Chemical Engineering Journal 138 (2008) 436–441

Chemical Engineering Journal

www.elsevier.com/locate/cej

Performance analysis of methanol-fueled solid oxide fuel cell system incorporated with palladium membrane reactor

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Received 3 January 2007; received in revised form 8 June 2007; accepted 25 June 2007

Abstract

The paper presents preliminary results from the performance analysis of a methanol-fueled solid oxide fuel cell (SOFC) system incorporated with a palladium membrane reactor. A conventional SOFC system comprises major components of preheaters, a reformer, an SOFC unit and a burner. The performance of the SOFC unit was dependent on operating current density, fuel utilization and temperature. When the conventional reformer is replaced by a palladium membrane reactor, pure hydrogen is extracted from the reformed gas and fed to the anode of the SOFC unit. It was demonstrated that the incorporation of the palladium membrane reactor to the SOFC system could improve the performance of the SOFC unit. When the membrane reactor is operated at a hydrogen recovery of 90%, the maximum power density is about 12.6% higher than that from the system with the conventional reformer. The performance comparison between the two SOFC systems which provide the same net electrical efficiency indicates that the SOFC system with the membrane reactor requires a smaller SOFC stack than the conventional SOFC system; however, the former requires an extra cost on palladium membranes and extra electrical power for operating the compressor for the membrane reactor. The preliminary economic analysis reveals that the implementation of the membrane reactor to the SOFC system is not cost-effective due to high cost of palladium membranes. Finally it was indicated that the use of the palladium membrane reactor in the SOFC system is still technically attractive even when an SOFC cell with lower resistance can be further developed.

Keywords: Solid oxide fuel cell; Palladium membrane reactor; Performance analysis

1. Introduction

Fuel cell is considered as an efficient electrical power generator compared to conventional heat engines, steam and gas turbine, and combined cycles. Among the various types of fuel cell, solid oxide fuel cell (SOFC) has attracted considerable interest as it offers wide application ranges, flexibility in the choice of fuel, high system efficiency and possibility of operation with an internal reformer. Hydrogen is a main fuel for most type of fuel cells. Nevertheless, other fuels such as methane, methanol, ethanol, gasoline and oil derivatives can also be used when a reformer is included in a fuel cell system for converting the fuel to hydrogen. A thermodynamic analysis was carried out to evaluate the performances of SOFCs fuelled by different fuels; that is, methane, methanol, ethanol and gasoline. The results obtained in terms of electromotive force and efficiency indicate that ethanol and methanol are very promising alternatives to hydrogen [1]. However, methanol is a preferable choice with respect to its availability, high energy density and ready storage and distribution [2,3].

A number of research efforts have been carried out on advanced SOFC operations such as development of intermediate temperature-SOFCs [4] and integration of SOFCs with intercool gas turbine [5]. Some researchers attempted to improve the performance of SOFC systems by focusing on the different integration modes of a reformer and an SOFC unit (i.e., external reforming, indirect internal reforming and direct internal reforming) [4]. Because it has been demonstrated that hydrogen

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doi:10.1016/j.cej.2007.06.021

Nomenclature

a	Constant in Eq. (8) (Ω m)
A	Area (m^2)
b	Constant in Eq. (8) (K)
$E_{A,pol}$	Activation energy involved in activation loss (kJ mol^{-1})
E_D	Activation energy for diffusion through membrane (kJ mol^{-1})
E_0	Open circuit voltage (V)
f	Volumetric flow rate of permeated hydrogen (m^3 s^{-1})
F	Faraday constant (C mol^{-1})
i	Current density (A cm^{-2})
n_i	Number of moles of component i (mol)
N_{H_2}	Permeation flux of hydrogen through membrane (mol m^{-2})
P	Total pressure (kPa)
P_{com}	Power requirement of the compression unit (kW)
p_i	Partial pressure of component i (Pa)
Q_0	Pre-exponential constant for membrane permeability (mol m^{-1} s^{-1} Pa$^{-0.5}$)
Q_i	Heat involved in each unit (kW)
R	Universal gas constant (8.31447×10^{-3}) (kJ mol^{-1} K^{-1})
T	Absolute temperature (K)
U_f	Fuel utilization (%)
V	Operating voltage (V)

Greeks letters

η	Overpotential (V)
δ	Thickness (m)
ϕ	Hydrogen recovery (%)
ψ_{com}	Efficiency of compressor (−)
ρ	Specific ohmic resistant (Ω m)
ξ	Level of SOFC cell resistance (%)

Subscripts

a	Anode
Act	Activation
c	Cathode
Conc	Concentration
Ohm	Ohmic
p	Permeate side
r	Reaction side

concentration in feed influences SOFC performance [6], the use of a palladium membrane reactor, which has been successfully implemented in a number of hydrogen-generating reactions [7], should provide potential advantages when it is incorporated with the SOFC system. It is expected that due to a high concentration of hydrogen obtained from the membrane reactor, the SOFC unit should be operated at a higher stack power density, and therefore a smaller SOFC stack as well as a cell area is required. However, the operation of the palladium membrane reactor requires additional costs on membrane and compressor. Unfortunately, there is still no effort in the literatures to analyze the potential benefits and economics of the incorporation of the palladium membrane reactor to the SOFC system.

In this study, the performances of the methanol-fuelled SOFC system incorporated with the palladium membrane reactor are compared with those of the conventional SOFC system. The benefits from the use of the membrane reactor and the preliminary economic analysis are investigated. The obtained information from this study is important for determining whether the research effort should be carried out further on this proposed system.

2. Theory

A conventional SOFC system normally consists of preheaters, a reformer, an SOFC unit, and a burner (Fig. 1(a)). As shown in the figure, a mixture of methanol and water is firstly preheated in Preheater I before being converted to hydrogen-rich gas in the reformer. Simultaneously, air is also preheated (in Preheater II) by the exhaust heat from Preheater I before feeding to the SOFC unit where electrical power is generated. Heat required in the system is obtained from the combustion of exhaust gases and the irreversible losses in the SOFC unit.

For the SOFC system with a palladium membrane reactor, the conventional reformer is replaced by the membrane reactor

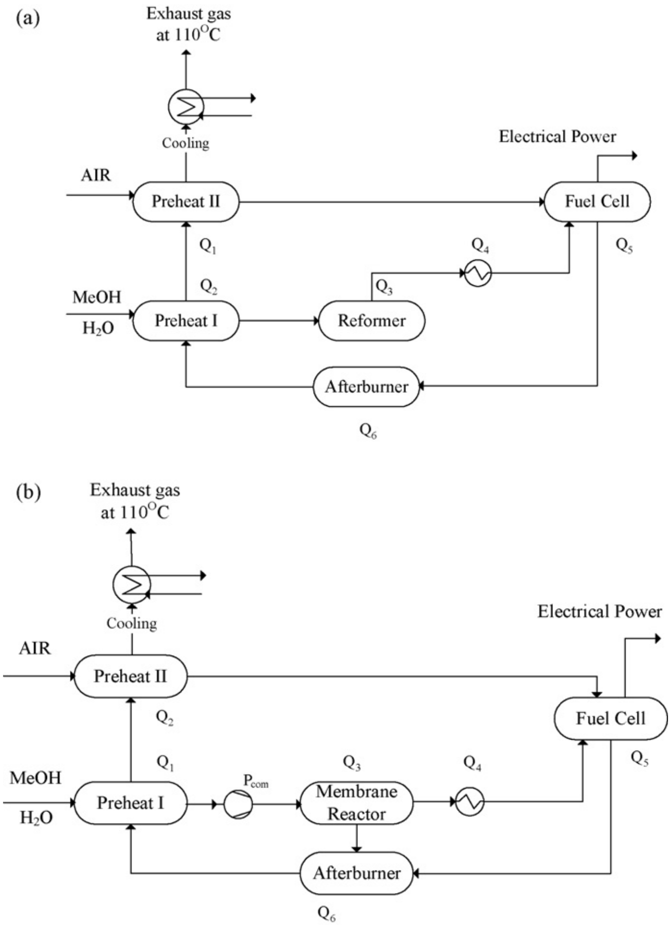

Fig. 1. Flow diagrams of SOFC systems; (a) a conventional SOFC system and (b) an SOFC system with a membrane reactor.

(Fig. 1(b)). In addition, a compressor is required for this system in order to increase the driving force for hydrogen separation. According to this operating system, pure hydrogen is extracted from the reformed gas and fed to the anode compartment of the SOFC unit, whereas the residual reformed gas is combined with the exhaust gases from the SOFC unit and combusted in the burner in order to supply heat to the system.

2.1.1. *Reformer/membrane reactor*

At the reformer/membrane reactor, the reactions involved in the production of hydrogen from the steam reforming of methanol can be represented by the following equations [8,9]

$$CH_3OH = 2H_2 + CO \tag{1}$$

$$CO + H_2O = H_2 + CO_2 \tag{2}$$

$$CO + 3H_2 = CH_4 + H_2O \tag{3}$$

In this work, the reactor is assumed to be operated at equilibrium condition. This assumption may be reasonable because the rates of methanol steam-reforming and the water gas shift reaction are fast, particularly at high temperature [10]. It was reported that the conversion of methanol from the methanol steam-reforming always close to 100% when the operating temperature above 623 K is performed [11]. According to the substantial works on developing selective hydrogen permeable membranes, a dense palladium-based membrane reactor has attracted many research interests. Recent research efforts have focused on the fabrication of thin membrane layers and determination of alloy compositions with better stability and resistance to poisonings. In the present work, the palladium membrane reactor with a membrane thickness of 10 μm was chosen due to its minimum in palladium material cost, defects and manufacturing difficulties of a thin membrane [12].

The hydrogen flux through a palladium membrane (N_{H_2}) is typically limited by the diffusion of hydrogen atoms through the membrane film, in which the flux can be represented by Eq. (4)

$$N_{H_2} = \frac{Q_0}{\delta}\exp\left(\frac{-E_D}{RT}\right)\left(p^{0.5}_{H_2,r} - p^{0.5}_{H_2p}\right) \tag{4}$$

The flux is inversely proportional to the membrane thickness (δ) and proportional to the difference in the square roots of the hydrogen partial pressure on the reaction side and the permeate side of the membrane. The resistance of the porous support is assumed negligible. The parameters of Eq. (4) are presented in Table 1. It should be noted that the required area of the palladium membrane can be calculated from the average hydrogen flux through the membrane as shown in the following equation:

$$\text{Area}_{\text{Mem}} = \frac{\text{molar flowrate of } H_2 \text{ recovered}}{\bar{N}_{H_2}} \tag{5}$$

Table 1
Parameters for hydrogen permeation through a palladium membrane [13]

Q_0 (mol m^{-1} s^{-1} Pa$^{-0.5}$)	4.40×10^{-7}
E_D (kJ mol^{-1})	15.7
Thickness (μm)	10

Table 2
Summary of parameters of ohmic resistance and thickness of each cell component [14]

Materials for anode/electrolyte/cathode	Ni–YSZ/YSZ/LSM–YSZ
Anode thickness (μm)	150
Constants for anode ohmic resistance	$a = 0.0000298$, $b = -1392$
Cathode thickness (μm)	200
Constants for cathode ohmic resistance	$a = 0.0000811$, $b = 600$
Electrolyte thickness (μm)	40
Constants for electrolyte ohmic resistance	$a = 0.0000294$, $b = 10350$
Interconnect thickness (μm)	100
Constants for interconnect ohmic resistance	$a = 0.001256$, $b = 4690$

As described earlier, the SOFC system with the palladium membrane reactor needs to install the compressor to operate in the palladium membrane reactor. The required power for the compressor (P_{com}) can be calculated from the following equation.

$$P_{\text{com}} = \frac{\Delta(Pf)}{\psi_{\text{com}}} \tag{6}$$

where f and P are volumetric flow rate and total pressure, respectively. It is assumed that the efficiency of compressor (ψ_{com}) is 80%.

2.2. *SOFC unit*

An SOFC unit consists of two porous ceramic electrodes (i.e. an anode and a cathode), a solid ceramic electrolyte, and an interconnector. The theoretical open-circuit voltage of the cell, which is the maximum voltage under specific operating conditions, can be calculated from the following equation:

$$V = E_0 - (\eta_{\text{ohm}} + \eta_{\text{Act,a}} + \eta_{\text{Act,c}} + \eta_{\text{Conc,a}} + \eta_{\text{Conc,c}}) \tag{7}$$

where E_0 is open circuit voltage determined by Nernst's equation and η_i is a polarization loss in the SOFC unit.

It is well established that several losses could occur during SOFC operation. The voltage drop is normally caused by three major irreversibilities; that is, ohmic polarization (Eq. (8)), activation polarization (Eq. (9)) and concentration polarization. The summaries of ohmic polarization and activation polarization parameters are given in Tables 2 and 3, respectively. In the present work, the concentration polarization is assumed to be negligible. This assumption is valid when the cell is not operated at too high current density or too low concentration [16].

$$\eta_{\text{Ohm}} = \frac{i\rho\delta}{A} \tag{8}$$

Table 3
Summary of activation polarization parameters [15]

	k (A m^{-2})	$E_{\text{A,pol}}$ (kJ mol^{-1})	m
Cathode	14.9×10^9	160	0.25
Anode	0.213×10^9	110	0.25

where $\rho = a\exp(b/T)$; a and b are the constant values dependent on a type of material.

$$\tilde{\eta}_{\text{Act}} = i\left[\left[\frac{4F}{RT}k_{\text{O}_2}(p_{\text{O}_2,c})^{m_{\text{O}_2}}\exp\left(-\frac{E_{\text{A,pol,O}_2}}{RT}\right)\right]^{-1} + \left[\frac{2F}{RT}k_{\text{H}_2}(p_{\text{H}_2,\text{a}})^{m_{\text{H}_2}}\exp\left(-\frac{E_{\text{A,pol,H}_2}}{RT}\right)\right]^{-1}\right] \quad (9)$$

The electrical power can be calculated by Eq. (10). Generally, the SOFC is suggested to operate at the relative power (ratio of power to the maximum achievable power at the specific condition) of 0.7 [17]. The fuel cell operation at lower power is attractive from the point of view that the higher efficiency is obtained. However, too low power is not practical due to high cost of SOFC cell.

$$\text{Electrical power} = \text{Current} \times \text{Operating Voltage} \quad (10)$$

The amount of heat involved in each unit (Q_i) shown in Fig. 1 can be calculated from the enthalpy change of each unit based on the assumption that no heat loss occurs in the unit.

3. Results and discussion

Various operating parameters influence the performance of SOFC stack. In operation, hydrogen in the fuel is consumed along the fuel channel by the electrochemical reaction. Fig. 2 shows the voltage (dashed lines) and average power density (solid lines) at different operating current density (i) and fuel utilization (U_f) for the conventional system fed by a feed with a H_2O:MeOH ratio of 1:1 at a temperature of 1173 K. The voltage decreases with the increase of operating current density due to the increased voltage loss from the irreversible SOFC cell resistances. Power density increases initially to a maximum value and then decreases. These characteristics are often observed in most SOFC systems. However, it should be noted that the values at high current density are likely to be overestimated because the concentration polarization is neglected. When the stack is operated at high fuel utilization, both the voltage and power density decrease. This is mainly due to the fuel depletion particularly near the exit of the anode chamber. Fig. 3 shows the effect of fuel utilization on the maximum power density (dashed lines) and its corresponding electrical efficiency (solid line) at three temperature levels. It is clearly shown that although the operation at high fuel utilization is desirable in term of achieving high electrical efficiency, the main drawback is its lower power density, implying that larger cell area is required to operate the system. Therefore, the fuel utilization should be carefully selected to achieve a high electrical efficiency at a reasonable stack power density. The fuel utilization of 80–95% has been reported in many studies [17–19]. It was also found that the temperature significantly influences the values of maximum power density. At high temperature the cell resistance becomes smaller and therefore the maximum power density increases. However, it does not affect the corresponding electrical efficiency at the maximum power density. It should be noted that high operating temperature is a favorable operating condition regarding the SOFC performance; however, it is limited by the presence of some technical constraint, such as availability of high temperature seal. The operating temperature of 1173 K is used in the further studies in this work.

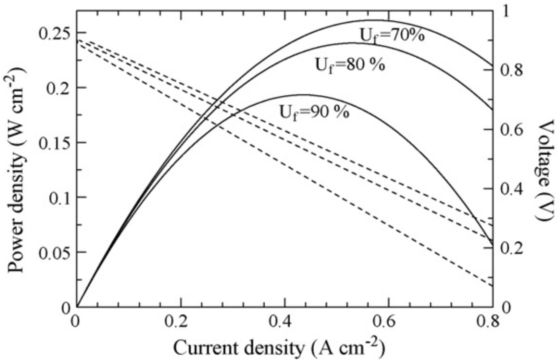

Fig. 2. Characteristic curves of SOFC stack at different fuel utilization (inlet H_2O:MeOH = 1:1 and T = 1173 K).

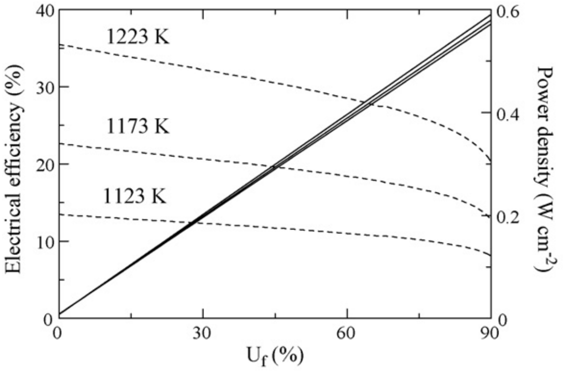

Fig. 3. Maximum power density and electrical efficiency at different operating fuel utilization and temperature (inlet H_2O:MeOH = 1:1).

When an SOFC system is incorporated with a palladium membrane reactor, pure hydrogen is extracted from the reformed gas and fed to the SOFC stack. The operating temperature of the palladium membrane was reported in a range of 673–873 K [20,21]. In this study, the operating temperature of 873 K was considered as it provided the highest hydrogen flux. Fig. 4 shows the characteristic curves of the SOFC unit fed by pure hydrogen at different hydrogen recovery (ϕ). The SOFC unit is operated at T = 1173 K and a fuel utilization of 80%. The dashed line and solid lines show the power density for the case of the conventional SOFC system and the case of the SOFC system with the membrane reactor, respectively. It is obvious that hydrogen recovery significantly influences the performance of the SOFC unit. The value must be sufficiently high to offer superior performance to the case with the conventional reformer. The maximum power density increases from 0.238 W cm^{-2} for the conventional SOFC system to 0.247 W cm^{-2} (3.8%) and 0.268 W cm^{-2} (12.6%), for the SOFC system with the palladium membrane operated at hydrogen recovery of 85% and 90%, respectively. When the SOFC unit is operated at constant fuel utilization, the hydrogen concentration along the fuel channel is governed by

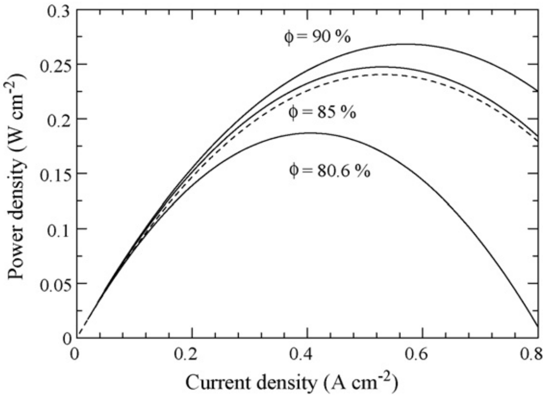

Fig. 4. Comparison of characteristic curves between the conventional SOFC system and the SOFC system with palladium membrane reactor operated at different values of percentage hydrogen recovery (ϕ; inlet H_2O:MeOH = 1:1, $U_f = 80\%$, $T = 1173$ K).

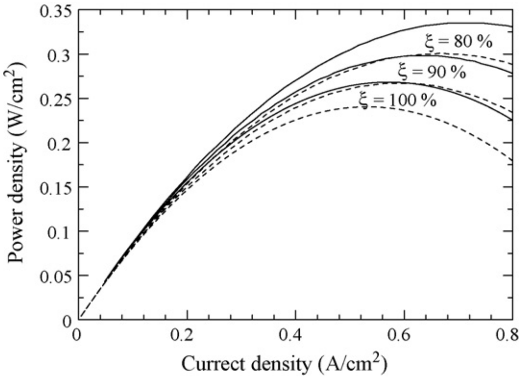

Fig. 5. Comparison of characteristic curves between the conventional SOFC system and the SOFC system with palladium membrane reactor at different cell resistance (inlet H_2O:MeOH = 1:1, $U_f = 80\%$, $\phi = 90\%$, $T = 1173$ K).

the value of hydrogen recovery. At low hydrogen recovery, the fuel depletion near the exit of the SOFC unit is pronounced, which deteriorates the SOFC performance as observed by the reduction of power density. From this study, it is obvious that the percentage hydrogen recovery is an important factor which determines whether the inclusion of the membrane reactor in the SOFC system is beneficial to the SOFC system.

Although it was clearly demonstrated that the use of the membrane reactor shows a potential technical benefit for the SOFC system, it requires additional cost on expensive palladium membranes and a compressor to operate the membrane reactor. A preliminary analysis is necessary to determine whether the SOFC system with the membrane reactor is economically feasible. Table 4 shows the calculation results of two cases; i.e., case I the conventional SOFC system and case II the SOFC system with a palladium membrane reactor. For both cases the SOFC is operated at 1173 K and a fuel utilization of 80%. Details of the other operating conditions are also provided in the table. The net electrical efficiency for both cases is 287.2 kW which is equivalent to an electrical efficiency of 45%. For the case II, the extra electrical power (21.6 kW) is generated in the SOFC stack to provide the electrical power for operating the compressor. It was found that the SOFC cell area for case II (131.7 m^2) is lower than that of case I (143.6 m^2), resulting in the reduction of SOFC cell area of 11.9 m^2 when using the membrane reactor in the system. However, the operation in case II requires a palladium membrane area of 120.1 m^2 at 873 K. From the literatures, the prices of SOFC cell and palladium membrane are 1,500 US\$/m^2 [22] and 746 US\$/m^2 [23], respectively. Assuming the equivalent life time for both the SOFC cell and the palladium membrane and neglecting the cost of the compressor, it is obvious that the saving of 62.2 US\$/kW from the reduction of the SOFC cell area is still much lower than the extra palladium membrane cost of 312.0 US\$/kW, indicating that the incorporation of the palladium membrane reactor in the SOFC system is not economical at the present state of art. To make it economical, significant effort is required to reduce the price of the membrane. However, it should be noted that nowadays an SOFC cell is also progressively developed to improve the cell performance as well as to reduce its price. The calculations of heat requirement in the system indicate that both systems can be operated without additional requirement of an external heat source.

Table 4
Performance comparison between the conventional SOFC system and the SOFC system with the palladium membrane reactor

Items	Unit	Case I	Case II
Inlet H_2O:MeOH ratio	–	1	1
Reformer/palladium membrane reactor			
Pressure	kPa	101.3	2026
Temperature	K	973	873
Afterburner stack data	K	1173	1173
Pressure	kPa	101.3	101.3
Temperature	K	1173	1173
Fuel utilization (U_f)	%	80	80
Cell voltage	V	0.62	0.67
Current density	A cm^{-2}	0.323	0.35
Power density	W cm^{-2}	0.203	0.234
Cell area	m^2	143.6	131.7
Palladium membrane reactor			
% recovery	%	–	90.0
Membrane area	m^2	–	120.1
Power production			
Electrical power	kW	287.2	308.8
Power consumption			
Compressor	kW	–	21.6
Net electrical efficiency	%	45	45

In order to determine whether the use of palladium membrane reactor is technically advantageous for the SOFC system when a better cell is developed, the characteristic curves of the SOFC at different levels of cell resistance ($\xi = 80\%$, 90% and 100%) are calculated (see Fig. 5). The dashed lines indicate the results for the conventional SOFC system while the solid lines represent those for the SOFC system with the palladium membrane reactor. The fuel utilization is kept at 80% for both cases and the hydrogen recovery is fixed at 90% for the case with the palladium membrane reactor. From the results, it is clear that when the cell is further developed to have lower resistance, the use of a palladium membrane reactor still shows a potential technical benefit to the SOFC system. It should be noted that the use of other membranes (such as zeolite membrane) which offer similar or slightly lower separation efficiency may be another attractive option to be considered.

4. Conclusions

Performance of the SOFC system fuelled by methanol was analyzed to investigate the potential benefit from incorporating a palladium membrane reactor to the system. The electrical efficiency and power density of the SOFC unit were governed by the operating current density, fuel utilization and temperature. It was demonstrated that the SOFC unit can be operated at higher power density when the system is equipped with the membrane reactor. Compared with the conventional SOFC system, the system with the membrane reactor requires lower SOFC cell area, resulting in lower cost of the stack. However, the cost of the required palladium membrane was found to be much more expensive than the saving cost. Therefore the SOFC system incorporated with the palladium membrane is not economically attractive unless the membrane can be made at much lower cost. Finally it was revealed that the improvement of the stack power density by the use of the palladium membrane reactor is still technically significant even when an advanced cell with lower cell resistance can be developed.

Acknowledgements

The supports from The Thailand Research Fund, Commission on Higher Education, and the Chulalongkorn University Graduate Scholarship commemorating the 72nd Anniversary of H.M. King RAMA IX are gratefully acknowledged. The authors also would like to acknowledge the support from Professor Piyasan Praserthdam.

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