Carbon Dioxide Reduction on a Metal-Supported Solid Oxide Electrolysis Cell

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Using iACRES, which is an ironmaking system based on the Active Carbon Recycling Energy System concept, to reduce or recycle CO₂ emitted from ironmaking processes, we electrolyzed CO₂ with a metal-supported solid oxide electrolysis cell (MS-SOEC) capable of providing a large cell surface area for the processing of large amounts of CO₂. The MS-SOEC current-density–voltage (I–V) curves reveal a change in slope at around 0.8 V, which is the theoretical decomposition voltage of CO₂. The CO production rate was 0.88 μmol cm^{−2} s^{−1} when 2.0 V was applied between the cathode and the anode at 800°C, while that for O₂ was 0.44 μmol cm^{−2} s^{−1}, which is consistent with the stoichiometry for CO₂ electrolysis. The Faraday efficiency was 48% at 900°C. Gas was observed to leak from the cell; this leakage will need to be overcome through improvements in the layer-production process in order to achieve an efficiency close to 100%. On the basis of the cell-based experimental results, the feasibility of a blast furnace based on iACRES and driven by an HTGR (high-temperature gas-cooled reactor) was evaluated. To reduce CO₂ emissions by 30.0%, the required MS-SOEC surface area was estimated to be 8.30×10⁴ and 3.98×10⁴ m² with 968 and 480 MWth of HTGR thermal output under Faraday efficiency of 48% and 100%, respectively. We confirmed that iACRES using MS-SOEC contributes to realizing low-carbon ironmaking by recycling CO₂ and reducing its emissions into the atmosphere.

KEY WORDS: carbon dioxide; carbon monoxide; metal-support; solid oxide electrolysis cell; carbon recycling.

1. Introduction

Ironmaking process and chemical industries emit large amount of carbon dioxide (CO₂) that causes global warming. Fossil-energy resources are imported in some countries, which economically suppresses those industries. To solve these problems, a new energy system referred to as the “Active Carbon Recycling Energy System” (ACRES)¹⁾ has been introduced. CO₂ is reduced chemically and recycled as a process material in ACRES. Carbon monoxide (CO) is a recycling-medium candidate for ACRES, as shown in Eq. (1), since CO has a higher exergy ratio ($\Delta G/\Delta H$) than hydrogen (H₂) produced through the reduction of water, and other hydrocarbons.

The co-product oxygen is also a useful industrial material. The ironmaking process that applies ACRES is referred to as “iACRES” (smart ironmaking process based on ACRES).²⁾ Exhausted CO₂ from the iACRES-based ironmaking process is recovered through a separation process, reduced to CO,

and reused in the process through recycling.

The reduction of CO₂ to CO is a key technology for the establishment of iACRES. CO₂ can be reduced to CO by a solid oxide electrolysis cell (SOEC) in which CO₂ electrolysis is carried out by the reverse operation of a solid oxide fuel cell (SOFC). A proposed iACRES for ironmaking is shown in Fig. 1. CO₂ is separated from the exhaust gas of the ironmaking process, and CO is regenerated by the SOEC. Since regenerated CO is recirculated in

Fig. 1. Schematic of the iACRES concept.

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the process, the quantity of coke (reducing agent) required is reduced. As an energy source for driving iACRES, renewable energy such as solar and wind power, high-temperature gas-cooled reactors (HTGRs),³⁾ and the waste heat from high-temperature industrial processes have been considered. In particular, HTGR is the main candidate for iACRES because it produces heat at high temperatures of up to 950°C, which are well matched to the needs of the SOEC process.

CO₂ electrolysis by SOEC has already been demonstrated.⁴⁾ A SOEC consists of anode/electrolyte/cathode layers. A conventional cell is constructed from ceramic materials because a ceramic electrolyte material has an efficient oxygen-ion (O²⁻) conductivity. Disk-type ceramic SOEC CO₂ electrolysis has been demonstrated,⁶⁾ which led to the conclusion that a cell surface area of the order of 10⁴ m² was required for the SOEC to achieve a blast-furnace-type iACRES.⁶⁾

However, the ceramic material in a SOEC is vulnerable to thermal and mechanical shock, which makes it difficult to create a cell structure with a large surface area. To overcome this, we developed a metal-supported SOEC (MS-SOEC) that can achieve a large surface area. This study experimentally examined the CO₂-electrolysis performance of the MS-SOEC, and its applicability to an ironmaking system based on iACRES was evaluated on the basis of the experimental SOEC results.

2. Experimental

Figure 2 displays the structure of the proposed MS-SOEC, which we refer to as “NYG4”. The SOEC was constructed on a 20-mm-diameter porous metal support, and has the following four layers on the metal substrate: anode | electrolyte | cathode | diffusion-barrier layer.

The porous metal support (prepared by Nippon Seisen Co., Ltd.) was made from SUS430 and SUS430 mesh with mesh-wire diameter of less 10 μm, and was welded at the center of the support. The anode, electrolyte, cathode, and diffusion-barrier layers were La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), yttria-stabilized zirconia (YSZ), NiO-YSZ, and La_{0.6}Sr_{0.2}Ca_{0.2}CrO₃ (LSCC), respectively. All layers are formed by the atmospheric plasma spray method (APS) (sprayed by TOCALO Co., Ltd.).

Figure 3 shows photographic images of the outside of the developed MS-SOEC, and an enlarged view of the cell mesh.

The MS-SOEC electrolyzes carbon dioxide by applying voltage on the cell,⁵⁾ as shown in **Fig. 4**.

CO₂ passes through the pores of the mesh and the diffusion-barrier layer, and reaches the cathode layer to receive electrons for the production of CO and O²⁻, according to:

O²⁻ is transported to the anode through the electrolyte and O₂ is generated:

Equation (1) is established through the progression of Eqs. (2) and (3).

Fig. 2. Structure of the NYG4 MS-SOEC.

Fig. 3. Photographic images of the developed MS-SOEC: (a) anode side, (b) cathode side, and (c) enlarged view of the cell mesh.

Fig. 4. MS-SOEC principles.

3. Experimental

3.1. SOEC Apparatus

The experimental apparatus was built to measure the performance of the SOEC. **Figure 5** displays the experimental SOEC system, while **Fig. 6** shows a schematic of the reactor cross-section. The cell is held by two outer alumina tubes with glass seal rings, and the reaction gases are supplied through the inner tubes.

CO₂ and N₂ are supplied to the cathode side as the feed gas; N₂ is also supplied to the anode as a sweep gas for the generated O₂. Gas compositions of the effluent gases from both electrodes were analyzed using a TCD gas chromatograph (GC-8AIT, Shimadzu CO.).

A potentiostat/galvanostat (HAL3001, Hokuto Denko), ammeter (HM-104A, Hokuto Denko), and voltmeter (HE-

104A, Hokuto Denko) were used to measure the electrochemical performance of the cell. Both electrical currents were collected by Pt mesh attached to the inner tubes, as shown in Fig. 6. The glass seal rings set between the cell and the alumina tube were melted at 950°C in advance to seal the cell to the tube in order to protect against gas leakage.

3.2. Electrolysis Process

Prior to any experiment, the NiO-YSZ in the cathode was reduced to Ni-YSZ with H₂ at 800°C for 1.0 h. During electrolysis, CO₂ (20 mL min⁻¹) and N₂ (20 mL min⁻¹) were supplied to the cathode side, and N₂ (30 mL min⁻¹) was supplied to the anode side. Current-voltage curves (I-V curves) were obtained by increasing the cathode-reference voltage over the 0.0–2.0 V range, at 800 and 900°C, in 0.1 V steps. The production rates of CO and O₂ were calculated from gas-composition analyses and flow rates.

3.3. Cell-Leakage Evaluation

The electrolyte layer produced by the APS method was prepared by the agglomeration of primary particles; consequently some porous paths still exist in this layer that facilitate the leakage of some gas through the whole cell. This leakage will be remediated in the future by improving the APS processing conditions that determine the thickness

of the layer, and the temperature of the plasma used to produce the layer. However, we first evaluated the current cell in order to demonstrate this new MS-SOEC process. The leakage factor, LF [%], was determined to show the relative level of leakage. For the MS-SOEC shown in Fig. 6, the cathode and anode sides were supplied with Ar (47.5 mL min⁻¹) and N₂ (30 mL min⁻¹), respectively. N₂ that leaked to the cathode side from the anode side was analyzed by gas chromatography, and the LF was calculated as the N₂ molar concentration at the cathode side in the Ar + N₂ mixture. As will be discussed in the following section about the SEM image in Fig. 10, some part of the boundary between cathode and electrolyte in the cell showed peeling-off which had possibility to cause cell reactivity fall. Then, the measurements in this study were performed after reaching stable condition to eliminate the effect of the initial change in the cell status.

4. Results and Discussion

4.1. Electrochemical Performance of the SOEC

Figure 7 displays I-V curves for NYG4 at 800 and 900°C; the LF was 5.6% at 800°C. This graph shows that the slope changes at around 0.5–1.0 V, which almost close to the theoretical decomposition voltage, V_{th} , of 0.98 V for CO₂, suggesting that CO₂ electrolysis has occurred. V_{th} was defined by the following equation:

$$V_{th} = \frac{\Delta G}{nF} \quad (4)$$

, where ΔG [kJ mol⁻¹], n [-] and F [C mol⁻¹] are the Gibbs's free energy for Eq. (1), the moles of migrated electrons in Eq. (1) of 2 and the Faraday constant equivalent to 96 500 C mol⁻¹, respectively.

A current density of 353.5 mA cm⁻² was flowed between the cathode and anode at 4.82 V/800°C; similarly, 339.8 mA cm⁻² was required at 4.38 V/900°C.

Figure 8 shows the effect of current density on the CO and O₂ production rates. The CO production rate was 0.88

Fig. 5. Schematic diagram of the experimental SOEC apparatus.

Fig. 6. Reactor cross-section.

Fig. 7. Current-density-voltage curves for NYG4. C-R: voltage between the cathode and the reference; C-A: voltage between the cathode and the anode.

$\mu\text{mol cm}^{-2} \text{ s}^{-1}$ at a current density of 353.5 mA cm^{-2} at 800°C ; similarly, the O_2 production rate was $0.44 \mu\text{mol cm}^{-2} \text{ s}^{-1}$ under the same conditions. The theoretical CO and O_2 production rate in Fig. 8 depend on current density, a consequence of Faraday's electrolysis law. The Faraday efficiency is defined by the following equation:

$$\text{Faraday efficiency} = \frac{\text{Production rate}}{\text{Theoretical value}} \dots\dots\dots (5)$$

In addition, the theoretical value is given by the following equation:

$$\text{Theoretical value} (\mu\text{mol s}^{-1} \text{ cm}^{-2}) = \frac{i}{nF} \dots\dots\dots (6)$$

where i is the current density [A cm^{-2}], n is the number of

Fig. 8. CO and O_2 production rates as functions of current density for NYG4.

reactive electrons $[-]$. When calculating the CO production rate, n in Eq. (6) is equal to 2, while $n = 4$ for O_2 . The calculated Faraday efficiencies of 48.1% for CO and 48.0% for O_2 (Fig. 8) are almost identical, which is consistent with the CO_2 -reduction stoichiometry and demonstrates that CO_2 reduction proceeds on the MS-SOEC. We ascribe the observation that the Faraday efficiency is less than 100% to the reformation of CO_2 from leaked CO and O_2 , although the amount of reformed CO_2 could not be evaluated using our apparatus. Remediation of this leakage through improvements in the layer-production process is required to achieve values close to 100%, which is the focus of our next study.

Figure 9 shows digital microscopy images of the cell surface before and after the experiment. The surface exhibited no cracks or breaks like ceramic materials, either before or after the experiment, suggesting that this cell was more durable physically than the ceramic-supported equivalent. SEM images of the cross-section of the cell after SOEC experiment are shown in Fig. 10. It is anxious that the boundary between anode and electrolyte has possibility to generate SrZrO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$ during the reaction, and also cathode and mesh-wire tend to react with CO. The boundaries between every layers can be observed clearly and every layers show homogeneous structures, then, it was thought that every layers kept original structure without side reactions during that reaction periods. However, some part of the boundary between cathode and electrolyte showed peeling-off which had possibility to cause cell reactivity fall. It was required to clarify the peeling-off generation cause and to remove the peeling-off between these layers by improvement of layer production procedure.

4.2. Evaluation of iACRES Using the Experimental Results

Based on above results, we evaluated a process that com-

Fig. 9. Digital images of the NYG4 MS-SOEC surface: (a) before the experiment and (b) after the experiment; (c) and (d) enlargements of the images in (a) and (b), respectively.

Fig. 10. SEM images of cross-section of the NYG4 MS-SOEC after SOEC experiment (a) Whole layers, (b) Cathode/electrolyte/Anode layers.

Table 1. Assumed specifications of the furnace used for the iACRES model based on a commercial blast furnace.⁹⁾

Annual pig-iron production [Mt y ⁻¹]	2.5
Blast furnace gas (BFG) emitted per pig-iron [Nm ³ t ⁻¹]	1.53 × 10 ³
CO ₂ emitted per pig-iron [Nm ³ t ⁻¹]	350
Total CO ₂ emissions [Nm ³ s ⁻¹]	27.7
CO ₂ content in BFG [vol.%]	22.8
CO content in BFG [vol.%]	22.0
H ₂ content in BFG [vol.%]	4.20
BFG outlet temperature [°C]	157

Table 2. Assumed HTGR operating conditions for the iACRES model based on the GTHTR-300.⁸⁾

Reactor thermal power [MWth]	600
Reactor core coolant	Helium gas
Core coolant flow [kg s ⁻¹]	439
Core inlet temperature [°C]	587
Core outlet temperature [°C]	850
Core coolant pressure [MPa]	6.9
Core power density [W mL ⁻¹]	5.4
Power conversion efficiency [%]	45
Electricity production [MWe]	270

biner MS-SOEC and iACRES for use in blast-furnace-class ironmaking. We assumed that part of the CO₂ generated from the furnace was reduced into CO by the MS-SOEC, and the heat and electricity generated from an HTGR with a 850°C secondary heat output and a 600 MWth heat output capacity (GTHTR-300⁸⁾) were used for SOEC electrolysis.⁸⁾ We calculated the required thermal output power of the HTGR and the cell surface area of the SOEC are necessary for the iACRES process.

The furnace specifications are based on those of a commercial large-scale blast furnace that produces pig iron at 2.5 Mt year⁻¹; **Table 1** lists the furnace model specifications based on this blast furnace.⁹⁾ The experimental electrolysis data from the SOEC at 800°C was employed for the MS-SOEC in this evaluation. **Table 2** lists the HTGR specifications based

Fig. 11. CO₂ balance in the iACRES model furnace.

on the GTHTR-300. The CO₂-recycle balance in the iACRES model is shown in **Fig. 11**. Half of the CO₂ generated from the furnace is recovered, while 60% of the CO₂ is reduced to CO by the MS-SOEC, and the generated mixed CO and CO₂ gas is supplied to the furnace as a part of the reduction gas; 30% of the total CO₂ is reduced to CO in the iACRES system. The MS-SOEC performance, based on the calculations for iACRES and the experimental data for NYG4, is shown in **Table 3**, assuming a Faraday efficiency of 48% as a measured value and 100% as a theoretical value. The overall simulation conditions and estimated values are shown in **Fig. 12**.

Table 4 shows the calculated results for the iACRES model; to achieve a reduction in CO₂ emissions of 30%, thermal output of 968 and 480 MWth from HTGR are required, and the necessary MS-SOEC surface area is calculated to be 8.30 × 10⁴ and 3.98 × 10⁴ m² under the efficiency of 48% and 100% as shown in Case 1 and 2, respectively. Improvement of Faraday efficiency was a practical subject for reduction of thermal power demand and required cell surface area. Then, the power density of the MS-SOEC needs to be enhanced through improvements in cell design in order to reduce further the surface area. This study reveals the potential scale of iACRES for realizing low-carbon ironmaking by recycling CO₂ and reducing CO₂ emissions into the atmosphere.

Table 3. MS-SOEC performance using the calculations for iACRES based on experimental data for NYG4 of SOEC.

Case	Case 1	Case 2
Faraday Efficiency [%]	48	100
Enthalpy efficiency of electrolysis [-]	0.900	
CO conversion efficiency [-]	0.600	
Operating temperature [°C]	800	
Applied voltage [V]	2.83	
Current density [A cm ⁻²]	0.180	
Power density [W cm ⁻²]	0.509	
CO production rate [$\mu\text{mol s}^{-1} \text{cm}^{-2}$]	0.448	0.933
O ₂ production rate [$\mu\text{mol s}^{-1} \text{cm}^{-2}$]	0.224	0.467

Table 4. Calculated results from the iACRES feasibility study based on experimental data for NYG4 of SOEC.

Case	Case 1	Case 2
Faraday Efficiency [%]	48	100
CO ₂ emission-reduction rate [%]	30.0	
SOEC electrical demand [MWe]	423	203
SOEC heat demand [MWth]	28.8	28.8
Required SOEC surface area [m ²]	8.30×10^4	3.98×10^4
Thermal demand from HTGR [MWth]	968	480

Fig. 12. Total material and energy balances of the iACRES system.

5. Conclusion

CO₂ electrolysis was demonstrated using an MS-SOEC extendable to a large surface area. I-V curves and gas-analysis data revealed that CO₂ electrolysis occurred on the MS-SOEC cell. CO and O₂ production rates of 0.88 and 0.44 $\mu\text{mol cm}^{-2} \text{s}^{-1}$, respectively, were obtained at 800°C by applying 2.0 V between the cathode and the reference. CO Faraday efficiencies of up to 48% were observed at 800 and 900°C. Gas leakage in the cell was detected; remediation of this leakage by improving the layer-production process is required to achieve a value close to 100%. A feasibility evaluation of iACRES based on a blast-furnace-class ironmaking system using HTGR outputs revealed that an MS-SOEC surface area of 8.30×10^4 and $3.98 \times 10^4 \text{ m}^2$, and 968 and 480 MWth of HTGR thermal output under Faraday efficiency of 48% and 100%, respectively, are required to reduce CO₂ emissions by 30.0%. We expect that MS-SOEC can be used to extend the surface area of SOEC for an iACRES system, and that iACRES with MS-SOEC will contribute to realizing low-carbon ironmaking through recycling CO₂ and reducing CO₂ emissions into the atmosphere.

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