. The exergy efficiency of photo energy-electrical energy/thermal energy is up to 25.7% in our solar hybrid system. Furthermore, the energy and exergy efficiencies have gone to 15.1% and 16.3% respectively by using the hybrid hydrogen production integrating solar energy and solid oxide electrolysis cell system. This energy efficiency is higher than that of using photovoltaic technology to electrolyze water at low temperature having efficiency only 9.3% [19].

V. CONCLUSIONS

Based on The conversion efficiency of photovoltaic power generation is low cost and high efficiency which applied to the great energy and exergy loss of the system. Moreover, the energy and exergy losses of the solar dish thermal engine system are relatively large.

The designed for high current density, the electrical energy input becomes very important and the electrical over potentials are the dominating factors governing the energy and exergy efficiencies, a scheme of approach is effective and has low hybrid system.

Compared with the existing, as the overall over potentials decrease with increasing operation temperature, the energy and exergy efficiencies increase with the increase of operation temperature at high current density. Consequently, high operating temperature is more effective to achieve high energy and exergy efficiencies at high current density

It is expected that the reported results will positively affect the development of advanced solid oxide electrolysis cells.

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