Possibility of Application of Solid Oxide Electrolysis Cell on a Smart Iron-making Process Based on an Active Carbon Recycling Energy System

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Efficient carbon dioxide (CO₂) reduction into carbon monoxide (CO) is required to establish a smart iron-making process based on an active carbon recycling energy system (iACRES). A disk-type solid oxide electrolysis cell (SOEC) was prepared and examined experimentally for application to the CO₂ reduction process in iACRES. A SOEC with a cathode|electrolyte|anode structure of Ni-YSZ|YSZ|La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} was fabricated. The electrolysis of carbon dioxide was conducted at 800–900°C. A current density of 107.1 mA cm⁻² was measured between the cathode and anode at 900°C and at 2.52 V. The production rates of CO and O₂ were in agreement with the theoretical values determined using Faraday's law. Evaluation of iACRES using the experimental results indicated that an estimated 0.73 high-temperature gas cooled reactor units as the primary energy source for CO₂ reduction and a SOEC surface area of 0.098 km² were required for the reduction of 30% CO₂ in blast furnace gas emitted from a conventional blast furnace.

KEY WORDS: carbon recycling; carbon dioxide reduction; carbon monoxide; high-temperature gas cooled reactor; iron-making system.

1. Introduction

The increase of carbon dioxide (CO₂) emissions due to the consumption of fossil fuels causes global environmental problems. In Japan, almost all primary energies are imported from other countries. Reductions of CO₂ emissions and primary energy imports have been difficult problems to be addressed. However, a new low-carbon energy system has been proposed, which is referred to as an active carbon recycling energy system (ACRES).¹⁾ With ACRES, carbon energy materials such as carbon monoxide (CO) are regenerated from CO₂ and reused cyclically. CO has a higher exergy ratio ($\Delta G/\Delta H$) than hydrogen (H₂) and methane, which makes CO an important candidate as a recycling media for ACRES. In ACRES, CO₂ separated from exhaust gas is reduced to CO, as shown in Eq. (1), and the regenerated CO is used cyclically as an energy medium.

CO₂ reduction into CO is a key technology for the establishment of ACRES. It is possible to reduce CO₂ into CO by an electrolysis process, such as with a solid oxide electrolysis cell (SOEC), which employs the opposite operation of a solid oxide fuel cell (SOFC).²⁾ CO₂ electrolysis in aque-

ous media at room temperature has been demonstrated.³⁾ High temperature CO₂ electrolysis by SOEC at 800–900°C has been reported for CO₂ and H₂ mixture,⁴⁾ and pure CO₂,⁵⁾ and tube-type cell⁶⁾ in previous studies. It was already shown that electrodes based on La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O₃ (LSCM) had high performance for CO₂ electrolysis in CO and CO₂ mixture,⁷⁾ a LaGaO₃-based electrolyte was capable to reduce CO₂ into CO at lower temperature up to 700°C.⁸⁾

ACRES is expected to be applicable with iron-making processes, because CO can be used directly for the reduction of iron ore. After CO₂ generated from a blast furnace is captured, CO is regenerated from CO₂ using the SOEC. The regenerated CO is recirculated in a blast furnace, so that the quantity of coke (reducing agent) required can be reduced. A proposed application of ACRES for an iron-making process referred to as a smart iron-making system based on ACRES (iACRES) is shown in Fig. 1. As primary energy sources for a high-temperature gas cooled reactor (HTGR) used for ACRES, renewable energies such as solar and wind, and waste heat from high-temperature industrial processes are proposed as candidates. The HTGR, in particular, is a chief candidate for iACRES because it is capable of sufficiently high-temperature heat production up to 950°C and stable heat output for iACRES.

Although previous studies demonstrated CO₂ electrolysis, knowledge about availability of SOEC CO₂ electrolysis under operation conditions of gas compositions and temper-

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Fig. 1. Schematic of the iACRES concept.

atures for iACRES was still small. Then, in this study, a disk-type SOEC was prepared and the SOEC electrolysis performance was measured experimentally at the laboratory scale. The availability of a practical iron-making system based on iACRES was evaluated using the experimental results for the SOEC.

2. Principle of SOEC

A SOEC electrolyzes carbon dioxide by the application of an overvoltage in the cell. SOEC has a three-layer structure of cathode|solid electrolyte|anode. CO₂ is supplied to a porous cathode and diffuses through the micropores of the electrode. CO₂ is then decomposed into CO and O²⁻ by electrons supplied to cathode, as shown in Eq. (2):

The oxygen ions generated are transported to the anode through ionic defects in the solid oxide electrolyte and oxygen is generated:

The overall reaction from Eqs. (2) and (3) gives Eq. (1). The energy change for Eq. (1) is given by

$$\Delta H = \Delta G + T\Delta S \quad (4)$$

where ΔH [J mol⁻¹], ΔG [J mol⁻¹], and ΔS [J mol⁻¹ K⁻¹] are the Gibbs free energy, enthalpy, and entropy changes for the reaction, respectively, and T [K] is the reaction temperature. For establishment of the reaction by the supply of ΔH , the ΔG term is covered by the use of electricity, while the $T\Delta S$ term is provided by thermal energy.

The decomposition voltage of CO₂ (E° [V]) is dependent on ΔG , which is expressed as

$$E^\circ = -\Delta G / (nF) \quad (5)$$

where n is the number of the valence electrons and F is Faraday's constant (= 96 500 C/mol). The catalytic reactions at the electrodes, gas diffusion in the electrode layer, and ohmic resistance must be considered for performance improvement of SOEC. Yttria-stabilized zirconia (YSZ) is mainly used as solid oxide electrolytes,⁹⁾ which become oxygen ion conductors at high temperatures around 700–1 000°C.

Fig. 2. Schematic diagram of the SOEC experimental apparatus.

Fig. 3. Cross-section of the SOEC reactor.

3. Experimental

3.1. SOEC Apparatus

The experimental apparatus shown in Fig. 2 was constructed to measure the performance of the SOEC. CO₂ gas is introduced to the reactor as a reaction gas, and Ar is used as a carrier gas at the cathode side. N₂ is used as a carrier gas for oxygen generated via electrolysis at the anode side. The reacted gases were analyzed using gas chromatography with a thermal conductivity detector (GC-8A, Shimadzu) attached with packed-columns of Porapak Q and Molecular Sieve 13x using argon for carrier gas.

A potentiostat/galvanostat (HAL3001, Hokuto Denko), ammeter (HM-104A, Hokuto Denko), and voltmeter (HE-104A, Hokuto Denko) were used to measure the electrochemical performance.

Figure 3 shows a cross-sectional schematic of the SOEC reactor. The SOEC (20 mm diameter and 1.0 mm thick) was held by two outer alumina tubes (20 mm outer diameter) and sealed with glass rings. The electrolyte cell thickness was relatively thicker than conventional cell, then, it was thought that IR loss of the cell was relatively larger than conventional one. It was expected that electrolysis performance would be improved by the reduction of the thickness. Reaction gases were supplied through inner tubes (6 mm outer diameter). The electrical current was collected using platinum mesh

(7×7 mm²) attached to each end of the inner tubes. The glass ring seals were melted at 950°C prior to operation of the SOEC.

3.2. Cell Preparation

In this study, a cell with the structure Ni-YSZ|YSZ|La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) was selected. For the cathode, Ni and YSZ were employed as the catalyst and oxygen ion conductor, respectively. LSCF, which is an ion-electron mixed conductor, was used as the anode. The YSZ oxygen ion conductor was used as the electrolyte. To prepare an electrolyte disk, YSZ powder (TZ-8Y, 40 nm particle diameter, Tosoh) was molded into a disk form (25 mm diameter and 1.2 mm thick, 1.6 g) by uniaxial pressing. The disk was placed in a protective cover and isostatically pressed with an oil pressure compressor at 200 MPa. The disk electrolyte sample was then sintered at 1400°C for 2 h in a high-temperature electric furnace.

The Ni-YSZ electrode was prepared by mixing NiO (99.9%, Wako) and YSZ (TZ-8Y) powders in a weight ratio of 8:2 by ball-milling with 10 mL of ethanol for 30 min. Graphite powder (16 wt%, 40 μm particle diameter, Wako) was added to the NiO-YSZ mixture as a pore former. This cathode material was mixed with dispersant consisting from α-terpineol (as solvent) 85 wt%, ethyl cellulose (as bonding) 7 wt%, carboxylic acid-based polymer (as surfactant) 2 wt%, polyethylene glycol (as plasticizer) 3 wt% and dibutyl phthalate (as plasticizer) 3 wt% to produce an ink having mixing weight ratio of the cathode material : dispersant of 4 : 6. The cathode ink mixture was painted with a brush on one side of the electrolyte disk to a diameter of 12 mm. At the anode side, the LSCF (1.2 μm particle diameter, Powrex) mixed conductor was applied as an ink using the same procedure as that for the cathode with the same mixing weight ratio. The quantities of coated NiO-YSZ and LSCF after drying were 4.7 and 3.9 mg, respectively. Pt wire (0.25 mm diameter, Nilaco) was wound around the edge of the electrolyte disk and adhered with Pt paste to form the reference electrode. The cell was then sintered at 1050°C for 2 h under H₂ flow to produce cathode cermet structure. Then, the cell was set between the two outer alumina tubes.

3.3. Electrolysis Process

Hydrogen was primarily flowed in cathode electrode for the reduction of NiO to Ni for formation of the Ni-YSZ cermet cathode at 900°C for 1 hour. During electrolysis, CO₂ and Ar were each supplied to the cathode side at 25 mL min⁻¹, and N₂ was supplied to the anode side at 30 mL min⁻¹. A three-electrode measurement was employed to obtain current density-voltage curves with 0.1 V steps from 0.0 V to 2.0 V. The polarization characteristics were measured at 800, 850, and 900°C. The compositions of the reactant gases were analyzed using gas chromatography and production rates of CO and O₂ were calculated using the measured composition and flow rate data.

4. Results and Discussion

4.1. Polarization Performance of SOEC

Figure 4 shows current density-voltage curves for the Ni-YSZ|YSZ|LSCF cell at various temperatures. At all temper-

Fig. 4. Current density-voltage curves for the Ni-YSZ|YSZ|LSCF cell at various temperatures.

Fig. 5. CO and O₂ production rate from the Ni-YSZ|YSZ|LSCF cell as a function of current density.

atures, the current density began to increase with voltage from the decomposition voltage of CO₂ at around 0.7 V. A current density of 107.1 mA cm⁻² was measured between the cathode and anode at 2.52 V and 900°C. The cell resistance increased with decreased temperatures because the oxygen ion conductivity was decreased.

Figure 5 shows the CO and O₂ production rate as a function of current density. The theoretical production rate is dependent on the current density according to Faraday's law. Faraday efficiencies showing the ratio of the calculated theoretical electrons for the reduction to the actually supplied electrons are depicted in Fig. 6 for the results in Fig. 5. The production rates obtained are almost in agreement with the theoretical rates. However, measured values of the efficiency were around 0.1 smaller than ideal value of 1.0. During measurement of the efficiency under each condition, degradation of the value and production of gas phase by-product were not observed. It was inferred that the loss of the efficiency did not come from carbon deposition, and would

depend on insufficiency of measurement accuracy. The CO production rate was $0.48 \mu\text{mol s}^{-1} \text{cm}^{-2}$ at 107.1 mA cm^{-2} and 900°C , which confirmed that the CO_2 reduction shown in Eq. (1) proceeded in the SOEC.

Figure 7 shows scanning electron microscopy (SEM) images of the Ni-YSZ and LSCF electrode surfaces after operation of the SOEC. Gas diffusion paths remained in both the cathode and anode after SOEC operation.

In the Ni-YSZ cathode, Ni particles with diameters of approximately $1\text{--}2 \mu\text{m}$ form an electronic conduction network to which fine YSZ particles are attached. In the LSCF anode, the LSCF particles were distributed uniformly, so

Fig. 6. Faraday efficiencies for CO and O_2 productions for the results in Fig. 5.

Fig. 7. SEM images of (a) Ni-YSZ cermet cathode and (b) LSCF anode electrode surfaces.

that there was sufficient space for gas diffusion. It is considered that these structures promoted the electrolysis reaction by allowing the diffusion of reactants and products.

4.2. Evaluation of Iron-making Process with iACRES using the Experimental Results

Based on the experimental results, iACRES as a combination of ACRES with a blast furnace was evaluated when CO_2 in the blast furnace gas (BFG) was reduced to CO by the SOEC. Heat and electricity generated from the HTGR were used together for the high-temperature CO_2 electrolysis in the SOEC. The required HTGR unit numbers and SOEC surface area for a blast furnace were calculated.

A blast furnace used conventionally in large ironworks¹⁰⁾ with an annual pig-iron production of 2.5 Mt y^{-1} was employed as a model for the evaluation. An HTGR plant, in which the secondary coolant has 600 MW-thermal (MWt) at 850°C ,¹¹⁾ was employed for the electrolysis. The electrolysis process of the SOEC was set to operate at 800°C . The experimental results for the SOEC at 800°C and assumption of enthalpy efficiency of the electrolysis of 90%, which is the value of conventional water electrolysis system for hydrogen production,¹²⁾ were thus employed in this evaluation. The CO and O_2 production rates were calculated using Faraday's law. **Table 1** shows the numerical calculation conditions and estimated values for the model presented in **Fig. 8**. It was estimated that $1.53 \times 10^3 \text{ m}^3$ of BFG was emitted for the production of 1 t of pig-iron, and 22% of the gas was carbon dioxide,¹³⁾ *i.e.*, $1.19 \times 10^3 \text{ mol s}^{-1}$ of CO_2 was emitted from the blast furnace. It was assumed that 50% of the generated CO_2 (358 mol s^{-1}) was reduced to CO with an elec-

Table 1. Numerical calculation conditions for iACRES as a combination of ACRES with a blast furnace.

Blast Furnace	
Annual iron production [$\text{Mt y}^{-1} \text{ BF-unit}^{-1}$]	2.50
BFG emission per pig-iron [$\text{m}^3 \text{ t}^{-1}$]	1.53×10^3
CO_2 content in BFG [vol.%]	22.0
CO_2 emission per pig-iron [$\text{m}^3 \text{ t}^{-1}$]	337
HTGR	
Output temperature [$^\circ\text{C}$] (Secondary cycle)	850
Thermal power [MWt]	600
Cycle efficiency [–]	0.380
He flow rate [kg s^{-1}]	439
SOEC	
Operation temperature [$^\circ\text{C}$]	800
Applied voltage [V]	2.47
Current density [A cm^{-2}]	0.071
Power density [W cm^{-2}]	0.174
CO production rate [$\mu\text{mol s}^{-1} \text{cm}^{-2}$]	0.366
O_2 production rate [$\mu\text{mol s}^{-1} \text{cm}^{-2}$]	0.183
CO conversion rate [–]	0.300
Enthalpy efficiency of electrolysis [–]	0.900

Fig. 8. Material and energy balances for the iron-making process based on iACRES.

blastolysis efficiency of 60%, *i.e.*, 30% of CO₂ emitted from the blast furnace was reduced to CO. Figure 8 shows calculation results. From measured current density of 0.071 A cm⁻² at 800°C, CO₂ decomposition rate of 0.37×10⁻⁶ mol s⁻¹ cm⁻² was calculated, and required surface area of SOEC cell was estimated as 0.098 km² for required CO₂ decomposition rate of 358.1 mol s⁻¹. 37.9 MWt and 171 MW of electricity (MWe) were required for the SOEC reduction of the CO₂. Then, total thermal output from HTGR of 493 MWt was needed. The thermal output was corresponding to output of 0.78 HTGR unit. If SOEC current density was improved to 1 A cm⁻², required SOEC cell surface area was expected to be reduced to 6.9×10³ m² (0.0069 km²). It was understood that the improvement of SOEC performance was important way for reduction of volume of CO₂ reduction facility. These evaluated values would be useful information for system scale evaluation in feasibility studies of iACRES.

5. Conclusions

SOEC experimental apparatus was fabricated for CO₂ reduction to CO. The SOEC experiment was conducted using a Ni-YSZ|YSZ|LSCF cell, and 107.1 mA cm⁻² of current density was provided at 2.52 V and 900°C. The iACRES evaluation indicated that 0.73 HTGR units and an electrode surface area of 0.098 km² were required for the reduction of 30% of the CO₂ in conventional blast furnace gas. These results indicate the validity of carbon cycling with iACRES.

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