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Short Communication

Performance Multiple Objective Optimization of Irreversible Direct Carbon Fuel Cell/Stirling Thermo-Mechanical Coupling System

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Modern Stirling engine has been paid more and more attention because of its wide adaptability of various energy sources and excellent environmental characteristics. In this paper, Stirling engine is selected as the secondary energy device of direct carbon fuel cell to construct a new coupling system. Through electrochemical and thermodynamic derivation, the performance expression of coupling system is obtained. The results show that the performance of the coupling system is positively correlated with the working temperature. At the same time, a multi-objective function is introduced to give the corresponding working interval according to the engineers' different preferences for the power output and efficiency.

Keywords: irreversible Stirling engine; Direct carbon fuel cell coupling system; Performance study, multiple objective optimization

1. INTRODUCTION

With the increasingly severe situation of global energy, environment and climate, the research, development and utilization of renewable green energy, such as solar energy, geothermal energy and biomass energy, has been paid more and more attention. However, under the background of high cost of new energy utilization and no large-scale application, conventional energy represented by coal still plays a pivotal role with its mature technology and low development cost. China is the world's largest coal producer. Over the past 40 years of reform and opening up, China's coal industry has made historic strides in keeping with the trend of The Times. China's coal output increased from 620 million tons in 1978 to 1.384 billion tons in 2000 and 3.68 billion tons in 2018, producing 77.3 billion tons of coal in total [1]. The reserves of identified coal resources in China increased from 596 million tons in 1978 to

167 trillion tons in 2017 [1]. Faced with such a large amount of coal reserves, the development of clean coal use technology has become the top priority of sustainable development of China's coal energy.

Direct carbon fuel cell (DCFC) is named for its ability to directly use solid carbon as fuel. Compared with traditional coal-fired power generation, DCFC does not require gasification or mobile fuel, but can convert the energy stored in solid carbon into electricity through a series of electrochemical oxidation reactions. The energy efficiency of direct carbon fuel cells is about two to three times that of traditional coal-fired power generation, and the CO_2 released per unit of power generation is only 50% of that of coal-fired power generation [2-5].Therefore, direct carbon fuel cells have great advantages and potential in the clean and efficient use of coal to generate electricity and alleviate energy shortage. At the same time, how to better improve the performance of direct carbon fuel cells has always been one of the most concerned issues for scientific researchers.

Due to the large amount of high-quality waste heat generated by the fuel cell during its operation, many researches [6-10] focus on how to utilize this part of energy. Many thermodynamic devices can be used as subordinate energy devices of fuel cells, such as vacuum thermionic generator [6], thermoelectric generator [7], thermal photovoltaic cell [8], Brayton engine [9], Stirling engine [10] and so on. In this paper, an irreversible Stirling engine is coupled with a direct carbon fuel cell in a similar way, and the waste heat generated in the working process of a direct carbon fuel cell is used to drive the Stirling engine, so as to improve the overall performance. The analytical expression of coupling system performance is deduced, and the performance boundary of coupling system is given by numerical calculation, which provides theoretical guidance for practical engineering application.

2. PERFORMANCE EXPRESSION OF COUPLED SYSTEM

Direct carbon fuel cells do not need to gasify fuel and can directly convert energy from solid carbon into electricity and heat. It is mainly composed of electron conductive cathode layer and anode layer, and ionic conductive electrolyte three parts. According to different electrolytes, direct carbon fuel cells can be divided into four basic types: (1) DCFC with molten alkali metal hydroxide as electrolyte; (2) DCFC with molten carbonate as electrolyte; (3) DCFC with molten carbonate (or liquid metal oxide) and solid oxide double electrolyte; (4) only solid oxide is used as electrolyte, i.e. direct carbon solid oxide fuel cell. The model adopted in this paper takes the molten Li₂CO₃/K₂CO₃ mixture as electrolyte, and the mixing molar ratio is 32:68. The whole electrochemical reaction process can be summarized as $C + O_2 \rightarrow CO_2$ + electrical energy + thermal energy. As described in the literature [11], because of the existence of a potential direct carbon fuel cell is always smaller than the open circuit voltage output voltage $E = -\frac{4g^0(T)}{n_eF} + \frac{RT}{n_eF} \ln \left[\frac{p_{O_2,cat}(p_{CO_2,cal})^2}{p_{CO_2,an}} \right]$, where $\Delta g^0(T)$ is the gibbs free energy change under normal atmospheric pressure, n_e is the electron number needed to transfer per mole charcoal, F is Faraday constant, R is gas constant, T is the operating temperature, subscript an and cat represent anode and cathode, p_x represents partial pressure of x substance, $V_{act} \setminus V_{ohm}$ and V_{con} represent activation overpotential, ohmic overpotential and concentration overpotential, respectively. Considering the

existence of overpotential, the analytic expressions of direct carbon fuel cell output voltage V, efficiency η_{cell} and the output power P_{cell} are as follow:

$$V = E - V_{\text{act,an}} - V_{\text{act,cat}} - V_{\text{ohm}} - V_{\text{con}}$$
(1)

$$P_{\text{cell}} = JA \left(E - V_{\text{act,an}} - V_{\text{act,cat}} - V_{\text{ohm}} - V_{\text{con}} \right)$$
(2)

$$\eta_{\text{cell}} = \frac{P_{\text{cell}}}{-\Delta \dot{H}} = -\frac{n_e F}{\Delta h} \left(E - V_{\text{act,an}} - V_{\text{act,cat}} - V_{\text{ohm}} - V_{\text{con}} \right)$$
(3)

where $-\Delta \dot{H}$ is the total energy output per unit time, Δh is molar enthalpy change, J is the operating current density and A is area.

When a direct carbon fuel cell is in operation, a lot of high-quality waste heat is generated. Some of this part of heat is released directly into the environment as heat leaks, and some is lost in the process of reheating. The rest part can be used by coupling a subordinate energy device. Regenerative device in the role of coupling system is preheating reactants, which can increase the temperature of reactants from the room temperature to reaction temperature. Many studies have shown that this part of the loss usually accounted for only $1\% \sim 2\%$ of the heat generated by the direct carbon fuel cell [12-14]. Therefore, this part of the loss can be neglected, and the heat flow rate to the subordinate energy device is

$$q_{\rm h} = -\Delta \dot{H} - P_{\rm cell} - \dot{Q}_{\rm loss} = -\Delta \dot{H} - P_{\rm cell} - \alpha A_{\rm l} (T - T_0) \tag{4}$$

 \dot{Q}_{loss} denotes heat leakage in direct carbon fuel cell in unit time, α is convection heat leakage coefficient, A_1 is effective heat exchange area and T_0 is ambient temperature.

Through a series of electrochemical derivations, for a given q_h , the maximum efficiency and the power of Stirling engine [15] can be expressed as:

$$\eta_{\text{engine}} = \frac{(m_1 - 1)T - m_1 T_0 + [J(1 - \eta_{\text{cell}}) - m_3(T - T_0)] + T_e}{2m_1 T + m_1 \{(m_1 - 1)T - m_1 T_0 + [Jm_2(1 - \eta_{\text{cell}}) - m_3(T - T_0)] + T_e\}}$$
(5)

$$P_{\text{engine}} = K[JAm_2(1 - \eta_{\text{cell}}) - m_3(T - T_0)] \times \eta_{\text{engine}}$$
(6)

where $m_1 = xC/[R \ln(V_2/V_1)]$ is the irreversibility of heat transfer, V_1 and V_2 are volume of Stirling heat engine in the two volume constant volume process respectively, *C* is the thermal heat capacity, $m_2 = -\frac{A}{n_e F K} \Delta h$ is the irreversibility associated with the system structure, $m_3 = \frac{\alpha A_1}{K}$ is the irreversibility of direct carbon fuel cell and the environment of heat transfer, $K = \frac{k_1}{(1+b)(1+\sqrt{k_1/k_2})^2}$, b is the time ratio of the reheating part in the isothermal branch; k_1 and k_2 are the thermal conductivity between the working material and the heat source at temperature *T* and T_0 , respectively.

The total energy of the whole coupling system during operation is the enthalpy change of the electrochemical reaction. The performance expression of the direct carbon fuel cell-Stirling thermomechanical coupling system can be obtained from the equations (2), (3), (5) and (6) :

$$\eta_{\text{hybrid}} = \eta_{\text{cell}} + \left[1 - \eta_{\text{cell}} + \frac{m_3}{Jm_2} \left(\frac{T}{T_0} - 1\right)\right] \eta_{\text{engine}}$$
(7)
$$P_{\text{hybrid}} = \left(-JT_0 m_1 m_2\right) \times \left\{\eta_{\text{cell}} + \left[1 - \eta_{\text{cell}} + \frac{m_3}{Jm_2} \left(\frac{T}{T_0} - 1\right)\right] \eta_{\text{engine}}\right\}$$
(8)
For a subscription (7) where the set $\left[1 - \eta_{\text{cell}} + \frac{m_3}{Jm_2} \left(\frac{T}{T_0} - 1\right)\right] \eta_{\text{engine}}$ (8)

From equation (7), the value of $\left[1 - \eta_{\text{cell}} + \frac{m_3}{Jm_2} \left(\frac{T}{T_0} - 1\right)\right] \eta_{\text{engine}}$ must be positive, so the efficiency of the coupling system must be greater than the single direct carbon fuel cell efficiency.

Similarly, a similar conclusion can be drawn from equation (8) : the power of the coupled system is higher than that of a single direct carbon fuel cell. It can also be known from equations (7) and (8) that the performance of the coupling system directly depends on the irreversibility of the direct carbon fuel

cell itself and various irreversibilities generated in the process of heat transfer from the direct carbon fuel cell to Stirling engine. Figure 1 shows the three-dimensional curve of the efficiency of the coupling system changing with the working current density and temperature, and figure 2 shows the three-dimensional curve of the output power of the coupling system changing with the working current density and temperature.



Figure 1. three-dimensional curve of the efficiency of the coupling system changing with the working current density and temperature



Figure 2. the three-dimensional curve of the output power of the coupling system changing with the working current density and temperature.

It can be seen from figure 1 and figure 2 that the efficiency and power of the system increase with the rise of temperature. It can be seen that the higher the temperature is, the better the performance of the system. Meanwhile, when the derivative of power function and efficiency is set to 0, the corresponding working current density can be found when the power and efficiency reach the extreme

value respectively. The working current density corresponding to the power extremum is not the same as that corresponding to the efficiency extremum.

3. MULTIPLE OBJECTIVE OPTIMIZATION OF THE COUPLING SYSTEM

In order to better describe the different preferences of engineers on power and efficiency in practical engineering practice, a new multi-objective function is introduced:

$$Z = \eta \times P^{\lambda} \tag{9}$$

where λ is the weighting factor, it represents the degree of preference for the power of the engineers, its scope is $[0,\infty)$. When $\lambda = 0$, means the engineers do not care the power output, only expect with maximum efficiency, corresponding to the point $D_{\lambda=\infty}$ in figure 3, and the maximum efficiency η_{max} will be achieved; when $\lambda = \infty$, shows that the engineers only care about the power output, without considering how much of the efficiency, the corresponding point is $D_{\lambda=\infty}$ in figure 3, the power density reached its maximum P_{max}^* ; when $\lambda = 1$, on behalf of the engineers of power and efficiency preference is the same. The power output density and efficiency are P_1^* and η_1 respectively, corresponding to the point $D_{\lambda=1}$ in figure 3. The interval $[D_{\lambda=0}, D_{\lambda=1})$ represents the efficiency preference choice; and interval $(D_{\lambda=1}, D_{\lambda=\infty}]$ represents a power output preference selection.



Figure 3 Curve of the efficiency versus the power density

Figure 4 shows the relation curve of power, efficiency and Z^* as the current density changes, where $Z^* = Z/A$, Z_1^* presents the value of Z^* when $\lambda = 1$. As can be seen from the figure, when the current density is $J_{Z_{1,max}^*}$, the optimal value of Z_1^* will be obtained. Therefore, when the engineer give the same emphasis to power output and efficiency, the working current of the direct carbon fuel cell

should be set as $J_{Z_{1,max}^*}$, meanwhile, the corresponding value of the efficiency and power can be presented respectively as $\eta_{Z_{1,max}^*}$ and $P_{Z_{1,max}^*}^*$.



Figure 4. The curves of the efficiency, power density, and Z^* varying with the current density.

4. CONCLUSIONS

In this paper, a new irreversible direct carbon fuel cells/stirling thermo-engine coupling system is constructed, in which the irreversible Stirling thermo-engine can utilize the high quality waste heat generated in the working process of direct carbon fuel cell to achieve the purpose of waste heat recovery and improving the overall working performance. Through electrochemical and thermodynamic methods, the analytical expression of the performance of the coupled system of irreversible direct carbon fuel cell and Stirling thermal engine is derived, and it is known that the performance of the coupled system is a monotonic function of temperature, the higher the temperature, the better the performance of the coupled system. In addition, multi-objective function is introduced to realize different preferences of engineers on power and efficiency, which can provide theoretical guidance for practical engineering applications.

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