

A solid oxide fuel cell system fed with hydrogen sulfide and natural gas

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Abstract

Hydrogen sulfide (H_2S) occurs naturally in crude petroleum, natural gas, volcanic gases, hot springs, and some lakes. Hydrogen sulfide can also result as a by-product from industrial activities, such as food processing, coke ovens, paper mills, tanneries, and petroleum refineries. Sometimes, it is considered to be an industrial pollutant. However, hydrogen can be decomposed from H_2S and then used as fuel for a solid oxide fuel cell (SOFC). This paper presents an examination of a simple hydrogen sulfide and natural gas-fed solid oxide fuel cell system. The possibility of utilization of hydrogen sulfide as a feedstock in a solid oxide fuel cell is discussed. A system configuration of an SOFC combined with an external H_2S decomposition device is proposed, where a certain amount of natural gas is supplied to the SOFC. The exhaust fuel gas of the SOFC is after-burned with exhaust air from the SOFC, and the heat of the combustion gas is utilized in the decomposition of H_2S in a decomposition reactor (DR) to produce hydrogen to feed the SOFC. The products are electricity and industry-usable sulfur. Through a mass and energy balance, a preliminary thermodynamic analysis of this system is performed, and the system efficiency is calculated. Also in this paper, the challenges in creating the proposed configuration are discussed, and the direction of future work is presented.

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1. Introduction

A fuel cell system provides a promising option for efficient and environmentally benign electric power generation. Among the several kinds of fuel cells, solid oxide fuel cells (SOFCs) are particularly suitable for integration with other types of bottoming cycles (such as gas turbine cycles and cogeneration) because of their high operating temperature (up to 1300 K). Furthermore, an SOFC has multiple fuel choices due to the high reaction temperature. In the last decade, solid oxide fuel cells using hydrogen or methane as a fuel have attained real maturity and may soon provide a viable commercial option for power generation [1,2]. Researchers are also exploring other fuel options. Hydrogen sulfide, which is considered to be an air pollutant, is a potential candidate as a fuel for SOFCs [3]. However, hydrogen sulfide is an extremely corrosive and noxious gas,

which puts stringent requirements on cell materials, especially at high temperatures [4]. Direct use of H_2S in solid oxide fuel cells with a platinum anode causes anode deterioration over time, and the performance of the SOFC therefore drops [3]. For an SOFC with Ni-YSZ cermet electrodes and a YSZ electrolyte, although material integrity is recoverable when H_2S is removed from the fuel, the performance loss will increase when the H_2S concentration exceeds 2 ppm at 1000 °C [5].

To circumvent some of these issues, an H_2S decomposition reactor (DR) integrated with an SOFC system becomes a possible choice. Production of hydrogen by direct thermal decomposition of hydrogen sulfide has been studied extensively. There are several good reviews of the subject available [4,6]. Thermal catalytic decomposition of H_2S in the temperature range of 500–1073 K has been investigated by many researchers [7–11]. Many kinds of membrane systems to separate hydrogen and sulfur decomposed from H_2S have also been studied extensively [12–15]. H_2S decomposition can occur quickly in the presence of certain catalysts and the conversion rate can be high. A laboratory-scale metal-membrane reactor can drive the decomposition of H_2S

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Nomenclature

[CH ₄]	molar flow rate of methane (mol s ⁻¹)
[CO]	molar flow rate of carbon monoxide (mol s ⁻¹)
[CO ₂]	molar flow rate of carbon dioxide (mol s ⁻¹)
C_p	specific heat at constant pressure (J mol ⁻¹ K ⁻¹)
f	hydrogen flow rate at the inlet of an SOFC stack (mol s ⁻¹)
h	enthalpy (J mol ⁻¹)
Δh_e	combustion heat of hydrogen (J mol ⁻¹)
Δh_{fuel}	combustion heat of fresh natural gas fed into system (J mol ⁻¹)
Δh_{hc}	combustion heat of consumed hydrogen in SOFC bundle (J s ⁻¹)
[H ₂]	molar flow rate of hydrogen (mol s ⁻¹)
[H ₂ O]	molar flow rate of steam (mol s ⁻¹)
K	reaction equilibrium constant
K_r	equilibrium constant for the reforming reaction
K_s	equilibrium constant for the shifting reaction
n	total molar flow rate of gas mixture (mol s ⁻¹)
p	pressure (bar)
P_{H_2}	partial pressure of hydrogen in the anode gas mixture
$P_{\text{H}_2\text{O}}$	partial pressure of steam in the anode gas mixture
P_{CH_4}	partial pressure of methane in the anode gas mixture
P_{CO}	partial pressure of carbon monoxide in the anode gas mixture
P_{CO_2}	partial pressure of carbon dioxide in the anode gas mixture
Q	heat (J)
T	temperature (K)
x	molar flow rate of the reacted methane in reforming reaction (mol s ⁻¹)
y	molar flow rate of the reacted carbon monoxide in shifting reaction (mol s ⁻¹)
z	molar flow rate of the reacted hydrogen in electrochemical reaction (mol s ⁻¹)
U_f	fuel utilization
w_{dc}	dc power generated from an SOFC power generation unit (W)
$w_{\text{H}_2\text{S}}$	molar flow rate of hydrogen decomposed from H ₂ S (mol s ⁻¹)

Greek letters

η_{dc}	dc efficiency for an SOFC power generation unit
η_{system}	efficiency of integrated system

Subscripts

e	electrochemical reaction
r	reforming
f	fuel
s	shifting
stack	fuel cell stack

Superscripts

i	inlet
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to greater than 99.4% of complete conversion at around 973 K [15]. Since the SOFC can be operated under a high temperature condition of about 1300 K, its exhaust flue gas has a heat utility high enough for H₂S decomposition. The hydrogen decomposed from H₂S can then be sent back to the SOFC as fuel.

In this investigation, a simple model of the integrated system is given, and thermodynamic analyses, including energy and mass balances, are performed. A computer code is developed to simulate the processes.

2. System configuration and description

The system configuration of the proposed SOFC system consuming natural gas and hydrogen sulfide is shown in Fig. 1. The system consists of an internal reforming SOFC stack, a combustor, a thermal H₂S decomposition reactor, a desulfurizer, and two recuperators. Natural gas is internally reformed, and the product, a hydrogen-rich gas mixture, is fed into the SOFC anodes. The air is pre-heated and fed into the SOFC cathodes. The electrochemical reaction occurs at the interface of the cathodes and anodes and produces oxygen ions flowing through the electrolytes and cathodes, and electrons flowing through the anodes and external circuit, which generates the electricity. The reaction heat is used to reform the natural gas and heat the incoming air and fuel streams. The depleted fuel and air streams are fed into the combustor where the residual fuel gases (hydrogen, carbon monoxide, and methane) are combusted with the excess oxygen from the depleted air stream. The high-temperature flue gas is used to decompose the H₂S and heat the air and fuel streams fed into the SOFC stack. The hydrogen sulfide is decomposed and separated in a decomposition reactor with a porous membrane. The separated hydrogen flows through a desulfurizer and is sent back to the SOFC stack as a fuel. Another by-product is sulfur, which can be used in industrial processes.

3. System modeling

This system model calculates the thermodynamic properties and chemical composition of the gases at the inlet and

Table 1
Coefficients for calculation of the equilibrium constants

	Reforming	Shifting
A	-2.63121×10^{-11}	5.47301×10^{-12}
B	1.24065×10^{-7}	-2.57479×10^{-8}
C	-2.25232×10^{-4}	4.63742×10^{-5}
D	1.95028×10^{-1}	-3.91500×10^{-2}
E	-6.61395×10^1	1.32097×10^1

reactions comes from the electrochemical reaction and can be calculated using following equations:

$$Q_r = x(h_{\text{CO}} + 3h_{\text{H}_2} - h_{\text{H}_2\text{O}} - h_{\text{CH}_4}) \quad (10)$$

$$Q_s = y(h_{\text{CO}_2} + h_{\text{H}_2} - h_{\text{CO}} - h_{\text{H}_2\text{O}}) \quad (11)$$

3.2. SOFC model

The SOFC model is based on a 100 kW tubular SOFC heat and power system (SOFC-CHP) developed by Siemens Westinghouse. The field performance parameters of this SOFC system are shown in Table 2 [1].

The η_{dc} in Table 2 is the dc efficiency of the SOFC bundle and is defined in Eq. (12), where w_{dc} is dc power produced by the SOFC power generation unit, and Δh_{hc} is the combustion heat of consumed hydrogen in the SOFC bundle.

$$\eta_{\text{dc}} = \frac{w_{\text{dc}}}{\Delta h_{\text{hc}}} \quad (12)$$

To simplify the study, this paper focuses on the thermodynamic aspects of the total SOFC system based on the available data in Table 2. The total heat generated in the SOFC stack Q_{stack} can be calculated from Eq. (13). This generated heat includes reversible electrochemical reaction heat and the heat due to the irreversibility of the process that provides the heat for internal reforming and heating the incoming reactant streams.

$$Q_{\text{stack}} = \frac{w_{\text{dc}}(1 - \eta_{\text{dc}})}{\eta_{\text{dc}}} \quad (13)$$

where η_{dc} is the dc efficiency of the SOFC bundle and w_{dc} is the dc power. The flow rate of hydrogen fed into the SOFC stack can be calculated as

$$f_{\text{stack}}^{\text{H}_2} = \frac{w_{\text{dc}}}{U_f \eta_{\text{dc}} \Delta h_e} \quad (14)$$

where Δh_e is the change of enthalpy of formation of the electrochemical reaction given in Eq. (3). The enthalpy changes of the reactants and products due to temperature variation

Table 2
The operating parameters of a 100 kW SOFC-CHP system

dc power (w_{dc}) (kW)	110
dc efficiency (η_{dc}) (%)	53
Fuel utilization (U_f) (%)	85
Stoichiometric air	~4
Stack temperature (K)	~1273

Table 3
The assumed performance values of the related system components

Parameters	Assumed values
Thermal efficiency of H ₂ S DR (%)	90
Recuperator efficiency (%)	90
Combustor isotropic efficiency (%)	95
H ₂ S conversion efficiency (%)	≤90
Temperature difference in various recuperators (°C)	≥100

are calculated using Eq. (15). In this study, the system efficiency is defined in Eq. (16), where Δh_{fuel} is the combustion energy of the fresh nature gas fed into the system.

$$\Delta h = \int_{T_2}^{T_1} C_p dT \quad (15)$$

$$\eta_{\text{system}} = \frac{w_{\text{dc}}}{\Delta h_{\text{fuel}}} \quad (16)$$

3.3. H₂S decomposition reactor and other system component models

The decomposition temperature range can be 200–1600 °C, which includes catalytic or direct thermal decomposition. In the temperature range of about 800–1500 °C, thermolysis of hydrogen sulfide can be treated simply in terms of the reaction shown in Eq. (17), where x equals 2 [18–20]. In this study, the temperature of H₂S decomposition is set as 800 °C, although the H₂S decomposition may occur at many different temperatures, including those lower than 800 °C, depending on the specific catalysts. The assumed parameters for the relevant system components are given in Table 3, where DR is the decomposition reactor.



4. System simulation

4.1. System simulation results

In this study, the pressures in all of the system components are assumed to be 1 bar, and the flow resistance in the pipelines and system components is neglected. The typical natural gas composition in the United States is 94.4% methane, 3.1% ethane, and 1.1% nitrogen and other components [21]. In this study, the natural gas is assumed to be 100% CH₄ for simplicity. The depleted fuel recalculation for internal reforming is set to 58%, which makes the C/H ratio in the reforming process in the range of 2.5–3.

In the particular case of an H₂S conversion efficiency of 90% and 85% fuel utilization for the SOFC, the temperature, gas flow rate, and composition at each node of the system (as shown in Fig. 1) are listed in Table 4. The flow rate of natural gas fed into the SOFC is 0.0034 kg/s, the corresponding flow rate of consumed H₂S is 0.0071 kg/s, and the molar ratio of the natural gas and H₂S is approximately 1.01.

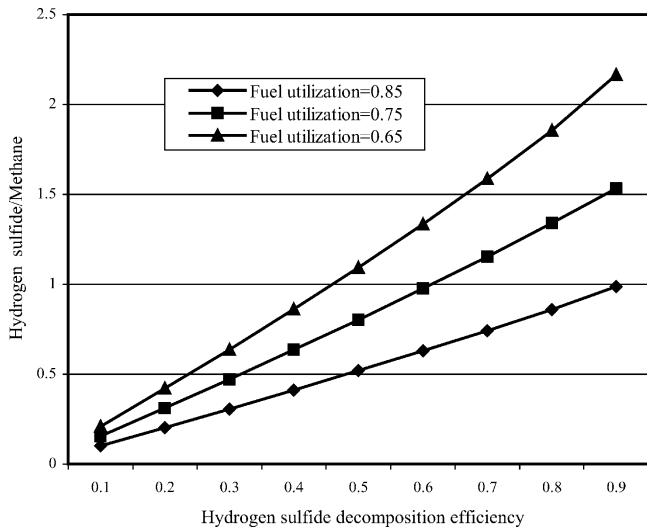


Fig. 4. Effect of the hydrogen sulfide decomposition efficiency on the H₂S/CH₄ ratio.

Improvement in the fuel utilization will increase system efficiency, and also a higher hydrogen sulfide decomposition efficiency will result in a higher system efficiency, as shown in Fig. 5. When the fuel utilization approaches a higher value, the improvement of the hydrogen sulfide decomposition efficiency will contribute less to the system efficiency. This is because there is less fuel in the depleted fuel gas combusted to produce heat. Similar to Fig. 4, the relation between the fuel utilization and system efficiency is not exactly linear, especially when the hydrogen sulfide decomposition efficiency is high. This is because when the fuel utilization increases, the fuel consumption rate increases but the hydrogen decomposed from H₂S decreases due to less fuel in depleted gas. Fig. 6 shows that increasing the fuel utilization will decrease the consumed H₂S/CH₄ ratio due to the same reason as stated above. When the fuel utiliza-

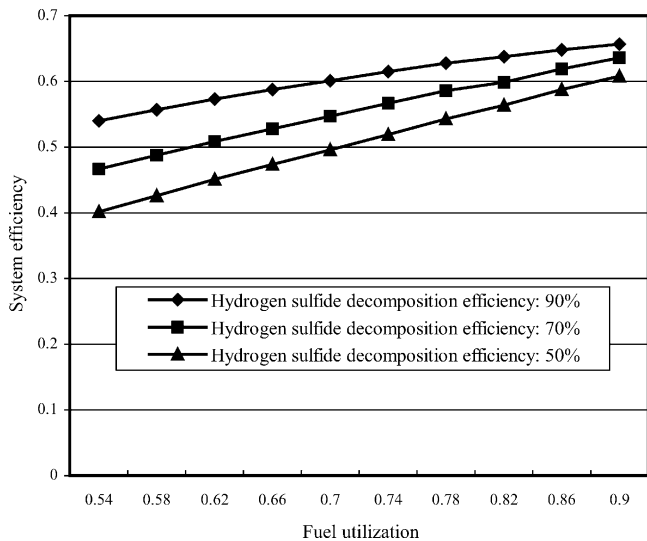


Fig. 5. Effect of fuel utilization on system efficiency.

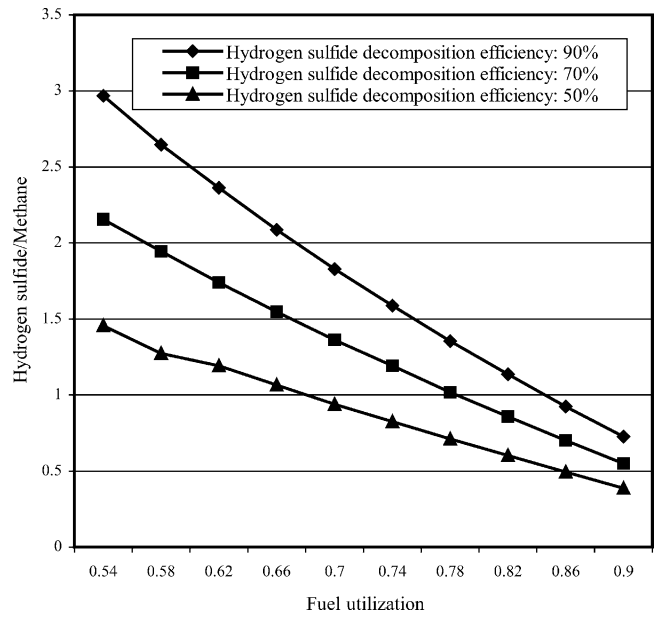


Fig. 6. Effect of fuel utilization on H₂S/CH₄ consumption ratio.

tion is low, the hydrogen sulfide decomposition efficiency affects the consumed H₂S/CH₄ ratio dramatically because of the large amount of heat used to decompose the H₂S.

4.4. System performance under differing SOFC dc efficiencies

Improvement in the dc efficiency of an SOFC directly enhances the conversion rate of fuel in the SOFC and hence increases the system efficiency as shown in Figs. 7 and 8. It is also indicated that the system efficiency increases with the H₂S decomposition efficiency and fuel utilization as shown in Figs. 3 and 5. As indicated in Figs. 9 and 10, the SOFC dc efficiency improvement will slightly decrease the H₂S/CH₄

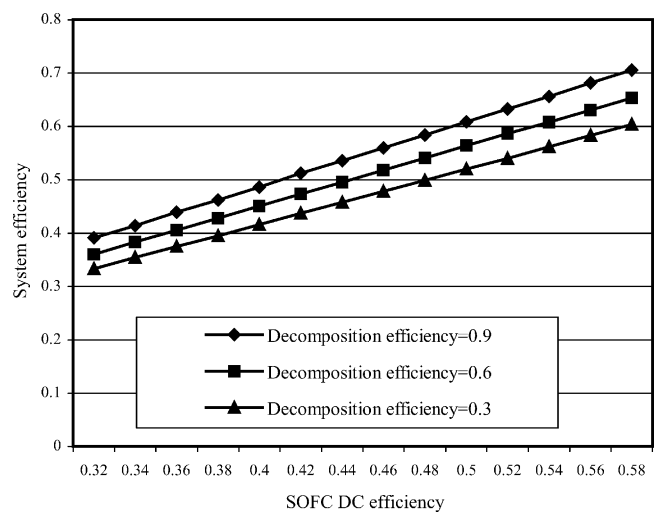


Fig. 7. Effect of the SOFC dc efficiency on system efficiency with differing H₂S decomposition efficiencies.

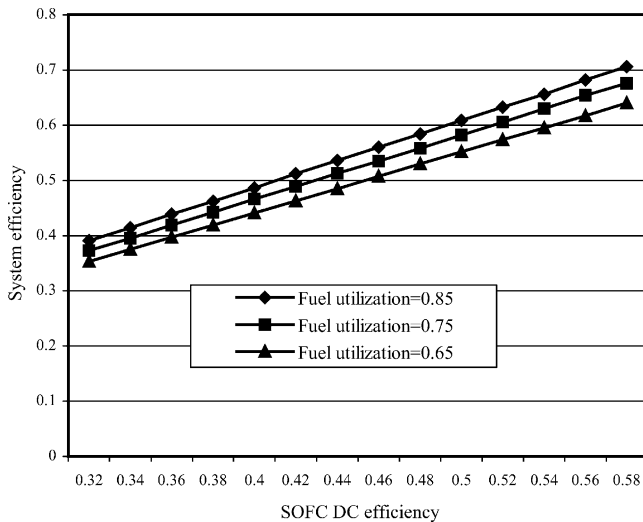


Fig. 8. Effect of the SOFC dc efficiency on system efficiency with differing fuel utilization percentages.

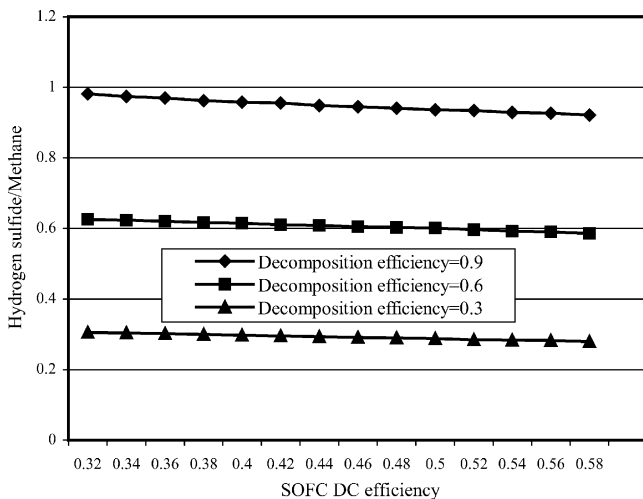


Fig. 9. Effect of the SOFC dc efficiency on the H₂S/CH₄ ratio with differing H₂S decomposition efficiencies.

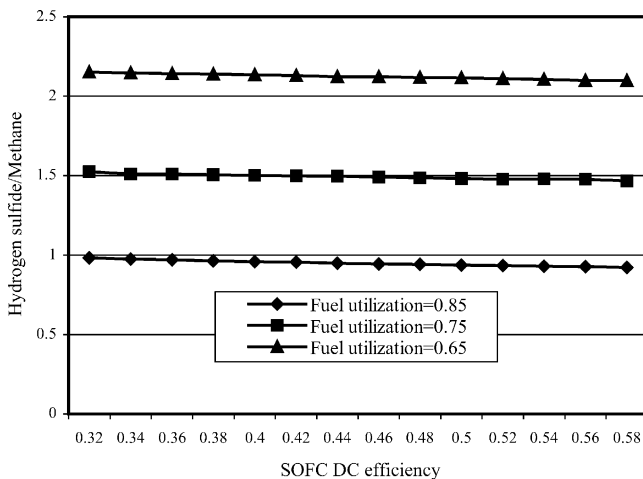


Fig. 10. Effect of the SOFC dc efficiency on the H₂S/CH₄ ratio with differing fuel utilization percentages.

ratio because a less irreversible reaction heat is used to decompose the H₂S. If the H₂S decomposition is set at a lower temperature, the effect of the SOFC dc efficiency on the H₂S/CH₄ ratio is expected to slightly increase because of the heat available for H₂S decomposition.

5. Conclusions

An integrated system that combines the SOFC power generation system with a direct thermal H₂S decomposition device with a membrane has been proposed and analyzed. The preliminary energy and mass balance analysis shows that from a thermodynamic analysis, such a system has the capacity to recover the heat from SOFC power generation system to decompose the hydrogen sulfide and thereby produce electrical power and industry-usable sulfur at same time. The system power generation efficiency is expected to reach 65% for the case of an SOFC dc efficiency of 53%, a fuel utilization of 85%, and an H₂S decomposition efficiency of 90%.

In the near future, with the quest for efficient and clean power sources, more and more SOFC-related power systems like the one proposed in this study will be developed. For this particular integrated system, with the advance toward commercialization of SOFC power generation technology, the proposed SOFC technology is becoming relatively mature. The challenges of building this proposed system focus on the H₂S decomposition device and the system integration. Although some laboratory-scale hydrogen decomposition membrane reactors exist, there are currently no such commercial devices available in the market. Expanded technical and economic studies are necessary to evaluate the feasibility and maturity of larger H₂S decomposition devices. Additionally, the system integration needs to be fine-tuned and the analysis of the overall system should be expanded. Finally, system control and other technical and economic issues should be considered further as well.

References

- [1] R.A. George, *J. Power Sources* 86 (2000) 134–139.
- [2] S.C. Singhal, *Solid State Ionics* 135 (2000) 305–313.
- [3] M. Liu, P. He, J.L. Luo, A.R. Sanger, K.T. Chuang, *J. Power Sources* 94 (2001) 20–25.
- [4] J. Zaman, A. Chakma, *Fuel Process. Technol.* 41 (1995) 159–198.
- [5] Y. Matsuzaki, I. Yasuda, *Solid State Ionics* 132 (2000) 261–269.
- [6] E. Luinstra, in: *The GRI Sulfur Recovery Conference*, Austin, TX, USA, 24–27 September 1995.
- [7] Y. Lai, C. Yeh, Y. Lin, W. Hung, *Surf. Sci.* 519 (2002) 150–156.
- [8] T.V. Reshetenko, S.R. Khairulin, Z.R. Ismagilov, V.V. Kuznetsov, *Int. J. Hydrogen Energy* 27 (2002) 387–394.
- [9] A.A. Adesina, V. Meeyoo, G. Foulds, *Int. J. Hydrogen Energy* 20 (1995) 777–783.
- [10] J.S. Foord, E.T. FitzGerald, *Surf. Sci.* 306 (1994) 29–36.
- [11] T. Chivers, C. Lau, *Int. J. Hydrogen Energy* 10 (1985) 21–25.
- [12] J. Fan, H. Ohashi, H. Ohya, M. Aihara, T. Takeuchi, Y. Negishi, S.I. Semenova, *J. Membr. Sci.* 166 (2000) 239–247.

- [13] H. Ohashi, H. Ohya, M. Aihara, Y. Negishi, S.I. Semenova, *J. Membr. Sci.* 146 (1998) 39–52.
- [14] C.P. Badra, *Int. J. Hydrogen Energy* 20 (1995) 717–721.
- [15] D. Edlund, D. Friesen, B. Johnson, W. Pledger, *Gas Sep. Purif.* 8 (1994) 131–136.
- [16] A.F. Massardo, F. Lubelli, *J. Eng. Gas Turbines Power* 122 (2000) 27–35.
- [17] U.G. Bossel, Final report on SOFC data facts and figures, Swiss Federal Office of Energy, Berne, CH, 1992.
- [18] A.T. Raissi, in: *Proceedings of the 2001 DOE Hydrogen Program Review*, NREL/CP-570-30535.
- [19] M.E.D. Rayment, Make hydrogen from hydrogen sulfide, *Hydrocarbon Process.* (July 1975) 139–142.
- [20] N.I. Dowling, J.B. Hyne, D.M. Brown, *Ind. Eng. Chem. Res.* 29 (1990) 2327–2332.
- [21] P.L. Spath, M.K. Mann, Life cycle assessment of a natural gas combined-cycle power generation system, September 2000, NREL/TP-570-27715, p. 10.