

Investigation of CO₂ and Steam Co-electrolysis Conditions for Synthesizing Carbon Recycled Methane

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ABSTRACT

An investigation of methane synthesis by co-electrolysis using renewable energy was conducted. The aim was to achieve highly efficient energy conversion in carbon recycling. Specifically, the investigation focused on the reaction conditions that apply when carbon dioxide and high-temperature steam are used to obtain syngas, which is a mixture of carbon monoxide and hydrogen made by co-electrolysis. First, the co-electrolysis performance of the electrolyte supported cell and of the fuel electrode supported cell were compared in order to determine the characteristics of a solid oxide electrolysis cell that are suited to syngas production. It was found from the results of that comparison that both the electrolysis current density and the syngas conversion rate are higher with the fuel electrode supported cell. Next, the relationship between the electrolysis current density and the source gas throughput quantity, which is a design parameter for the solid oxide electrolysis cell reactor, was obtained using a fuel electrode supported cell. Confirmation was also obtained of the source gas composition needed to match the syngas composition to the theoretical molar ratio for producing methane gas, which is an operation criterion for such reactors.

1. Introduction

Countries around the world have declared ambitious targets and initiatives oriented to achieving carbon neutrality by the year 2050 as a measure to counter the climate change caused by carbon dioxide (CO₂) and other greenhouse gases⁽¹⁾.

One of the measures being investigated is carbon dioxide recycling (carbon recycling) using renewable energy, and attention is being directed to technology for methane production (methanation) by the power to gas (P2G) approach. P2G is a technology for converting the electricity from renewable energy into gaseous fuel. The source gas for methanation is CO₂, and exhaust gases from steelworks⁽²⁾, garbage incinerating facilities⁽³⁾, thermal power plants, and other such facilities are considered valuable sources for that CO₂. Methane (CH₄) that has been produced using electricity from 100% renewable energy is defined as carbon neutral green methane, which has prospects for conversion to city gas or use as an alternative fuel⁽⁴⁾. Since the composition of city gas is approximately 90% CH₄, green methane can be injected into existing natural gas and city gas pipelines for transport and storage.

The aim of the present research, therefore, is the kind

of highly efficient carbon recycled CH₄ synthesis shown in Fig. 1. In co-electrolysis, simultaneous electrolytic reactions in CO₂ and high-temperature steam (H₂O) yield syngas. In other words, this is a system to synthesize CH₄ by means of the mixture of carbon monoxide (CO) and hydrogen (H₂) that is syngas.

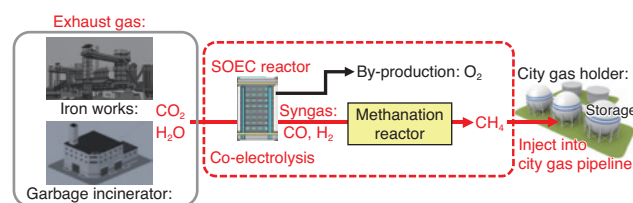


Fig. 1 Co-electrolysis methanation system via syngas

2. Achieving High-efficiency Methane Production

2.1. Methane Synthesizing Process

There are two main methods of CH₄ production by P2G, as shown in Fig. 2, that are being investigated⁽⁴⁾.

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In the method in Fig. 2(a), H₂ is produced by steam electrolysis or alkaline water electrolysis carried out upstream. Next, the produced H₂ and CO₂ are mixed together and supplied to a downstream thermochemistry reactor where CH₄ synthesis is carried out by the Sabatier reaction.

In the method in Fig. 2(b)⁽⁵⁾⁻⁽⁷⁾, the co-electrolysis reaction of CO₂ and H₂O upstream produces syngas that is supplied to a downstream methanation reactor. There CH₄ synthesis is carried out by thermochemical reaction.

Comparison of these two methods with attention to the chemical species involved in the reactions shows that for the method in Fig. 2(a), it is necessary to temporarily store the H₂ produced upstream by electrolysis and mix it with CO₂ so that it matches the mol number needed for CH₄ synthesis downstream. It can then be introduced into the thermochemistry reactor. When large-scale production of CH₄ is envisioned, therefore, it will be necessary to install new storage tanks and pipelines for the electrolyzed H₂. Preparation of the related statutes and technical regulations associated with that activity will also be an issue.

In Europe, the possibility of injecting electrolyzed H₂ into city gas pipelines and using it as a part of city gas is also being considered. However, as H₂ has a lower heat value per volume than CH₄, there are limits on the amount of H₂ that can be mixed in, and its use has not been expanding⁽⁸⁾.

With the approach in Fig. 2(b), on the other hand, if the composition of the syngas produced upstream by co-electrolysis can have a mol number that matches what is needed for CH₄ synthesis downstream, then that total amount can be introduced directly into the methanation reactor and there will be no need for intermediate gas storage. It is also the case that the source gases in Fig. 2(b) have lower mol numbers so that the energy needed to raise the pressure and temperature of the source gas supply can be limited proportionately. The H₂O that is produced as a by-product simultaneously with CH₄ following the synthesis reaction also has a lower mol number, so the dehydration energy can be reduced.

For the present research, therefore, it was decided to use the method in Fig. 2(b), which can be expected to consume less energy outside the reaction path and to involve more

highly efficient methanation.

2.2. Syngas Production by Co-electrolysis

In order to more efficiently obtain syngas to serve as source gas for methane synthesis, a solid oxide electrolysis cell (SOEC) was used as the co-electrolysis reactor for the present research.

Figure 3 shows a conceptual diagram of co-electrolysis by an SOEC reactor. The CO₂ and H₂O that serve as source gases are simultaneously subjected to electrolysis reduction and the syngas that will serve as a source for the CH₄ synthesis reaction is obtained.

In co-electrolysis, the reactions shown in Eqs. (1) and (2) occur simultaneously in the fuel electrode. CO, H₂, and oxygen ions (O²⁻) are produced from the source gas and electrons (e⁻).



The aqueous shift reaction shown in Eq. (3) also occurs in parallel as by-production.



At the oxygen electrode, oxygen (O₂) is generated from O²⁻ as shown in Eq. (4).



Syngas production by co-electrolysis occurs as an endothermic reaction, as shown in Fig. 4. The energy required for this co-electrolysis reaction is shown in Eq. (5).

$$\Delta H = \Delta G + T\Delta S \quad (5)$$

ΔH : Enthalpy [kJ]

ΔG : Gibbs energy [kJ]

T : Operating temperature [K]

ΔS : Entropy [kJ/K]

Here ΔH is defined as the total energy needed for the reaction, ΔG as the energy supplied as electricity, and $T\Delta S$ as the energy supplied as heat. As a portion of the reaction energy can also be supplied as heat in this way, the use, for example, of waste heat from steelworks, garbage incinerating facilities, thermal power plants, and other such

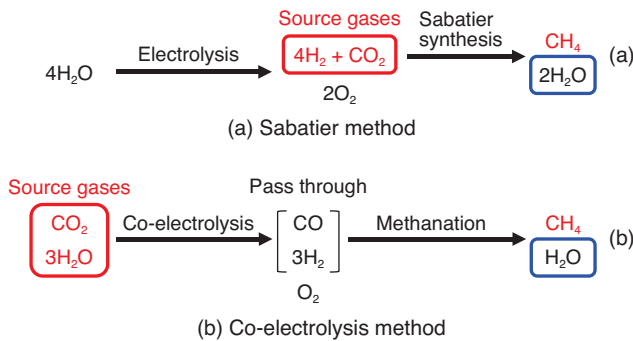


Fig. 2 Comparison of methane synthesis processes

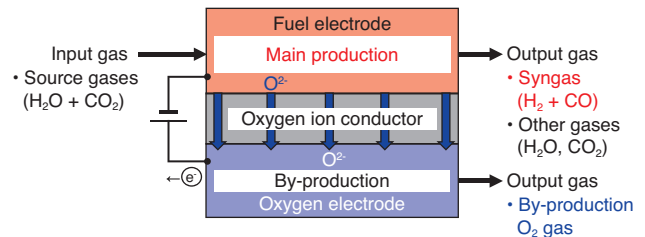


Fig. 3 Structure and material flow in SOEC co-electrolysis reactor

facilities could reduce the input energy. This is anticipated as an advantage of SOEC over other methods⁽⁹⁾. This may result in the apparent P2G energy conversion efficiency exceeding 100% when SOEC is used, so the heat balance needs to be taken into consideration when comparing with other methods.

The SOEC requires an operating temperature of at least 650°C or more in order to lower the resistance for O^{2-} transport in the ion conductor⁽¹⁰⁾. On the other hand, the heat generated by the overvoltage that accompanies this lowering of O^{2-} transport resistance can be used for endothermic reaction. The potential at which the heat absorbed by a high-temperature electrolytic reaction is in balance with the heat generated by electrolytic cells is called the thermo-neutral voltage. The electrolytic voltage is around 1.3 V/cell. When the voltage exceeds this, therefore, self-sustaining operation becomes possible and a supply of heat from outside becomes unnecessary.

2.3. Design Parameters for SOEC Reactors Using Co-electrolysis

The size of an SOEC reactor used for syngas production is decided on the basis of the CO_2 target throughput quantity ($Ta\ CO_2\ tqr$), as shown in Eq. (6)⁽¹¹⁾. To make the SOEC reactor more compact and reduce its manufacturing cost, it is effective to reduce the cell stacking number ($No\ cr$). For that purpose, it is necessary to raise the electrolysis current density and increase the CO_2 throughput quantity ($CO_2\ tra$) per unit active area.

$$Ta\ CO_2\ tqr = CO_2\ tra \cdot S\ ac \cdot No\ cr \quad (6)$$

$Ta\ CO_2\ tqr$: CO_2 target throughput quantity per minute per SOEC reactor [t - CO_2 /min/Reactor]

$CO_2\ tra$: CO_2 throughput quantity per minute per unit active area [t - CO_2 /min/ m^2]

$S\ ac$: Active area of cell [m^2 /Cell]

$No\ cr$: Cell stacking number per SOEC reactor [Cells/Reactor]

On the other hand, increasing the flow rate of source

gas input to the SOEC reactor in order to increase the CO_2 throughput quantity may lower the rate of conversion to syngas⁽¹²⁾. It has been conjectured that this occurs because when source gas exceeding the throughput capacity of the SOEC reactor is input, blow-by ends up occurring. This is why it is important to ascertain the source gas throughput quantity from the electrolysis current density and to ascertain the blow-by source gas quantity from the syngas conversion rate in order to determine the electrode area per cell and cell stacking numbers.

2.4. Operation Criteria for SOEC Reactors Using Co-electrolysis

With syngas production using an SOEC reactor, the aqueous shift reaction in Eq. (3) occurs in parallel with the electrolytic reactions of CO_2 and H_2O shown in Eqs. (1) and (2). For this reason, it is possible that the amount of H_2O in the source gas input to the SOEC reactor that is converted to H_2 , and the amount of CO_2 that is converted to CO , may not be equal to each other. The theoretical molar ratio required to carry out CH_4 synthesis in the downstream methanation reactor is $H_2/CO:3$. In order to have the gas output from the SOEC reactor match this ratio, therefore, it is important to adjust the H_2O/CO_2 molar ratio in the source gas that is input upstream to the SOEC reactor as well as to ascertain the temperature dependence of the aqueous shift reaction.

3. Research Goals

With regard to methanation carried out through syngas production by co-electrolysis of CO_2 and H_2O using an SOEC reactor, the following matters constituting SOEC reactor design parameters and operation criteria were investigated with the aim of increasing the efficiency of methanation systems.

- (1) Selection of SOEC type suited to syngas production and grasp of that SOEC type's structure
- (2) Confirmation of electrolysis current density characteristics, source gas throughput quantity, and syngas conversion rate
- (3) Confirmation of source gas H_2O/CO_2 molar ratio for syngas production that provides the theoretical ratio for CH_4 synthesis and confirmation of reaction conditions

4. SOEC and Test Apparatus

4.1. Selection of SOEC Type Suited to Syngas Production

The basic structure of an SOEC is as shown in Fig. 5. It is made up of three main layers, which are the fuel electrode layer, the electrolyte layer, and the oxygen electrode layer.

At present, no SOEC designed for dedicated co-electrolysis use exists. Therefore a solid oxide fuel cell (SOFC) was put to use as an SOEC. The fuel electrode layer is a combination of the nickel (Ni) catalyst, which has e^- conductivity, and a porous structure of oxide ceramic

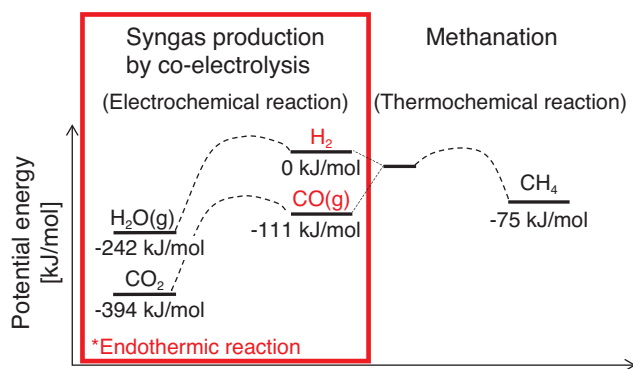


Fig. 4 Potential energy diagram in syngas synthesis and methanation

(YSZ, GDC) with O²⁻ conductivity. Here the e⁻ are received, the CO₂ and H₂O source gases go through reduction by co-electrolysis reaction, and syngas is produced. The electrolyte layer (ScSZ, YSZ) is the layer that transports the O²⁻ produced in the fuel electrode to the oxygen electrode that is the positive electrode by electrical field. It also functions as a barrier that blocks the permeation of gas between the fuel electrode and the oxygen electrode. The oxygen electrode layer is an oxide ceramic (LSM, GDC, LSC) that includes lanthanum (La) and strontium (Sr), forming a porous structure that has O²⁻ conductivity and e⁻ conductivity. This is where O²⁻ transported from the fuel electrode is oxidized and produces O₂ and e⁻.

When the structures of the two types of SOEC shown in Fig. 5 are compared, the electrolyte supported cell (ESC) is a structure in which the electrolyte layer is thick and the fuel electrode layer is thin. The fuel electrode supported cell (FSC) is a structure in which the electrolyte layer is thin and the fuel electrode layer is thick. As the FSC has a thinner electrolyte layer, it can also be considered to have lower O²⁻ transport resistance, but when used as an SOEC, it is not known which of the ESC and FSC has the advantageous structure. For the present research, therefore, the ESC and FSC were first compared and a selection made.

4.2. SOEC Reactor for Co-electrolysis Testing

The structure of the SOEC reactor used for the present research is shown in Fig. 6.

A tubular type of SOEC also exists⁽¹¹⁾. For the present research, however, a planar SOEC was selected in order to simplify the comparison of different SOEC materials and structures, the expansion of electrode area (active area) by stacking, and so on.

In exterior shape and size, the SOEC is 50 mm square and the electrode is 40 mm square. The SOEC is sandwiched between collectors (mesh of 100 0.7-mm diameter Au wires), and outside that is an inter connector made of alumina, with piping attached, in a structure that holds the contents in place. The inter connector is formed with 10 straight gas channels that are rectangular in cross-section, 2 mm wide and 0.4 mm deep. Their flow paths are arranged so that the fuel electrode gas channels and oxygen electrode gas channels form counter flows with each other.

Type	ESC	FSC
Cross-sectional view		
Plan view		

Fig. 5 Layer structure and materials in SOEC

4.3. Test Apparatus

Figure 7 shows an overview of the co-electrolysis test apparatus. The CO₂ for use as source gas is supplied at 99.99% purity from a gas cylinder. After having the supply flow rate of the CO₂ adjusted by a mass flow controller (MFC), it is humidified by being passed through a pure water bubbler that is heated to 90°C or higher. The H₂O/CO₂ molar ratio is adjusted using the dew point setting of the bubbler, and is then input as source gas to the fuel electrode gas channel intake of the SOEC reactor. The oxygen electrode gas channel intake of the SOEC reactor was supplied with a carrier gas consisting of inert argon (Ar) gas with 5% of O₂ by volume. Gas was input to the SOEC reactor with the reactor outlets of both electrodes open to atmospheric pressure.

Electrolysis current was applied by the parallel operation of intelligent bipolar power supplies (PBZ20-20 from Kikusui Electronics Corp.). The volume flow of the gas output from the SOEC reactor after co-electrolysis reaction was measured using high-accuracy film flow meters (SF-U Series VP-3U, VP-4U from HORIBA STEC Co., Ltd.). After dehumidification, the gas was injected into

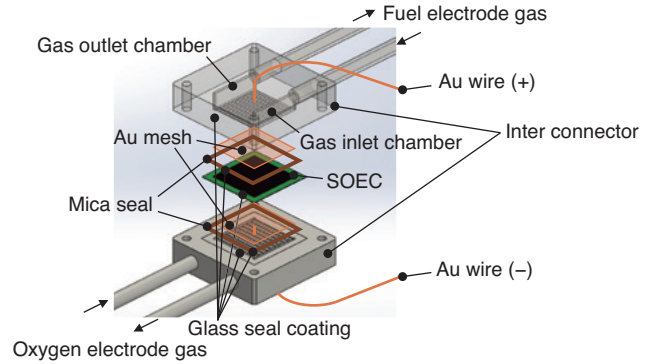


Fig. 6 SOEC reactor test rig structure

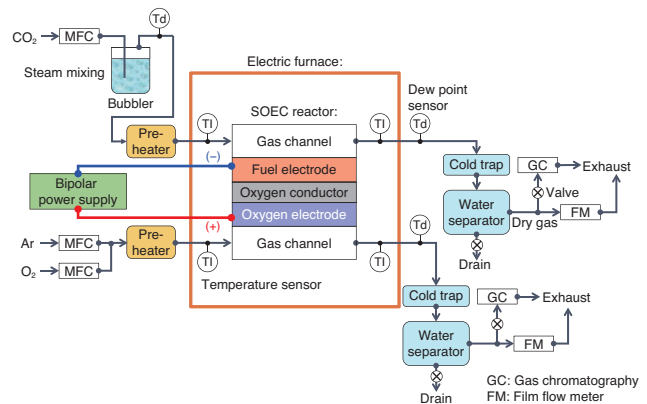


Fig. 7 Co-electrolysis test apparatus

a micro gas chromatograph (990 Micro GC from Agilent Technologies) and its composition was analyzed. Gas analysis of H_2 , O_2 , N_2 , CH_4 , and CO was carried out with Ar gas as the carrier gas, with molecular sieve 5A in the separation column, using a thermal conductivity detector (TCD) for measurement. For CO_2 analysis, measurement was made with a TCD using helium (He) gas as the carrier gas and Pora PLOT Q in the separation column.

5. Test Conditions

The present research was carried out as described in Sections 5.1. to 5.3., in that order.

5.1. Selection of SOEC Type

To select an SOEC type that is suited to syngas production, the ESC and FSC were compared by the syngas conversion rate, which is expressed as the proportion of output syngas quantity by co-electrolysis reaction per input source gas quantity. The test conditions are shown in Table 1.

The H_2O/CO_2 molar ratio for the source gas input to the SOEC reactor was set at 3, the same value as the theoretical molar ratio for CH_4 production. The operating temperature was set at $800^\circ C$, taking O^{2-} transport resistance in the ion conductor into consideration. The flow rate of source gas input to the SOEC reactor was set at 1.12 NL/M, which is 10% of source gas utilization at an electrolysis current density of $1.0 A/cm^2$. The electrolysis current was adjusted so that the cell voltage reached a thermo-neutral voltage of 1.3 V/cell and maintained this level under these conditions. Next, the source gas flow rate was gradually reduced from this point and the conditions under which electrolysis current density and syngas conversion rate reach their highest level at thermo-neutral voltage were confirmed.

5.2. Evaluation of Electrolysis Current Density Characteristics

Electrolysis current density characteristics were evaluated in order to obtain design parameters for the SOEC reactor. The test conditions are shown in Table 2.

The H_2O/CO_2 molar ratio for the source gas input to the SOEC reactor was set at 3, the same value as the theoretical molar ratio for CH_4 production. The operating temperature was set at $850^\circ C$, taking the heat resistance temperature of the cell into consideration. The cell voltage was adjusted to a thermo-neutral voltage of 1.3 V/cell.

5.3. Evaluation of Source Gas H_2O/CO_2 Molar Ratio Characteristics

The source gas H_2O/CO_2 molar ratio characteristics were evaluated in order to obtain criteria for the SOEC reactor operating conditions. The test conditions are shown in Table 3.

The operating temperature was set at 700, 800, and $850^\circ C$ in order to determine the temperature dependence of the aqueous shift reaction. Here again the cell voltage was

Table 1 Evaluation conditions for selection of SOEC type

Parameters	Values	Units
Steam/ CO_2 molar ratio	3	N.A.
Operating temperature	800	$^\circ C$
Source gas flow rate	0.16-1.12	NLM*
Operating pressure	No pressurization	N.A.
Cell voltage	1.3	V

*NLM: Normal liters per minute

Table 2 Evaluation conditions for characteristics of electrolysis current density

Parameters	Values	Units
H_2O/CO_2 molar ratio	3	N.A.
Operating temperature	850	$^\circ C$
Source gas flow rate	0.16-0.56	NLM
Operating pressure	No pressurization	N.A.
Cell voltage	1.3	V
Current density	1.3-2.2	A/cm^2

Table 3 Evaluation conditions for characteristics of source gas H_2O/CO_2 molar ratio

Parameters	Values	Units
H_2O/CO_2 molar ratio	0.1-5	N.A.
Operating temperature	700, 800, 850	$^\circ C$
Source gas flow rate	0.16	NLM
Operating pressure	No pressurization	N.A.
Cell voltage	1.3	V

Table 4 Indices for evaluating co-electrolysis performance

Evaluation index	Definition
Current density	Current per unit active area
H_2 conversion rate	Molar number of production H_2 / Molar number of input H_2O
CO conversion rate	Molar number of production CO / Molar number of input CO_2
Syngas conversion rate	Molar number of production H_2 and CO / Molar number of input $H_2O + CO_2$
Faraday efficiency	Reaction electrons of production gas / Supplied electrons
Conversion energy efficiency	Combustion heat value of production gas (HHV) / Supplied electricity

adjusted to the thermo-neutral voltage of 1.3 V/cell.

The indices used to evaluate co-electrolysis performance are shown in Table 4⁽¹³⁾.

Electrolysis current density is the electrolysis current per unit active area. The greater the current density, the higher the source gas (mixture of CO_2 and H_2O) throughput quantity will be.

The rate of H₂ conversion by co-electrolysis expresses the conversion rate of H₂O in the source gas input to the SOEC reactor into H₂. Similarly, the CO conversion rate expresses the conversion rate of CO₂ into CO. The syngas conversion rate is the sum of the H₂ conversion rate and CO conversion rate, and it expresses the conversion rate of source gas into syngas. Higher conversion rates can be said to indicate higher performance as a reactor.

The Faraday efficiency expresses the reaction electron number as converted from the amount of syngas production per input electron number, and the directly produced CH₄ was also included in the reaction electron number. The conversion energy efficiency expresses the rate of energy conversion to the high heating value (HHV) of the gas that was produced from the amount of electricity input to electrolysis. Since the heat energy indicated in Eq. (5) is also used in the co-electrolysis reactions for the present research, the energy in the produced gas may at times exceed the input electricity.

6. Results and Discussion

6.1. Selection of SOEC Type

The results from comparison of co-electrolysis performance by ESC and FSC are shown in Fig. 8. This shows the relationship between the syngas conversion rate and the electrolysis current density with respect to the flow rate of source gas input to the SOEC reactor.

When the source gas input flow rate was increased, the electrolysis current density increased regardless of differences in SOEC structure. Conversely, the syngas conversion rate went down. In the results of this test, the electrolysis current density reached its highest level under the condition of a source gas flow rate of 1.12 NLM. With the FSC type, the figure was 1.4 A/cm², and with the ESC type, it was 0.2 A/cm², indicating that the former can be expected to achieve throughput quantities that are

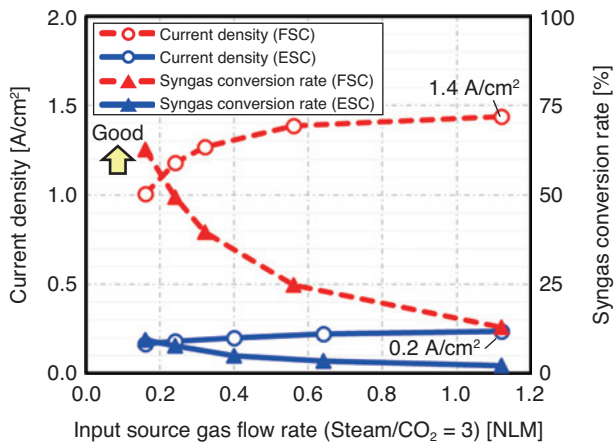


Fig. 8 Comparison of co-electrolysis performance ESC vs FSC at 800°C

Table 5 Comparison of co-electrolysis performance ESC vs FSC at 0.16 NLM

Parameters	ESC	FSC	Units
Syngas conversion rate	10	63	%
Current density	0.2	1.0	A/cm ²

seven times greater. The FSC is thought to have a greater throughput quantity than the ESC because, as shown by the cross-sectional view in Fig. 5, the electrolyte layer thickness of 3 μm in the FSC is thinner than the 150 μm in the ESC, so that this layer in the FSC has lower transport resistance of O²⁻.

On the other hand, the source gas input flow rate that yielded the highest syngas conversion rate was 0.16 NLM. The electrolysis current densities in ESC and FSC under this condition are shown in Table 5.

As for the syngas conversion rate, the ESC figure was 10% while the FSC figure was six times greater at 63%. Under this condition, the FSC also achieved an electrolysis current density of 1.0 A/cm², for five times larger throughput quantity than the ESC, at 0.2 A/cm². This difference in the conversion rate is thought to be due to the fuel electrode layer thickness, which is 50 μm in the ESC but 400 μm in the FSC, eight times thicker because it includes a support structure function, so that the amount of catalyst is correspondingly greater, and this promoted electrochemical reaction.

In light of the above results, the FSC type of SOEC was selected as suited to syngas production. Subsequent investigation of syngas production conditions was also carried out using the FSC type.

6.2. Evaluation of Electrolysis Current Density Characteristics

Figure 9 shows the changes occurring in electrolysis current density and in the amounts of H₂, CO, and CH₄ synthesized when the source gas input flow rate was gradually increased from 0.16 NLM. When the source gas

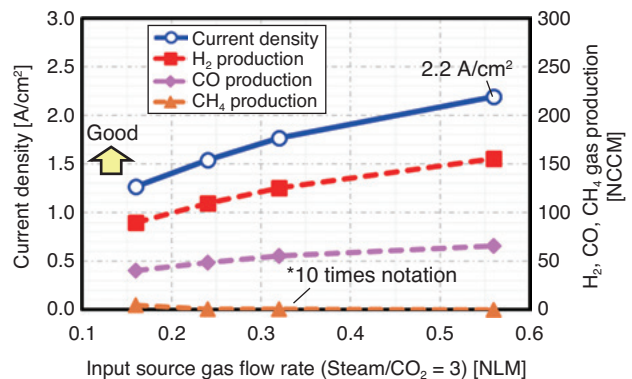


Fig. 9 Current density and produced gases at various input source gas flows at 850°C

flow rate was increased, the electrolysis current density increased so that the amounts of H_2 and CO synthesized also increased. However, it was found that the increase in amounts slowed down on the higher flow rate side so that it did not increase proportionately. Traces of CH_4 production were also detected, but a decrease in the amount produced was observed on the high flow rate side.

Next, Fig. 10 shows the results for calculation of the syngas conversion rate with respect to electrolysis current density from the test results in Fig. 9.

It was found that when the electrolysis current density increases, the syngas conversion rate decreases. This is thought to occur because the unreacted source gas that the SOEC reactor was unable to process completely was subject to blow-by. Source gas blow-by wastes the heating and humidifying energy for that blow-by amount, which lowers system efficiency. It is for this reason that SOEC reactor design gives priority to the syngas conversion rate.

The characteristics of source gas throughput quantity and syngas conversion rate, which constitute SOEC reactor design parameters, were successfully determined from the above. In order to increase the source gas throughput quantity, it is necessary to investigate SOEC reactor structure and related matters that will promote the supply of source gas to the catalyst in a way that reduces the amount of unreacted source gas.

6.3. Evaluation of Source Gas H_2O/CO_2 Molar Ratio Characteristics

Figure 11 shows the results when the H_2O/CO_2 molar ratio of the source gas input to the SOEC reactor is changed so that the composition of the output syngas will be $H_2/CO:3$, which is the theoretical molar ratio for CH_4 synthesis.

It was found that in order to make the output gas have a molar ratio of $H_2/CO:3$, it was necessary to increase the H_2O/CO_2 molar ratio of the input source gas to excess H_2O as the operating temperature rose higher. It has been conjectured that because the aqueous shift reaction from the right side to the left side of Eq. (3) takes place in parallel

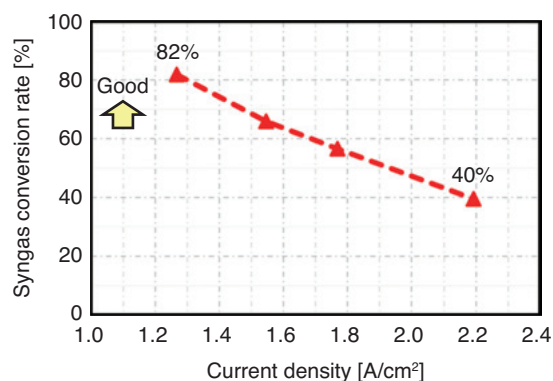


Fig. 10 Syngas conversion rate at various current densities at 850°C

with the co-electrolysis reaction. It is thought that the higher the temperature rises, the more the reactions that produce H_2O and CO from the H_2 produced by co-electrolysis and from the CO_2 in the unreacted source gas are promoted. The H_2O/CO_2 molar ratio that the input source gas should have in order for the output gas to have the theoretical molar ratio for CH_4 synthesis was 3.0 at 700°C, 3.3 at 800°C, and 4.2 at 850°C.

Figure 12 shows the Faraday efficiency and conversion energy efficiency at the various temperatures when this is done.

The Faraday efficiency was from 90% to 92% at the various temperatures, indicating high electrolysis performance. It was also found that the conversion energy efficiency exceeded 100%, at from 102% to 103%. This was because syngas was produced by an endothermic reaction that, in addition to the electricity directly involved

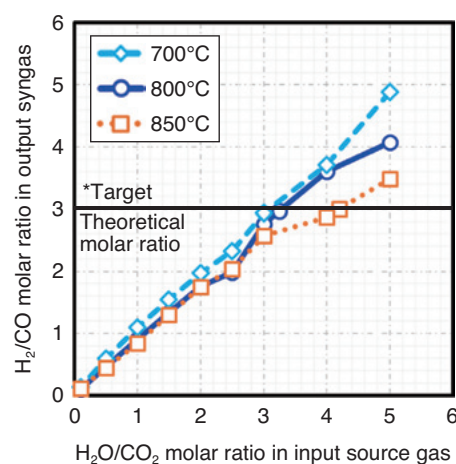


Fig. 11 H_2/CO output molar ratio vs H_2O/CO_2 input molar ratio at various temperatures

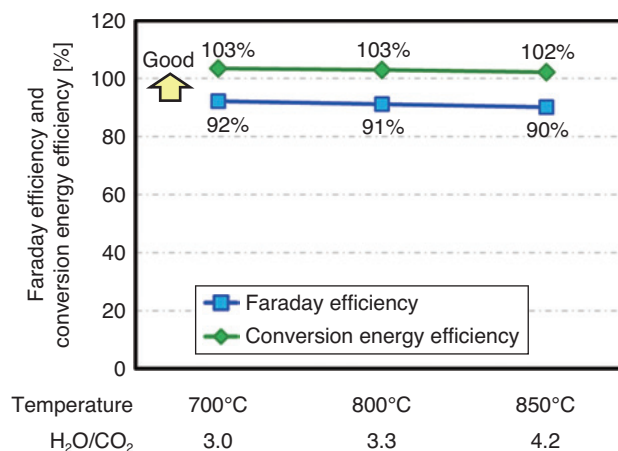


Fig. 12 Faraday efficiency and conversion energy efficiency at various temperatures

in the reaction, was also able to use the heat energy added to the SOEC.

Next, the highest electrolysis current density reached at the various temperatures is shown in Fig. 13. The highest electrolysis current density signifies the source gas throughput quantity, and it was found to reach its highest point at 800°C.

Similarly, the syngas conversion rate at the various temperatures is shown in Fig. 14. The syngas conversion rate shows the same tendency as the electrolysis current density with regard to temperature characteristics, and here also it was found to reach its highest point at 800°C.

It is conceivable that the syngas conversion rate was higher at 800°C than at 700°C because the rise in temperature caused the O²⁻ transport resistance to diminish so that the electrolysis current density increased and the source gas throughput quantity increased. At 850°C, however, the syngas conversion rate decreased, and it is conceivable that this was because the aqueous shift reaction in Eq. (3) caused the amount of H₂O produced to increase, causing an excess of H₂O in the source gas, leading to the decrease in the conversion rate.

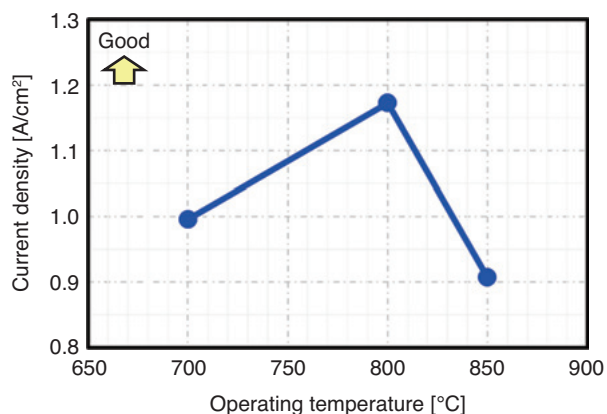


Fig. 13 Current density at various temperatures

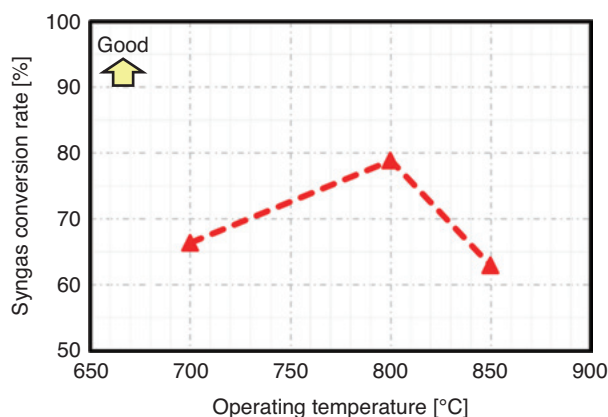


Fig. 14 Syngas conversion rate at various temperatures

7. Conclusion

With the aim of achieving highly efficient carbon recycled CH₄ synthesis, an investigation of the operation criteria and reaction conditions was conducted for an SOEC reactor that yields syngas as a mixture of CO and H₂ produced by co-electrolysis of CO₂ and H₂O. The following results were obtained.

- (1) The results from comparison of ESC and FSC co-electrolysis performance showed that FSC achieved higher CO₂ throughput quantity per unit active area, as expressed by electrolysis current density and syngas conversion rate, and FSC was found to be suited to syngas production.
- (2) Although increasing the input source gas quantity caused electrolysis current density to increase, the syngas conversion rate went down. This suggested that, in order to aim for a highly efficient CH₄ synthesizing system, it would be more advantageous to operate at a lower flow rate even if the size of the SOEC reactor is increased.
- (3) It was found that in order to produce an output gas composition of H₂/CO:3, which is the theoretical molar ratio for CH₄ synthesis, it was necessary to increase the H₂O/CO₂ molar ratio of the source gas to excess H₂O. It was also found that as the electrolysis current density and the syngas conversion rate were both higher at an operating temperature around 800°C, there is a temperature suited to SOEC co-electrolysis operation.

It was found from the above that in order to achieve highly efficient CH₄ synthesis, an SOEC reactor with FSC installed should be operated at around 800°C at a low flow rate. For greater compactness of the SOEC reactor, the desired aim would be a high source gas flow rate, or in other words, high electrolysis current density operation. Under present conditions, however, this conflicts with the syngas conversion rate, and it is hoped that research with a view to optimization can be continued in future.

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