

System calculation of integrated coal gasification/molten carbonate fuel cell combined cycle

Reflection of electricity generating performances of practical cell

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Abstract

Materials and heat balance of integrated coal gasification/molten carbonate fuel cell (IG/MCFC) combined system are calculated considering the electricity generating performance of the practical cell. The considered gas conditions that are required to stabilise the electricity generation of MCFCs are the non-carbon deposition condition, the lower limit of H₂ concentration at the anode outlet of 1 mol% and the upper limit of CO₂ partial pressure on the cathode inlet gas of 0.1 MPa. The anode gas recycling system and the anode heat exchange system have been studied supposing a not-equilibrium state of water–gas shift reaction in anode gas channel.

From the investigation on carbon deposition at the anode inlet gas, the anode gas recycling system requires approximately 80% re-circulation of the anode outlet gas, whereas the anode heat exchange system needs 60% humidity of the fuel gas. The fuel utilisation in the anode gas recycling system should be set lower than in the anode heat exchange system. The net thermal efficiency of the anode gas recycling system has a peak for CO₂ partial pressure where the net thermal efficiency of the anode heat exchange system increases as the CO₂ partial pressure of the cathode gas decreases.

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1. Introduction

Molten carbonate fuel cells (MCFC) are operated in high temperature (600–700 °C) environments, and it is possible to combine them with gas turbine systems, which leads to a high efficiency energy conversion. Since the CO in the fuel gas is changed into CO₂ and H₂ by performing a water–gas shift reaction in high temperatures, CO rich fuel has been adapted to operate with MCFCs. Therefore, it has been considered to install an integrated coal gasification/molten carbonate fuel cell (IG/MCFC) system as the central utility station.

If natural gas is supplied to the MCFC system, the fuel gas should be reformed to produce H₂-enriched gas. Since the reforming reaction is an endothermic reaction, the exhausted anode gas is supplied into the reforming subsystem. Due to this reason, the fuel utilisation of the natural gas/MCFC system is set at approximately 70–80%. From the point of view of energy flow, the combustion of

exhausted anode gas in the reformer is a kind of chemical energy re-circulation. Whereas in the IG/MCFC system, the coal gasification subsystem is isolated from the fuel cell system, so that the discharged fuel gas is not fed into the coal gasification subsystem. The fact that chemical energy re-circulation is impossible, increases the fuel utilisation of the IG/MCFC system in comparison to the natural gas system to achieve a better efficiency of the total plant system.

The other important feature of coal gas is the possibility to deposit carbon in the anode inlet gas of MCFCs. The outlet gas composition of the gasification subsystem is unstable for carbon deposition, which would plug up the pipe at the anode inlet. Concerning the cathode gas composition, another problem has occurred in MCFCs in the meantime: the NiO dissolution, which causes the Ni shortening of the anode and the cathode. The NiO dissolution rate is proportional to the partial pressure of the CO₂ gas in the cathode gas [1,2]. For the purpose of performing long-term electricity generation without Ni shortening, a lower value is maintained for the partial pressure of the cathode CO₂ gas.

Reinstrom [3] studied IG/MCFC systems with anode gas recycling and anode steam injection systems. Both pieces of equipment for anode gas recycling and steam injection

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Nomenclature

A_a	frequency factor of anode resistance
A_{C1}, A_{C2}, A_{C3}	frequency factor of cathode resistance
A_{ir}	frequency factor of internal resistance
E	Nernst voltage
E^0	standard electro-motive force
F	Faraday's constant
ΔH_a	activation energy of anode resistance
$\Delta H_{C1}, \Delta H_{C2}, \Delta H_{C3}$	activation energy of cathode resistance
ΔH_{ir}	activation energy of internal resistance
j	current density
m_i	molar fraction of species i
p	partial pressure of species i
R	universal gas constant
R_a	anode resistance
R_c	cathode resistance
R_{ir}	internal resistance
T	temperature
V	cell voltage

Subscript

a	anode
c	cathode

are designed to prevent carbon deposition at the anode inlet of the cell. In his study, the efficiency of the total power plant is discussed, and the coal-to-pile-bar efficiency of the two systems is calculated to be 47% HHV. Marconi and his co-authors [4] calculated thermal efficiency of IG/MCFC systems and concluded that de-carbonated feed of fuel gas is effective for better thermal efficiency. He also mentioned that the steam addition of fuel gas does not seem to produce any improvement of thermal efficiency, mainly because of the additional enthalpy required to produce steam, which is not balanced by a corresponding increase of cell performances. Nakayama et al. [5] estimated the thermal efficiency of the IG/MCFC system for three different kinds of gas clean-up subsystems. In his calculation, the CO and H₂ utilisation of anode gas had been set at 95%, and the thermal efficiency evaluated to be over 50% HHV. However, the composition of hydrogen, which remains at the anode outlet, amounts to be slightly less.

On the other hand, some practical MCFC bench scale cells are presently being tested which supply simulated coal gas. Kawase et al. [6] reported that the value of $([H_2] \cdot [CO_2]) / ([CO] \cdot [H_2O])$ in the anode gas channel may not be in thermodynamic equilibrium when the cell generates electricity with simulated coal gas including H₂S. Due to the gas composition analysis of the anode outlet gas by using gas chromatography, the value of $([H_2] \cdot [CO_2]) / ([CO] \cdot [H_2O])$ in the anode gas channel of the tested cell is estimated to be approximately 0.2–0.4 times

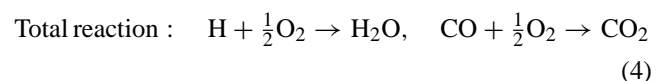
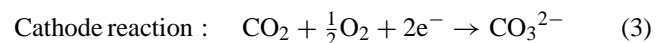
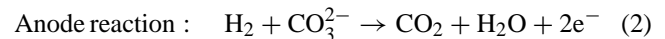
the value of $([H_2] \cdot [CO_2]) / ([CO] \cdot [H_2O])$ if the water–gas shift reaction is in complete equilibrium when the current density is set at 100 mA cm². This result proves that the water–gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, is in a thermodynamic not-equilibrium state when CO-rich gas with H₂S is supplied into the anode gas, and the production of H₂ is insufficient for the reaction of generating electricity. From the other bench scale cell tests, which supply simulated coal gas to the author's research laboratory, the cell voltage gradually drops once the H₂ concentration of the anode outlet gas becomes less than approximately 1 mol%.

Considering this background information, the IG/MCFC system calculation should be revised in order to evaluate the influence of a not-equilibrium state in the anode gas channel in comparison to the total power plant efficiency. In this paper, the materials and the heat balance are calculated considering the electricity generating performance of the practical cell. The considered gas condition of MCFCs is the non-carbon deposition condition, the lower limit of H₂ concentration at the anode outlet of 1 mol% and the upper limit of CO₂ partial pressure in the cathode inlet gas of 0.1 MPa. The calculated systems are the anode gas recycling system and the anode heat exchange system.

2. Calculation of material and heat balance in IG/MCFC system

2.1. Analysed system construction

The calculated anode gas recycling IG/MCFC system is illustrated in Fig. 1. Coal fed into the gasification subsystem is oxidised by 95% O₂ purified air. The coal gas is cooled down by a gas cooler. Particles included in the coal gas are removed by a porous filter. H₂S is withdrawn by a de-sulfuriser using the MDEA wet method. The outlet anode gas is re-circulated to the anode inlet, and the exhausted anode gas is combusted in the catalytic combustor. In an MCFC system, CO₂ is needed for the cathode reaction, so that combusted gas can be supplied to the cathode, and a part of the outlet cathode gas can be re-circulated to the cathode inlet. The electrochemical and chemical reaction in the MCFC is as follows:



The cathode re-circulating line is equipped with a gas cooler (steam generator), which has the effect of cooling the MCFC. The exhausted cathode gas is diverted to the expander, and the outlet gas from the expander is supplied

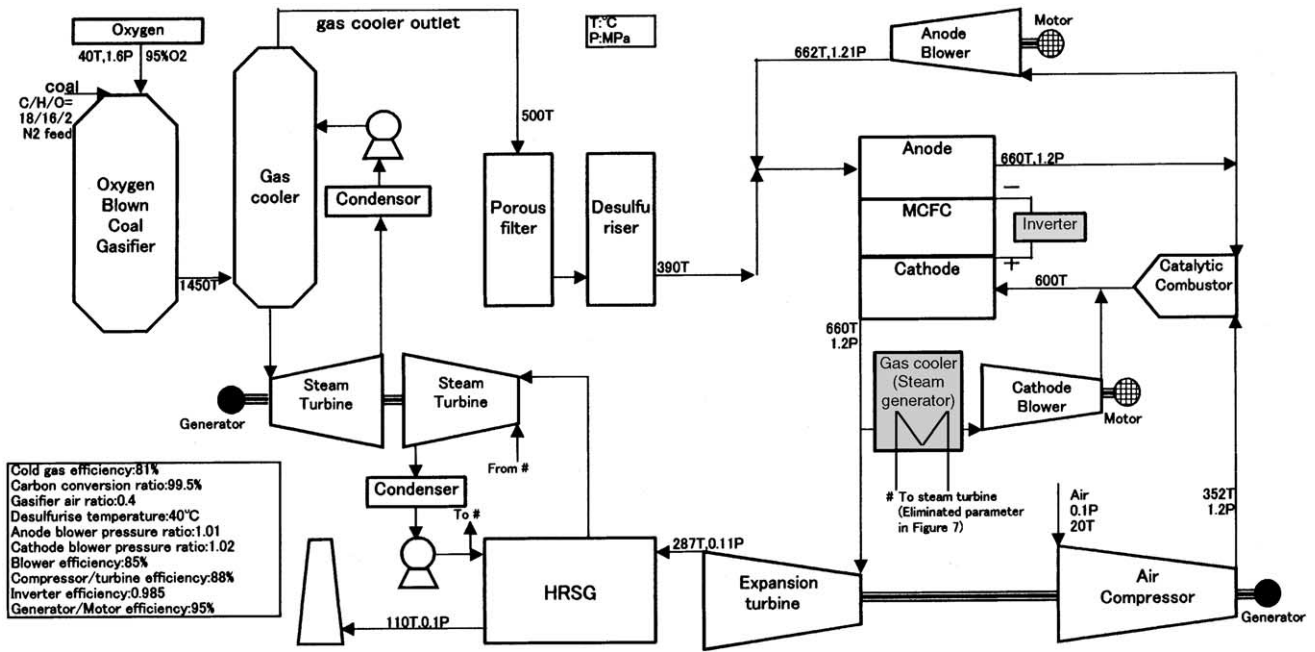


Fig. 1. Schematic design of anode gas recycling IG/MCFC system.

to the HRSG. The operating pressure of the gasification subsystem is set at 1.6 MPa, whereas the MCFC operating pressure is 1.2 MPa. The air compressor, which supplies the cathode air, is powered by the shaft power of the expander. The steam turbine is driven by the steam coming from the gas cooler of the gasification subsystem, HRSG and the cathode recycling gas cooler (steam generator).

The outlet gas composition of the gas-clean-up equipment is listed in Table 1. In the table, the reformed natural gas composition is also indicated as a reference. The CO concentration of the coal gas is much higher than that of the reformed natural gas. There is a schematic diagram of the anode heat exchange system in Fig. 2. In this system, the anode gas recycling is abbreviated, and the steam is supplied by the HRSG. In order to maintain the gas temperature at the anode inlet of the MCFC, the anode gas line is equipped with a heat exchanger, and the heat is transferred from the anode outlet gas.

2.2. Calculation of the MCFC performance

In ordinary MCFC-operating conditions, the relation between the cell voltage and the current density is written as

follows:

$$V \cong E - (R_{ir} + R_a + R_c)j \quad (5)$$

V and E are the cell voltage and the Nernst voltage, respectively, R_{ir} , R_a , and R_c represent the cell resistance, and j refers to the current density. The Nernst voltage and the cell resistance are written as follows:

$$E = E^0 + \frac{RT}{2F} \ln \frac{P_{H_2,a} P_{CO_2,c} P_{CO_2,c}^{1/2}}{P_{CO_2,a} P_{H_2O,a}} \quad (6)$$

$$R_{ir} = A_{ir} \exp\left(-\frac{\Delta H_{ir}}{RT}\right) \quad (7)$$

$$R_a = A_a T \exp\left(\frac{\Delta H_a}{RT}\right) P_{H_2,a}^{-0.5} \quad (8)$$

$$R_c = A_{C1} T \exp\left(-\frac{\Delta H_{C1}}{RT}\right) P_{O_2,c}^{-0.75} P_{CO_2,c}^{0.5} + A_{C2} T \exp\left(\frac{\Delta H_{C2}}{RT}\right) \times \left\{ m_{CO_2,c} + A_{C3} m_{H_2O,c} \exp\left(\frac{\Delta H_{C3}}{RT}\right) \right\}^{-1} \quad (9)$$

Here E^0 reveals the standard electro-motive force at the average cell temperature. P_i and m_i designate the partial pressure and the mole fraction of gas species i , respectively, and T expresses the average temperature of the cell. The constants, R and F , are the gas constant and the Faraday's constant, and the subscripts, a and c, denote the anode and cathode gas, respectively. A_{ir} , ΔH_{ir} denote the frequency coefficient of internal resistance and the activation energy, respectively.

Table 1
Gas composition of coal gas and reformed natural gas (mol%)

Gas species	Coal gas	Reformed natural gas
H ₂	24.6	47.0
CO	57.6	7.6
CO ₂	1.0	6.6
H ₂ O	0.6	34.5
N ₂	16.2	0

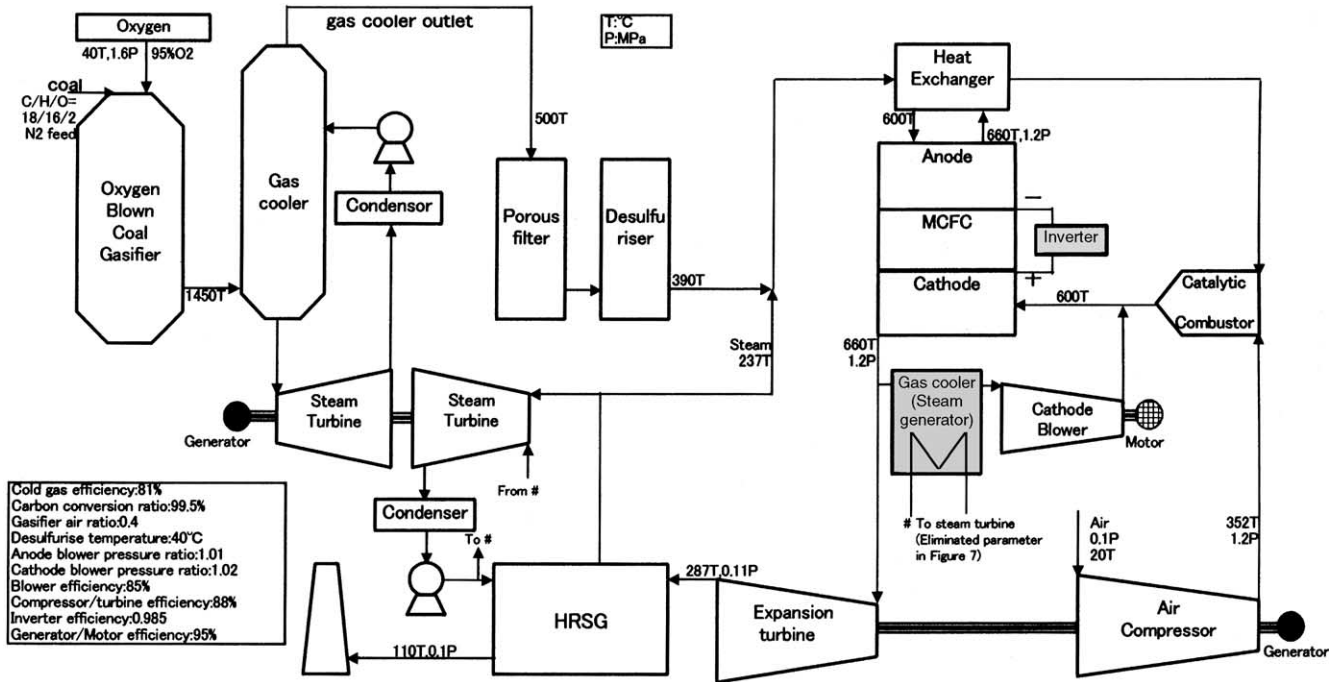


Fig. 2. Schematic design of anode heat exchange IG/MCFC system.

ΔH_a , ΔH_{C1} , ΔH_{C2} , ΔH_{C3} give an indication of the activation energy, and A_a , A_{C1} , A_{C2} , A_{C3} , are the coefficients derived from tests on single cells, which have a reactive area of 100 cm². Each parameter appearing in the equations regarding the cell performance is listed in Table 2.

2.3. Limit of gas condition and definition of *K* value

In this paper, the gas conditions that are required for the electricity generation with the practical cell are supposed. The supposed conditions are the non-carbon deposition at the anode inlet, 1 mol% of remaining H₂ at the anode outlet, and 0.1 MPa of the CO₂ partial pressure at the cathode inlet. The assumed cell conditions are summarised in Table 3.

As mentioned above, the water–gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ in the anode gas channel does not completely amount to the equilibrium once the CO-rich gas with H₂S is supplied. To reflect the not-equilibrium state of the

Table 2
Coefficients and activation energy of cell

	Magnitude
A_{ir} (Ohm cm ²)	9.84e–3
ΔH_{ir} (kJ mol ⁻¹)	23.8
A_a (Ohm cm ² atm ^{0.5} K ⁻¹)	9.5e–7
ΔH_a (kJ mol ⁻¹)	27.9
A_{C1} (Ohm cm ² atm ^{0.25} K ⁻¹)	6.91e–15
ΔH_{C1} (kJ mol ⁻¹)	179.2
A_{C2} (Ohm cm ² K ⁻¹)	3.75e–9
ΔH_{C2} (kJ mol ⁻¹)	67.2
A_{C3}	1.07e–6
ΔH_{C3} (kJ mol ⁻¹)	95.2

Table 3
Supposed gas condition required to stable operation

Location	Required gas condition	Purpose
Anode inlet	Non-carbon deposition	Stable supply of fuel
Anode outlet	H ₂ concentration >1 mol%	Stable generation of cell
Cathode inlet	CO ₂ partial pressure <0.1 MPa	Prevent NiO dissolution

water–gas shift reaction of the cell performance, the *K* value is introduced as follows:

$$K = \frac{\{([H_2] \cdot [CO_2]) / ([CO] \cdot [H_2O])\}_{not-equilibrium}}{\{([H_2] \cdot [CO_2]) / ([CO] \cdot [H_2O])\}_{equilibrium}} \quad (10)$$

Here the subscript ‘equilibrium’ means the equilibrium value at an average cell temperature of 630 °C. The magnitude of value *K* corresponds to the not-equilibrium state when *K* is less than 1.

The net thermal efficiency in this study is defined as follows:

$$\begin{aligned} \text{Net thermal efficiency} = & \{[\text{MCFC AC output}] \\ & + [\text{Gas turbine output}] + [\text{Steam turbine output}] \\ & - [\text{Cathode blower consumption}] \\ & - [\text{Anode blower consumption}] \\ & - [\text{Feed water pump consumption}]\} / \\ & [\text{Calorific value of supplied coal}] \\ & - \text{Other consumption (2\% of Calorific value of supplied} \\ & \text{coal)}. \end{aligned} \quad (11)$$

3. Results and discussions

3.1. Carbon deposition

The outlet gas composition of the coal gas is presented in the carbon–hydrogen–oxygen equilateral ternary diagram in Fig. 3. The dividing line between the carbon deposition and the non-deposition area is calculated in consideration of the water–gas shift and the Boudard reaction. If the anode gas recycling ratio rises to 100% in the anode gas recycling system, the anode inlet gas composition moves to CO₃ in the diagram. On the other hand, the added steam ratio is infinite in the anode heat exchange system, and the anode inlet gas should be 100% H₂O, which is pointed out in the diagram. Therefore, the point of the anode inlet gas composition moves to the point of H₂O with the multiplication of the steam ratio. By the result of the gas composition at the anode inlet, it has been evaluated that the anode gas recycling system requires approximately 80% anode gas recycling, and the anode heat exchange system requires 60% humidity.

3.2. Investigation of the not-equilibrium state

Material and heat balance of the anode gas recycling system is calculated by using the parameter *K*. In Fig. 4, the H₂ concentration in the anode outlet gas and the net thermal efficiency is presented versus *K* for a fuel utilisation of 80, 90 and 95%. The H₂ concentration of the anode outlet gas and the net thermal efficiency decreases with the reduction of the value *K*. Because H₂ has an important function in the electricity generating reaction, CO needs to be water–gas shifted to H₂ to be used as fuel in the electricity generating reaction. The reduction of the *K* value leads to a shortage of

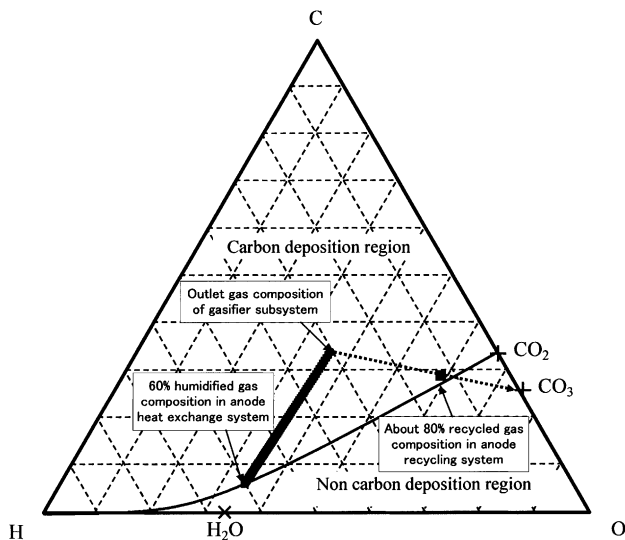


Fig. 3. Carbon–hydrogen–oxygen equilateral ternary diagram in anode recycling system and anode heat exchange system. Calculated temperature is 600°C and pressure is 1.2 MPa.

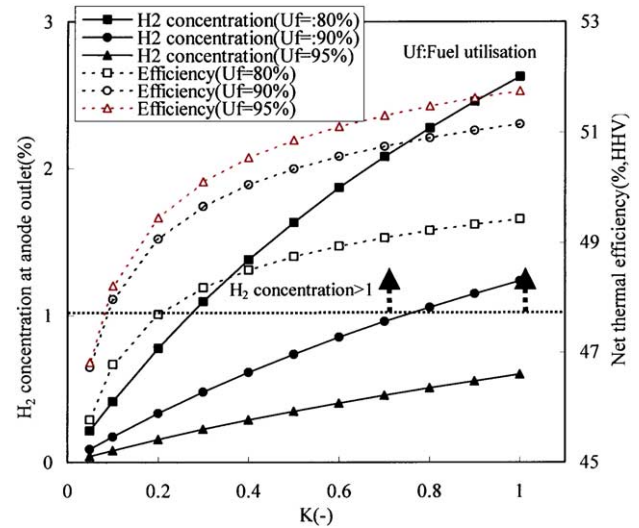


Fig. 4. H₂ concentration at anode outlet and net thermal efficiency vs. *K* in anode recycling system.

H₂ supply in the anode gas channel. As a consequent, the cell voltage drops and the net thermal efficiency of the total power plant decreases. If the value *K* is less than approximately 0.3, the H₂ concentration is less than 1 mol% in the anode outlet gas, when the operated fuel utilisation is 90 and 95%. Therefore, the anode gas recycling system should be operated at an approximate fuel utilisation of 80%.

A similar study has been carried out for the anode heat exchange system, and the results are presented in Fig. 5, which has the same format as in Fig. 4. The difference is in the tendency of decreasing the rate of the anode outlet H₂ concentration, and of changing the rate in its absolute value of net thermal efficiency. Since the fuel gas of the anode heat exchange system should be mixed with steam from

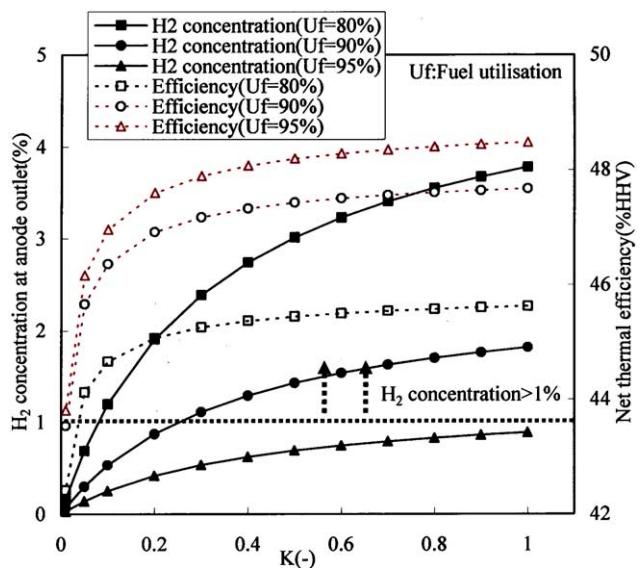


Fig. 5. H₂ concentration at anode outlet and net thermal efficiency vs. *K* in anode heat exchange system.

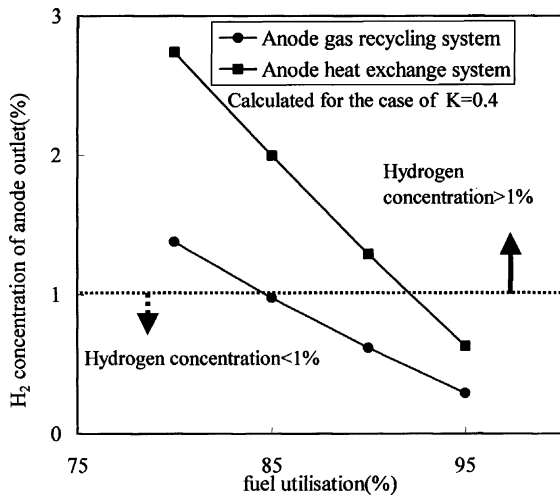


Fig. 6. H₂ concentration of anode outlet gas vs. fuel utilisation.

HRSG so as to avoid the carbon deposition problem, the H₂O concentration is great in the anode inlet gas. The addition of steam makes progress in the water–gas shift reaction easier, and the H₂ concentration is kept higher compared to the anode gas recycling system. Therefore, the H₂ concentration of the anode outlet gas remains at more than 1 mol%, even if *K* decreases to be approximately 0.3 and the fuel utilisation is set to be 90%.

In Fig. 6, the H₂ concentration of the anode outlet gas is described versus the fuel utilisation for the case that the *K* value is set at 0.4, for the discussed two different systems. By looking at this comparison, it is obvious that the anode heat exchange system should be operated with a higher fuel utilisation than the anode gas recycling system.

3.3. Study of the heat removal rate from the cathode gas recycling equipment to the steam cycle

The inlet and outlet gas temperature of MCFCs should be controlled due to the fact that the operating temperature range is limited, i.e. from 600 to 660 °C. To keep the cathode outlet gas temperature at the defined value (660 °C), the volume of airflow from the air compressor is regulated. To set the cathode inlet gas at the prescribed temperature (600 °C), the cathode gas recycling flow rate is adjusted. If heat is removed from the cathode gas recycling line to the gas cooler (steam generator), the MCFC system requires a smaller amount of air supplied by the air compressor, because the amount of heat that should be removed by the air is smaller. The diminution of the airflow leads to a smaller amount of energy consumption for the air compressor, and the net thermal efficiency of the plant is improved. However, a decrease of the air supply rate leads to a relative increase of the cathode CO₂ partial pressure. From the point of view of NiO dissolution, a low partial pressure of CO₂ is preferable.

In this section, the cathode CO₂ partial pressure is examined with the parameter of the removed heat, which is transferred by the gas cooler (steam generator) equipped in the cathode gas recycling line. The calculated systems are the anode gas recycling system and the anode heat exchange system. The net thermal efficiency is estimated for the different *K* values, which have been mentioned above. The net thermal efficiency is drawn against the CO₂ partial pressure of the cathode gas in Fig. 7; the removed heat from cathode gas recycling line to the steam turbine by the gas cooler (steam generator) is eliminated as a parameter. If the *K* value changes, the H₂ concentration of the anode outlet gas also

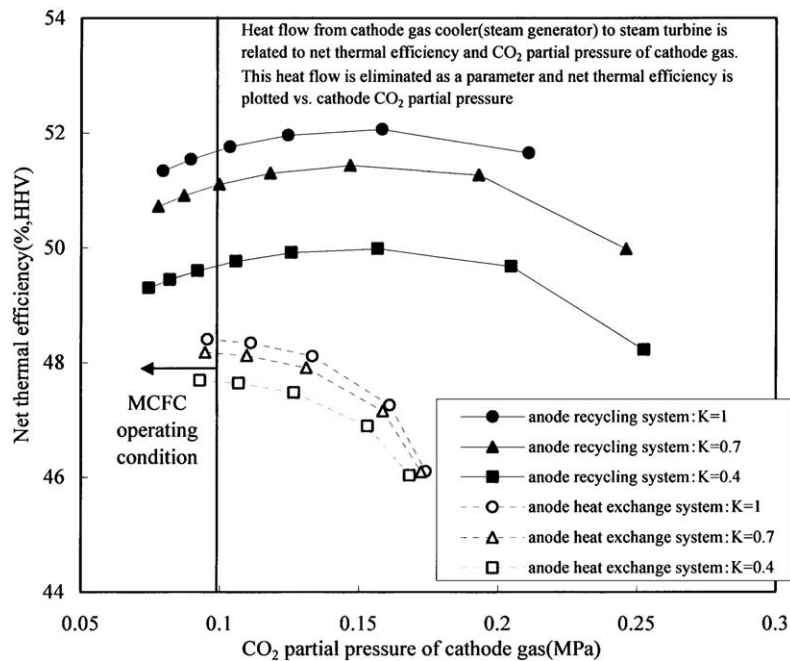


Fig. 7. Net thermal efficiency vs. CO₂ partial pressure of cathode gas with the parameter of removed heat from cathode gas cooler (boiler) to steam turbine. Set plant fuel utilisation is adjusted so that the anode outlet H₂ concentration is estimated to be 1 mol%.

Table 4
Maximum fuel utilisation that maintains H₂ concentration of 1 mol% at the anode outlet gas, with corresponding value *K*

Value <i>K</i>	Anode recycling system (%)	Anode heat exchange system (%)
1	91.5	94.4
0.7	89.5	93.7
0.4	84.7	92.2

changes. Therefore, the maximum fuel utilisation also varies to maintain the H₂ concentration in the anode outlet gas at more than 1 mol%. In the figure, the fuel utilisation corresponds to each *K* value selected, so that the H₂ concentration of the anode outlet gas is calculated to be 1 mol%. Calculated fuel utilisations with the corresponding *K* value can be gathered from Table 4.

In the anode gas recycling system, the net thermal efficiency has a peak in the CO₂ partial pressure where the net thermal efficiency of the anode heat exchange system increases as the CO₂ partial pressure of the cathode gas decreases. The range of cathode gas CO₂ partial pressure is different in each system, which is mainly caused by the difference of supplied fuel gas flow rate. The fuel gas in the anode heat exchange system is 60% humidified, so that the heat removed from MCFC by the anode gas is more than that in the anode gas recycling system; supplied air flow rate required to remove heat out of MCFC is different in each system. The calculated net thermal efficiency in the anode heat exchange system is lower than that in the anode gas recycling system, because the production of steam waists the net thermal efficiency in the anode heat exchange system. However, the anode heat exchange system has the advantage of stabilising the electricity generation with practical MCFCs.

4. Conclusions

Material and heat balance of the IG/MCFC system has been calculated. The estimation has been carried out considering the gas conditions that are required to stabilise the

electricity generation with practical cells. The discussed systems are the anode gas recycling and the anode heat exchange system. Not-equilibrium state of water–gas shift reaction has been supposed in anode gas channel and the following can be concluded.

- (1) In order to avoid the carbon deposition problem at the anode inlet, the anode gas recycling system requires approximately 80% re-circulation of the anode outlet gas, whereas the anode heat exchange system requires 60% humidity of the fuel gas.
- (2) The anode heat exchange system should be operated with a higher fuel utilisation than the anode gas recycling system, because the addition of steam makes progress in the water–gas shift reaction easier, and the H₂ concentration is kept higher compared to the anode gas recycling system.
- (3) Due to the examination of the heat removed from the gas cooler (steam generator) in cathode gas recycling line to the steam turbine, the net thermal efficiency of the anode gas recycling system has a peak for CO₂ partial pressure where the net thermal efficiency of the anode heat exchange system increases as the CO₂ partial pressure of the cathode gas decreases.

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