Carbon Dioxide Electrolysis for a Carbon-recycling Iron-making System

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A new energy transformation system based on carbon recycling has been proposed; it is called the active carbon recycling energy system (ACRES) and has been developed in order to reduce the emission of carbon dioxide (CO₂) to the atmosphere. An experimental study based on the ACRES concept for carbon monoxide (CO) regeneration via high-temperature electrolysis of CO₂ was carried out using several solid oxide electrolysis cells (SOECs). Experimental results showed that a cell with the structure Pt-LSM cermet|YSZ|Pt-LSM cermet exhibited the highest current density and CO production rates of 0.52 mA·cm⁻² and 0.75 μmol·min⁻¹·cm⁻² respectively, at 900°C. On the basis of the cell's electrolytic characteristics, the scale of a combined ACRES CO₂ electrolysis/iron-making facility was estimated.

KEY WORDS: carbon dioxide; carbon monoxide; high temperature; electrolysis; SOECs; carbon recycling; iron-making system.

1. Introduction

The carbon content in the fossil fuels that are used as the primary energy resources that have sustained the economic growth of our society has caused a significant increase in the carbon dioxide (CO₂) concentration in the atmosphere. The excessive CO₂ levels have disturbed the delicate balance in the atmosphere, resulting in an atmospheric accumulation of solar thermal energy attributed to the greenhouse gases; this causes the average temperature of the earth to rise and the global climate to change.¹⁾ In Japan, the supply of fossil fuels used as primary energy resources depends mainly on imports. Energy in the imported fuels is 82% (18.9×10^{18} J) of all the primary energy used in Japan. Here, 7% of the fossil fuel is consumed in the iron-making process.²⁾ Japan undertook the obligation to follow the Kyoto protocol and is required to drastically reduce its CO₂ emissions. Any limit imposed on CO₂ emissions will directly affect the manufacturing and service industries. To deal with this problem a new carbon recycling energy system has been proposed and developed in order to reduce the emission of CO₂ into the atmosphere from industrial processes. In this new energy system, which is called the active carbon recycling energy system (ACRES), carbon is reused, cyclically consuming the CO₂ emissions at a large industrial facility; thus, it can reduce the emission of CO₂ to the atmosphere.^{2,3)}

A proposed application of ACRES to an iron-making process is shown in Fig. 1. The system is assumed to be ideal iron-making process. The system is powered by electricity and thermal energy generated from a high-temperature gas-

cooled reactor (HTGR). The regenerated carbon monoxide (CO) is recycled and used for the reduction of iron oxide into pure iron. CO₂ produced by the reduction process is regenerated into CO by the CO₂ electrolysis process using energy from the HTGR. Oxygen (O₂), a by-product of the CO regeneration process, can be a useful material for other oxidation processes. One promising aspect of CO regeneration using ACRES is that CO₂ electrolysis using a solid oxide electrolysis cell (SOEC) occurs at high temperatures. **Figure 2** shows the principal structure of an SOEC. CO₂ is fed to the cathode side and diffused through a layer of cathode material to the cathode-electrolyte interface where it is decomposed into CO and oxygen ions (O²⁻) by the input of electrons (e⁻). The CO molecules generated in the cathode side are collected, while the O²⁻ ions permeate through the dense electrolyte to the anode side. At the anode-electrolyte interface, the O²⁻ ions are oxidized to form O₂ and electrons. The electrons are transported to the cathode through the

Fig. 1. Schematic of the ACRES concept as applied to the iron-making process.

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Fig. 2. The CO₂ electrolysis process in the SOEC.

external circuit to complete the cycle. The reactions involved in CO₂ electrolysis by an SOEC can be expressed as follows:

The energy change for the reaction in Eq. (3) is given by

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

where T is the absolute temperature; ΔH , the enthalpy change; and ΔG , the Gibb's free energy. $T\Delta S$ can be considered as the amount of thermal energy required to reduce CO₂ to CO.

As shown in Fig. 2, electrolysis is performed by applying a sufficient electric potential to the SOEC. The procedure was carried out experimentally on the basis of the ACRES concept for CO regeneration via high-temperature electrolysis of CO₂ and CO regeneration by a SOEC was demonstrated. As yet, SOECs have attracted much interest owing to their high efficiency in producing H₂ and other synthetic fuels via high-temperature processes.⁴⁻⁸⁾ The principal goal of this work is to investigate the performance of a CO₂ electrolysis process that utilizes a tubular SOEC. Given the results of the SOEC experiments using different electrode materials, the performance of an ACRES system using the most effective SOEC electrode material is evaluated.

2. Experimental

An SOEC test apparatus, as described in Fig. 3, was built to study the performance of high-temperature electrolysis of CO₂. This test apparatus enables the use of the gases CO₂, CO, H₂, and Ar on the cathode side, while O₂ and N₂ can be used on the anode side.

2.1. Cell Preparation

In this study, three types of electrode materials, namely La_{0.8}Sr_{0.2}MnO₃ (LSM) with a diameter of 1 μm , platinum in the form of Pt paste, and Pt-LSM in *cermet* form, were tested. These materials were attached to a Y₂O₃-ZrO₂ (yttria-stabilized zirconia, YSZ), electrolyte tube and were structured as described below.

Cell-1 had a Pt-LSM *cermet*|YSZ|Pt-LSM *cermet* structure for the cathode|electrolyte|anode. The structures of

Fig. 3. Experimental SOEC apparatus for CO₂ electrolysis.

Cells 2 and 3 were LSM|YSZ|LSM and Pt|YSZ|LSM, respectively. The outer and inner surfaces of YSZ tubes were used as the locations for the cathode and anode electrodes, respectively.

For Cell-1, the Pt-LSM *cermet* paste was prepared by mixing together 10.0 g LSM powder, 0.5 g Pt paste (TR-7907 from Tanaka Kikinzoku Kogyo), 1.0 g binder, and 2.0 g dispersant. An appropriate amount of distilled water was added to the mixture. The binder and dispersant were added to the mixture to improve the adhesion to the electrolyte surface and to adjust the viscosity. The components were mixed thoroughly and the resulting paste was coated onto the cathode and anode sides by a dip-coating method. The electrolyte tube was composed of YSZ (ZR-8Y from Nikkato Corporation) and had outer (cathode) and inner (anode) diameters of 8 mm and 5 mm, respectively. The effective surface area for the cathode electrode was 25.1 cm². The cell was then dried at room temperature for several hours before being light sintered at 800°C under inert atmosphere for 4 h.

In the case of Cell-2, the LSM paste was prepared by mixing 10.0 g LSM powder (Powlex), 1.0 g binder, 2.0 g dispersant, and distilled water. The components of the mixture were dispersed with a dual-frequency ultrasonic cleaner. The resulting paste was coated onto the cathode and anode sides by a dip-coating method. The cell was then dried at room temperature for several hours and sintered at 1150°C under inert conditions for 4 h.

In the case of Cell-3, platinum paste was used for the cathode. Here, 0.5 g of the paste was mixed with appropriate amounts of ethanol and binder. The mixture was dispersed by using an ultrasonic disperser. The resulting mixture was coated onto the cathode side surface of the YSZ tube by a dip-coating method. The LSM paste for the anode surface of Cell-3 was prepared using the same method as for the anode material prepared for Cell-2. After coating, the cell was then light sintered at 800°C under inert conditions for 4 h in order to remove any inorganic material that might have been present in the Pt paste.

2.2. Electrolysis Process

A stainless steel mesh (SUS 304) was used as the current collector. Electric current was supplied to the cell using a Galvanostat (Hokuto Denko HAL 3001). Prior to starting the electrolysis experiments, hydrogen reduction was performed as a pretreatment for each cathode for about 5 h at 800°C. During the electrolysis process, pure CO₂ at a flow rate of 25 mL·min⁻¹ and argon at 25 mL·min⁻¹ were supplied to the cathode while nitrogen at 25 mL·min⁻¹ flowed into the

anode. The CO and O₂ production rates were analyzed using a gas chromatograph with a thermal conductivity detector (TCD).

3. Results and Discussion

3.1. Current Densities for Different Electrode Materials

The relationships between the current density at the cathode side standard and the cell voltage during electrolysis at 900°C for Cell-1, Cell-2, and Cell-3 are shown in Fig. 4.

Fig. 4. Current density as a function of applied cell voltage for Cell-1, cell-2, and cell-3 at 800°C and 900°C.

Fig. 5. SEM photographs of a cross section of Cell-1. (a) Interface between Pt-LSM cermet and YSZ electrolyte, cathode electrode and (b) interface between YSZ electrolyte and Pt-LSM cermet, anode electrode.

Current densities at the same applied cell voltage were strongly affected by the choice of electrode materials.

Cell-1 showed a higher current density of 0.52 mA·cm⁻² compared to the current densities of Cell-2 and Cell-3. This may be attributed to the lower area specific resistance, as reported by Lohsoontorn *et al.*,⁹⁾ in the Cell-1 electrode as compared with Cell-2 and Cell-3.

Furthermore, for Cell-2 and Cell-3, cathodic and anodic overpotentials might have caused high levels of resistance in the LSM cathode and anode electrodes.^{10,11)}

The Pt-LSM cermet used for both the cathode and anode in Cell-1 exhibited the highest current density. The current density performance in Cell-1 was caused by the special structure of the Pt-LSM cermet electrodes. Since Pt has a low overpotential and LSM had good ionic conductivity and mechanical/chemical compatibility with the YSZ electrolyte, the mixture of Pt and LSM in the cermet form resulted in an improved current density for Cell-1.¹²⁾ The similar coefficients of thermal expansion for the Pt-LSM cermet electrodes and the YSZ electrolyte helped to reduce contact resistance, which in turn reduced the cathode resistance and resulted in higher current density levels. Scanning electron microscope (SEM) micrographs showed that the Pt-LSM cermet cathode and anode were intact and adhered well to the YSZ electrolyte (see Fig. 5). No gap was found between cathode electrode-YSZ electrolyte interface and between anode electrode-YSZ electrolyte interfaces of Cell-1. Therefore, no delamination between electrodes and YSZ electrolyte was occurred at 800°C or 900°C which in turn resulted into higher current density of Cell-1. It was also suggested that during electrolysis, the Pt and LSM particles in the cermet form remained in good condition.

Observations of SEM micrographs of the cross sections

Fig. 6. SEM photographs of a cross section of Cell-2. (a) Interface between LSM and YSZ electrolyte, cathode electrode and (b) interface between YSZ electrolyte and LSM, anode electrode.

Fig. 7. SEM photographs of a cross section of Cell-3. (a) Interface between Pt and YSZ electrolyte, cathode electrode and (b) interface between YSZ electrolyte and LSM, anode electrode.

of Cell-2 after electrolysis (see Fig. 6) showed that small gaps had formed between the interfaces of both the cathode and anode electrodes and the YSZ electrolyte. This indicated that delamination of the LSM and the YSZ electrolyte had occurred during electrolysis. The delamination of the LSM electrodes resulted in higher ohmic resistance in Cell-2 and eventually resulted in low current densities. Pt, the cathode material in Cell-3, has exhibited generally higher current densities in other SOEC electrolysis applications,¹³⁾ thus it showed higher current density. The SEM micrograph of the Cell-3 cross section in Fig. 7 showed that there was no gap along the interface between the LSM anode side and the electrolyte and therefore such delamination might not have occurred. Further, it was observed that Pt was intact and adhered well to the surface of the YSZ electrolyte.

Overall, the Cell-1 SOEC with Pt-LSM *cermet* electrodes had better performance and higher current density than in the case of Cell-2 and Cell-3.

3.2. Effect of Operating Temperature on CO and O₂ Production Rates

Cell-1 exhibited the highest current density levels as it performed electrolysis. Therefore, it was chosen as the subject for further analysis of CO₂ electrolysis in this study. Figure 8 shows the CO and O₂ production rates for Cell-1 as functions of current density at 800°C and 900°C. CO production rates at 900°C seemed to be proportional to the current passing through the cell. However, at 800°C CO production was almost the same as that produced at 900°C. There have been relatively few reports on *cermet* that contained a noble metal such as Pt or perovskite oxide (LaMnO₃ or SrMnO₃). This was presumably due to the

Fig. 8. CO and O₂ production rates of Cell-1 as a function of current density at 800°C and 900°C.

high cost of the noble metals.¹⁴⁾ However, as reported by Ni *et al.*,¹⁵⁾ the Pt electrode exhibited a lower overpotential resulting in a higher current density. The mixture of Pt and LSM in *cermet* form for the cathode and anode electrodes in Cell-1 worked well under a high operating temperature. Both the ionic conduction and chemical kinetics of the CO₂ decomposition reaction increased with increasing temperature. The highest CO production rate that occurred during this work was 0.75 μmol·min⁻¹·cm⁻², which was achieved at an operating temperature of 900°C and a current density of 0.52 mA·cm⁻².

However, O₂ production rates at 800°C and 900°C were invariant. It was predicted that the anode side was the rate-determining step for O₂ production during the electrolysis process. In addition, LSM in the anode has been reported to have poor ionic conductivity. Thereafter, it was assumed that a relatively small amount of O²⁻ ions permeated the anode and formed O₂ molecules. In order to improve the reaction rate in the anode, the addition of YSZ into the LSM mixture would be required. The mixture of LSM and YSZ would improve the adhesion between the anode electrode and YSZ electrolyte. This improved adhesion would effectively increase the electrochemically active area of the LSM-YSZ-gas triple phase boundary.⁵⁾

3.3. Relationship between Cell Voltage and the Production Ratio of O₂/CO

The relationship between current density and the production ratio of O₂/CO is shown in Fig. 9. The production ratio of O₂/CO is close to the stoichiometric ratio of 0.5.

At lower current density levels, the O₂/CO production ratio was slightly higher. After passing the initial stage of CO₂ electrolysis, the current density increased with increasing cell voltage and then the production ratio of O₂/CO became stable and remained lower than the stoichiometric ratio of 0.5. This result also indicated that the reactions in Eqs. (1), (2) and (3) were proceeded mainly on the cell.

3.4. Relationship between Cell Voltage and the CO/Electrons Mole Ratio

According to the reaction in Eq. (1), during the decomposition process, 2 mol electrons are needed to decompose

Fig. 9. Relationship between cell voltage and production ratio of O_2/CO in Cell-1.

Fig. 10. Relationships between applied cell voltage and mole ratio of produced CO and electrons in Cell-1.

1 mol CO_2 into 1 mol CO and O^{2-} . This means that the ratio between the CO produced and electrons flowing in will ideally be 0.5. The relation between applied cell voltage and the mole ratio of Cell-1 is shown in Fig. 10. At lower applied cell voltage levels and corresponding lower current densities, the ratios were somewhat higher, close to 0.5, than ratios at higher current densities. At higher voltage levels and higher current densities, the ratios decreased.

At lower applied voltages, electrons were consumed primarily for CO production. On the other hand, at higher voltage levels, electrons could be consumed in unknown reactions, and thus, the ratio was reduced. Carbonation would be one of the candidates for the unknown reaction:

The carbonation reaction will be discussed in the next study.

3.5. Scale Estimation for an ACRES Facility

A combined system with an ACRES CO_2 electrolysis system using heat and power generated from an HTGR within an iron-making facility has been proposed^{2,3)} and is depicted in Fig. 11. An evaluation of such a combined system based on the experimental results for the Cell-1 SOEC provided

Fig. 11. Estimates of the scale of an ACRES carbon recycling system at an iron-making facility.

Table 1. Estimated ACRES energy balances for iron-making processes.

Parameter	Values
Electrolysis temperature for SOEC [$^{\circ}C$]	800
CO regeneration rate from SOEC experiment [$mol-CO \cdot s^{-1} \cdot cm^{-2}$]	9.94×10^{-9}
Electricity demand for electrolysis of CO_2 at $800^{\circ}C$ [$kJ \cdot (mol-CO_2)^{-1} \cdot s^3$]	210.7
HTGR heat output rate [$MWt \cdot (HTGR \text{ unit})^{-1}$]	600
HTGR electricity output for CO_2 reduction [$MWe \cdot (HTGR \text{ unit})^{-1} \cdot s^3$]	215.5
CO regeneration rate per an HTGR [$mol-CO \cdot s^{-1} \cdot (HTGR \text{ unit})^{-1} \cdot s^3$]	1021
CO_2 emission rate from the crude iron production per a blast furnace [$mol-CO_2 \cdot s^{-1} \cdot (BF \text{ unit})^{-1} \cdot s^3$]	2954
Electrode surface area per a blast furnace [$km^2 \cdot (BF \text{ unit})^{-1}$]	29.7
HTGR reactor units for a blast furnace [unit]	2.89

some estimates for the scale of the system. For the evaluation, it was assumed that electrolysis was performed at a high temperature using the high-temperature thermal output from the HTGR to first heat the electrolysis reaction cell and then be utilized for power production at the gas-turbine power generator.³⁾ The results of the energy balance evaluation for the combined system, taking into account the present SOEC experiment results, are shown in Table 1 and the estimated values are also indicated in Fig. 11.

The current density required for efficient electrolysis was $0.44 \text{ mA} \cdot \text{cm}^{-2}$ at $800^{\circ}C$, based on the results of Cell-1 evaluation. A SOEC based on the Cell-1 electrodes could produce $9.94 \times 10^{-9} \text{ mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$ of CO. Electricity consumption for electrolysis at 2.0 V was $2.81 \text{ mW} \cdot \text{cm}^{-2}$. In the scale estimation, an HTGR providing 600 MW of thermal output was able to produce enough power for high-temperature electrolysis in an ACRES. A conventional blast furnace (BF) for crude steel production in Japan emits an average of $1.12 \times 10^4 \text{ ton} \cdot \text{CO}_2 \cdot \text{day}^{-1}$. When an HTGR was introduced into the combined system, 3 HTGR units were required for the high-temperature electrolysis reactions. It was estimated that about $29.7 \text{ km}^2 \cdot (\text{BF unit})^{-1}$ of cell surface area would be required to support CO regeneration by the system.

4. Conclusion

Three CO₂ electrolysis processes were demonstrated using different electrode materials on a YSZ-based electrolyte. Cell-1, with a structure of Pt-LSM cermet|YSZ|Pt-LSM cermet for the cathode|electrolyte|anode, had higher current density levels than those of Cell-2, with a LSM|YSZ|LSM structure, and Cell-3, with a Pt|YSZ|LSM structure. The CO production rate was higher at 900°C than at 800°C. A CO production rate of 0.75 μmol·min⁻¹·cm⁻² was measured at an operating temperature of 900°C with a current density of 0.52 mA·cm⁻². On the other hand, the O₂ production rate was invariant at 800°C and 900°C. It was thought that the anodic reaction was the rate-determining step for O₂ production during the electrolysis process. The scale of a combined ACRES with CO regeneration by electrolysis of CO₂ driven by an HTGR for an iron-making process was estimated on the basis of the experimental results. The required surface area of the SOEC cells was estimated to be 29.7 km²·(BF unit)⁻¹ for a conventional BF. The reactivity of the cell has to be improved to reduce the necessary surface area. The combined system may contribute to the establishment of carbon supply security and a low-carbon society.

REFERENCES

- 1) Y. A. Cengel and M. A. Boles: THERMODYNAMICS, An Engineering Approach, McGraw-Hill, Singapore, (2007), 89.
- 2) Y. Kato: *ISIJ Int.*, **50** (2010), 181.
- 3) Y. Kato, T. Obara, I. Yamanaka, S. Mori, A. L. Dipu, J. Ryu, Y. Ujisawa and M. Suzuki: *Prog. Nucl. Energ.*, **53** (2011), 1017.
- 4) A. Brisse, J. Schefold and M. Zahid: *Int. J. Hydrogen Energ.*, **33** (2008), 5375.
- 5) C. Yang, A. Coffin and F. Chen: *Int. J. Hydrogen Energ.*, **35** (2010), 3221.
- 6) S. H. Jensen, X. Sun, S. D. Ebbesen, R. Knibbe and M. Mogensen: *Int. J. Hydrogen Energ.*, **35** (2010), 9544.
- 7) S. D. Ebbesen and M. Mogensen: *J. Power Sources*, **193** (2009), 349.
- 8) Z. Zhan and L. Zhao: *J. Power Sources*, **195** (2010), 7250.
- 9) P. K. Lohsoontorn, D. J. L. Brett, N. Laosiripojana, Y.-M. Kim and J.-M. Bae: *Int. J. Hydrogen Energ.*, **35** (2010), 3958.
- 10) Y. Huang, J. M. Vohs and R. J. Gorte: *Electrochem. Solid St.*, **9** (2006), No. 5, A237.
- 11) K. Chen and S. P. Jiang: *Int. J. Hydrogen Energ.*, **36** (2011), 10541.
- 12) M. Liang, B. Yu, M. Wen, J. Chen, J. Xu and Y. Zhai: *J. Power Sources*, **190** (2009), 341.
- 13) T. Ishihara, N. Jirathiwathanakul and H. Zong: *J. Royal Soc. Chem.*, **3** (2010), 665.
- 14) L. S. Wang and S. A. Barnett: *J. Solid State Ionics*, **76** (1995), 103.
- 15) M. Ni, M. K. H. Leung and D. Y. C. Leung: *Int. J. Hydrogen Energ.*, **33** (2008), 2337.
- 16) G. Tao, K. R. Sridhar and C. L. Chan: *J. Solid State Ionics*, **175** (2004), 615.