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An efficient hybrid system using a thermionic generator to harvest waste heat from a reforming molten carbonate fuel cell



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ABSTRACT

A new hybrid system consisting of an internal reforming molten carbonate fuel cell (IR-MCFC) and a vacuum thermionic generator (TIG) is constructed. By considering the main irreversible losses in two subsystems and the coupling process, general expressions for the power output and efficiency of the hybrid system are derived. The performance characteristics of the hybrid system are revealed, and the optimal regions, including the power output, efficiency, and load resistances, are determined. It is found that the maximum power output density of the IR-MCFC/TIG system increases by 22% compared to that of a single MCFC, and among the IR-MCFC- and MCFC-based hybrid systems reported in the literature, the present hybrid system can most efficiently harvest the waste heat from the MCFC.

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1. Introduction

Fuel cells represent a class of efficient energy converting systems that directly turn chemical energy into electricity [1,2]. To date, various types of fuel cells have been proposed, investigated, and constructed [3–6]. Among them, the molten carbonate fuel cell (MCFC), developed in the 1950s, is one of the most promising fuel cells because of its stationary power output and high efficiency [7,8]. Many comprehensive studies have been performed in both theory and experiment [9–14].

Currently, much attention has been paid to reducing the costs of MCFCs and improving the efficiency of MCFCs [15–17]. Traditional fuel cells fueled by H_2 have the difficulties of hydrogen production, preservation, and transportation. By applying internal [18–23] or external reforming technology [24,25], the MCFCs, working at high temperatures of nearly 600–800 °C, can directly utilize other inexpensive and resourceful gases as fuel, such as natural gas, biogas, landfill gas, and methane [26–31]. This is an attractive business prospect. Moreover, the recovery of the waste heat produced by MCFCs is another significant issue in the investigation of the performance of fuel cells. Coupling MCFCs with different thermodynamic systems, such as gas turbines [32–37] and heat engines [38–42], has been intensively discussed, but the complex structure

and low efficiency of these systems may limit their actual use. In comparison, as one type of high-temperature solid state generator, the vacuum thermionic generator uses electrons as the working substance and has advantages that include no mechanically moving parts, a small device size, and high power density [43–46], and it may be a better device for using the waste heat from MCFCs.

In the present paper, we establish a new hybrid model composed of an IR-MCFC and a vacuum TIG. Some irreversible losses in the hybrid system are considered. The expressions of the power outputs and efficiencies for the two subsystems and hybrid system are analytically derived. According to the first law of thermodynamics, an important energy equilibrium equation between the two subsystems is obtained. The graphs of the power output, efficiency, and load resistances, varying with different parameters, are generated. The performance characteristics of the IR-MCFC/TIG hybrid system are revealed, and the optimal regions of some important parameters are determined. The results obtained here are compared with those of other IR-MCFC- or MCFC-based hybrid systems reported in the literature.

2. The hybrid system consisting of an IR-MCFC and a TIG

Fig. 1 shows the hybrid system composed of an IR-MCFC and a vacuum TIG, where P_f and P_t are, respectively, the power outputs of the MCFC and the TIG; q_r is the reforming energy; q_t is the heat loss from the MCFC to the environment; q_c is the heat absorbed by the cathode of the TIG; and q_a is the heat released by the anode of the

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Nomenclature A_0 Richardson-Dushmann constant (A m⁻² K⁻²) T_a anode temperature of the TIG (K) molar heat capacity of component k at constant presvoltage of the MCFC (V) $C_{p,k}$ sure $(J \text{ mol}^{-1} \text{ K}^{-1})$ U_0 ideal equilibrium potential (V) unit charge (C) U_{ohm} ohm overpotential (V) ρ activation energy ($I \text{ mol}^{-1}$) voltage of the TIG (V) E_{act} ideal standard potential (V) optimal voltage of the TIG (V) E_0 Faraday constant ($C \text{ mol}^{-1}$) F molar Gibbs energy change (J mol⁻¹) Δg Greek symbols molar enthalpy change (J mol⁻¹) Λh molar fraction of methane χ_{CH_4} ΔĤ enthalpy change rate (W) thermal emissivity current density of the TIG (A m⁻²) Stefen-Boltzmann constant (W m⁻² K⁻⁴) σ current density of the MCFC (A m^{-2}) heat loss ratio in reforming process δ_r cut-off current density (A m⁻²) heat conductivity coefficient (W m^{-2} K $^{-1}$) j_{co} к start-work current density (A m⁻²) Ĵst n area ratio k_1 anode work function of the TIG (eV) Φ_a Boltzmann constant ($J K^{-1}$) k_B molar latent heat of H₂O (J mol⁻¹) L_m Subscripts number of electrons n_e anode \dot{n}_f molar rate of fuel flowing (mol s⁻¹) cathode c hydrogen expended rate (mol s⁻¹) \dot{n}_H **MCFC** partial pressure of constituent α (atm) p_{α} heat loss power output (W) m maximum power output density P* power output density (W m⁻²) S hybrid system heat released by the TIG anode (W) q_a TIG t heat absorbed by the TIG cathode (W) q_c 1, 2 two states of $P_s^* = P_{fm}^*$ heat loss rate (W) q_l reforming energy rate (W) q_r **Abbreviations** waste heat rate (W) q_w molten carbonate fuel cell **MCFC** load resistance (Ω) TIG thermionic generator universal gas constant ($I \text{ mol}^{-1} \text{ K}^{-1}$) R GT gas turbine R_0 reforming energy of methane per mole (I mol⁻¹) IR internal reforming S surface area (m²) SCO₂ supercritical CO₂ working temperature of the MCFC (K) Τ environment temperature (K) T_0

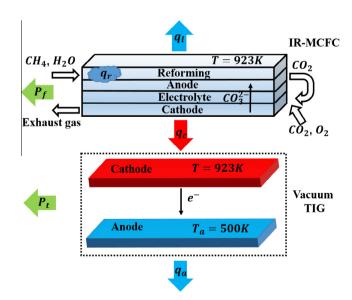


Fig. 1. The schematic diagram of the hybrid system composed of an internal reforming molten carbonate fuel cell and a vacuum thermionic generator.

TIG. Identical TIGs can be set in both the top and bottom sides of the MCFC. For simplicity, we only draw one equivalent TIG, shown in Fig. 1.

2.1. Model description of an IR-MCFC

The IR-MCFC shown in Fig. 1 has no extra supply heat for reforming a reaction and no extra structure for reforming product transportation. During the reforming process, pure methane and steam are utilized as the fuel. The two main reforming reactions are the steam/methane reforming reaction (SMR): CH₄+ $H_2O \leftrightarrow CO + 3H_2$ and the water–gas shift reaction (WGS): CO+ $H_2O \leftrightarrow CO_2 + H_2$ [19,23,31]. The overall reforming reaction is written as

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2. \tag{1}$$

In reality, the fuel utilization and the chemical reactivity in the internal reforming process are incomplete and depend on the size of the fuel cell stack, operating conditions, catalyst activity, etc. Such some incompleteness will reduce the performance of the IR-MCFC system [18,19,47,48]. In the present model, the effect of the fuel utilization and the incomplete chemical reactions on the system performance will be not discussed quantitatively. The methane is assumed to be completely used because we mainly focus on the recovery of the waste heat. Thus, the extra heat provided by the MCFC during the reforming process can be calculated by

$$\begin{split} q_{r} &= \dot{n}_{f} \chi_{\text{CH}_{4}} \left\{ 4 \left[\Delta h_{f}^{0}(\text{H}_{2}) + \int_{T_{0}}^{T} C_{p,\text{H}_{2}} d\tau \right] + \left[\Delta h_{f}^{0}(\text{CO}_{2}) + \int_{T_{0}}^{T} C_{p,\text{CO}_{2}} d\tau \right] \right. \\ &\left. - \left[\Delta h_{f}^{0}(\text{CH}_{4}) + \int_{T_{0}}^{T} C_{p,\text{CH}_{4}} d\tau \right] - 2 \left[\Delta h_{f}^{0}(\text{H}_{2}\text{O}) + L_{m} + \int_{T_{0}}^{T} C_{p,\text{H}_{2}\text{O}} d\tau \right] \right\}, \end{split} \tag{2}$$

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