FULL PAPER

Solid oxide fuel cell using CO–H₂O mixed gas fuelYoshinobu KITAZAKI¹, Taro SHIMONOSONO¹, Yoshihiro HIRATA^{1,†},
Soichiro SAMESHIMA¹ and Katsuhiko YAMAJI²¹Department of Chemistry, Biotechnology, and Chemical Engineering, Kagoshima University,
1–21–40 Korimoto, Kagoshima 890–0065, Japan²Fuel Cell Materials Group, Research Institute for Energy Conservation, National Institute of Advanced Industrial Science
and Technology (AIST), AIST Tsukuba Central 5, 1–1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan*

A solid oxide fuel cell with an yttria-stabilized zirconia (YSZ) electrolyte, Ni–YSZ anode and Ru–YSZ cathode was fabricated to measure the cell performance at 500–800°C using a H₂, CO or CO–H₂O fuel and air oxidant. The terminal voltage drop at a larger current density was due to the overpotential at the electrodes. A part of CO fuel was electrochemically oxidized to produce an electric power and some fractions of CO fuel were decomposed to form CO₂ gas and solid carbon (disproportionation reaction, 2CO → CO₂ + C). In the CO–H₂O fuel, electrochemical oxidation of a CO fuel, CO disproportionation, the water–gas shift reaction (CO + H₂O → H₂ + CO₂) and oxidation of deposited carbon (C + H₂O → H₂ + CO) proceeded in the anode. It is possible to produce an electric power and a H₂ fuel at the same time during the operation of a SOFC using a CO–H₂O fuel.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words : Solid oxide fuel cell, Hydrogen formation, CO fuel, Water–gas shift reaction, Yttria-stabilized zirconia

[Received April 2, 2018; Accepted July 2, 2018]

1. Introduction

The household fuel cell has been already commercialized in Japan, and its hydrogen fuel is produced by the steam reforming of city gas (i.e. methane, CH₄ + H₂O → 3H₂ + CO). In a polymer electrolyte fuel cell, CO gas formed by the steam reforming of methane causes CO poisoning of a platinum catalyst in the anode. On the other hand, CO gas is available as a fuel for a solid oxide fuel cell (SOFC). While the SOFC performance with a CO fuel is usually lower than that with a H₂ fuel, addition of Cu metal to Ni–YSZ (yttria-stabilized zirconia) anode enhances the SOFC performance with a CO fuel.¹⁾ However, addition of H₂O vapor to a CO fuel reduces the open circuit voltage (OCV) and increases the polarization resistance.²⁾ The mixing of H₂ gas to a CO fuel promotes carbon deposition in the Ni–YSZ anode and decreases the current density.³⁾

In our previous paper,⁴⁾ the performance of a YSZ fuel cell was examined for five kinds of gas systems: (a) the H₂ (fuel)–O₂ (oxidant) system, (b) the H₂–CO₂ system, (c) the H₂–H₂O system, (d) the CO–O₂ system, (e) the CO–H₂O system. A large or small electric power was measured in the gas systems of (a), (b) and (d). The gas systems of

(c) and (e) are attractive because the cathode outlet gas includes a H₂ fuel during the operation of a SOFC [(c) H₂ (anode) + H₂O (cathode) → H₂O (anode) + H₂ (cathode), (e) CO (anode) + H₂O (cathode) → CO₂ (anode) + H₂ (cathode)]. Although relatively high OCV values were measured in the gas systems of (c) and (e), no electric power was measured. In this paper, the CO–H₂O fuel/O₂ oxidant gas system for a SOFC was examined to produce an electric power and a H₂ fuel in the anode at the same time. When a CO fuel and a H₂O oxidant are supplied to the anode, a part of CO fuel is used for the SOFC power generation and the other part of CO reacts with H₂O vapor to produce H₂ and CO₂ gases (water–gas shift reaction). The formed H₂ fuel may be partly consumed as a fuel in the SOFC to increase the electric power and the remaining H₂ gas of the outlet gas can be separated as a fresh fuel. This paper reports the challenge of the CO–H₂O fuel/O₂ oxidant gas system for a SOFC to achieve the generation of an electric power and a H₂ fuel in a single operation process.

2. Experimental procedure

2.1 Fabrication of anode-supported SOFC

In the fabrication of anode powder, an yttria-stabilized zirconia powder (YSZ, 92 mol % ZrO₂–8 mol % Y₂O₃, specific surface area 11.6 m²/g, corresponding particle size 88 nm, TZ-8Y, Tosoh Co. Ltd., Japan) was dispersed in a 1.4 M Ni(NO₃)₂ aqueous solution at a volume ratio of YSZ:Ni = 70:30. The YSZ suspension of 2.1 vol % solid at pH 3 was stirred for 24 h and then freeze-dried. The freeze-dried powder was calcined at 600°C for 2 h in air.

† Corresponding author: Y. Hirata; E-mail: hirata@cen.kagoshima-u.ac.jp‡ Preface for this article: DOI <http://doi.org/10.2109/jcersj2.126.P10-1>

* Present affiliate: Energy Conversion Technology Group of AIST

In the fabrication of RuO₂-YSZ cathode, the YSZ powder was dispersed in a 1.0 M RuCl₃ aqueous solution at a volume ratio of YSZ:Ru = 70:30. The pH value of the YSZ suspension of 2.0 vol % solid was adjusted to 10 to precipitate Ru(OH)₃. After stirring for 24 h, the YSZ suspension was freeze-dried and then calcined at 800°C for 1 h in air to form a RuO₂-YSZ powder. The electrical resistivity of RuO₂ ($3.5 \times 10^{-7} \Omega \cdot \text{m}$ at room temperature⁵⁾) is as low as metal. In addition, the Ru electrode exhibited a high catalytic activity in the electrochemical dry reforming of methane with carbon dioxide ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$), which promoted the cathodic reaction of $\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-}$ and also the anodic reaction of $\text{CH}_4 + \text{O}^{2-} \rightarrow \text{CO} + 2\text{H}_2 + 2\text{e}^-$.^{6,7)} From the view point of the reduction of an oxidant gas, the RuO₂ cathode was expected to have a high catalytic property in the electrochemical reduction of an O₂ oxidant gas. Furthermore, a perovskite oxide SrRuO₃ which is a kind of ruthenium oxide, exhibited a high performance as a cathode of SOFC in our previous paper.⁸⁾ To fabricate an electrolyte film, the YSZ powder was dispersed at the solid content 25 vol % in a non-aqueous solution of 33 vol % toluene–67 vol % isopropanol. Nine mass % of polyethylene glycol and 5 mass % of polyvinyl butyral against the mass of YSZ powder were added to the YSZ suspension as a lubricant and a plasticizer, respectively. The suspension was stirred and then formed into a film of 80 μm thickness by a doctor blade method. The clearances of front and rear blades were 130 and 300 μm, respectively. The forming rate of the YSZ film was 5 cm/sec. The YSZ electrolyte film was placed on the NiO-YSZ anode powder bed (10 mm diameter, 5 mm thickness) to press uniaxially at 80 MPa, followed by an isostatic pressing at 300 MPa. The NiO-YSZ powder compact with a YSZ film was co-sintered at 1400°C for 4 h in air to form a dense YSZ electrolyte on the NiO-YSZ anode. The cathode powder was dispersed at 15 vol % solid content in a solvent of 50 vol % ethanol–50 vol % polyethylene glycol. The prepared paste of the cathode powder was spread on the surface of the YSZ electrolyte and then heated at 1100°C for 1 h in an argon atmosphere to form the RuO₂-YSZ cathode. A Pt mesh welded to a Pt lead wire was attached to each electrode with a Pt paste by heating at 1000°C for 1 h.

2.2 Measurement of cell performance

Before a cell test, NiO in the anode was reduced to Ni metal by supplying a H₂ gas at 800°C for 12 h. The cell performance was examined at 500–800°C by supplying several fuels of H₂, CO and CO–H₂O (molar ratio of CO:H₂O = 1:3.4) at 20–50 ml/min. The used CO gas was diluted to 10 vol % with an Ar gas. Air was used as an oxidant and supplied at 20–100 ml/min. The terminal voltage was controlled to measure the cell performance by a potentiostat (HAL-3001, Hokuto Denko Corp., Japan). The composition of the outlet gas at the anode side was measured using a gas chromatograph equipped with an active-carbon column and a thermal conductivity detector (GC7100T, J-Science Lab Co. Ltd., Japan) using an Ar carrier gas. The cell after the experiment was analyzed by electron probe micro-analyser (EPMA, JXA-8230, JEOL Ltd., Japan).

3. Results and discussion

3.1 H₂–O₂ gas system

Figure 1 shows the surface of YSZ electrolyte film and the cross section of the anode-supported YSZ cell. The YSZ electrolyte film with about 50 μm thickness consisted of 2–7 μm grains and was completely densified. No pin holes and cracks were observed. The thickness of Ru-YSZ cathode was about 110 μm.

The electrochemical reactions at the cathode and the anode are expressed as $0.5\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ and $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$, respectively. The total reaction of H₂ (anode) + 0.5O₂ (cathode) → H₂O (anode) proceeds in the YSZ cell. **Figure 2** shows the terminal voltage and power density of the YSZ cell using a gas system of a H₂–3 vol % H₂O fuel/air oxidant as a function of current density at 800°C. The OCV was 1.103 V and was in agreement with the Nernst voltage of 1.070 V which was calculated by Eq. (1),

$$\begin{aligned} E &= -\frac{\Delta G}{2F} \\ &= -\frac{1}{2F} \left[\Delta G^\circ + RT \ln \frac{P_{\text{H}_2\text{O}}(\text{anode})}{P_{\text{H}_2}(\text{anode}) P_{\text{O}_2}^{1/2}(\text{cathode})} \right] \\ &= E^\circ - \frac{RT}{2F} \ln \frac{P_{\text{H}_2\text{O}}(\text{a})}{P_{\text{H}_2}(\text{a}) P_{\text{O}_2}^{1/2}(\text{c})} \end{aligned} \quad (1)$$

Fig. 1. Microstructures of (a) surface of YSZ electrolyte film and (b) cross section of the anode-supported YSZ cell.

Fig. 2. (a) Terminal voltage and (b) power density of the YSZ fuel cell using a gas system of H₂–3 vol % H₂O fuel/air oxidant at 800°C.

where ΔG , F , R , T and P are the Gibbs free energy change for H₂O formation, the Faraday's constant, the gas constant, the absolute temperature and the partial pressure of gas, respectively. Under the operation of the YSZ cell, the partial pressures of H₂, H₂O and O₂ gases vary with the current density, and are expressed by Eqs. (2)–(4), respectively,

$$P_{\text{H}_2}(\text{a}) = \frac{s_{\text{H}_2} - c_{\text{H}_2}}{s_{\text{H}_2} + s_{\text{H}_2\text{O}} - c_{\text{H}_2} + f_{\text{H}_2\text{O}}} \quad (2)$$

$$P_{\text{H}_2\text{O}}(\text{a}) = \frac{s_{\text{H}_2\text{O}} + f_{\text{H}_2\text{O}}}{s_{\text{H}_2} + s_{\text{H}_2\text{O}} - c_{\text{H}_2} + f_{\text{H}_2\text{O}}} \quad (3)$$

$$P_{\text{O}_2}(\text{c}) = \frac{s_{\text{O}_2} - c_{\text{O}_2}}{s_{\text{O}_2} + s_{\text{N}_2} - c_{\text{O}_2}} \quad (4)$$

where s , c and f are the mole numbers of supplied, consumed and formed gases per one second, respectively, in the oxidation of H₂ fuel [H₂ (anode) + 0.5O₂ (cathode) → H₂O (anode)]. The denominator for Eqs. (2) and (3) represents the total mole number of the anode outlet gas. Similarly, the denominator for Eq. (4) represents the total mole number of the cathode outlet gas. The mole numbers of consumed and formed gases are related to the electric current by the Faraday's law,

$$c_{\text{H}_2} \text{ (or } f_{\text{H}_2\text{O}}) = \frac{i}{nF} \quad (5)$$

$$c_{\text{O}_2} = \frac{1}{2} \frac{i}{nF} \quad (6)$$

where i and n are the electric current and the number of electrons which contribute to the oxidation of 1 mol H₂ fuel (i.e., $n = 2$). The terminal voltage based on the Nernst equation was calculated by Eqs. (1)–(6) for the measured current density in Fig. 2. The $f_{\text{H}_2\text{O}}$ value was calculated to be 2.91×10^{-7} mol/s at 56.1 mA (198.4 mA/cm²) and was 28.5% of the $s_{\text{H}_2\text{O}}$ value (1.02×10^{-6} mol/s) for the

H₂–3 vol % H₂O fuel at 50 ml/min. On the other hand, either c_{H_2} or c_{O_2} value was about 1% of s_{H_2} or s_{O_2} value, respectively, and was negligible in Eqs. (2)–(4). The terminal voltage was calculated by Eq. (1) using the partial pressures of inlet H₂ and O₂ gases and the partial pressure of H₂O by Eq. (3). The calculated terminal voltage and electric power were plotted in Fig. 2, and were significantly higher than the measured values. The measured terminal voltage decreased rapidly at a larger current density. The maximum power density was 66.7 mW/cm² at 167 mA/cm² of current density.

The area specific resistance of YSZ electrolyte, RuO₂ cathode and Ni–YSZ anode were calculated to be 0.16, 3.9×10^{-7} and $5 \times 10^{-3} \Omega\cdot\text{cm}^2$, respectively, using the measured thickness (50 μm for electrolyte, 110 μm for the cathode and 5 mm for the anode) and the reported electrical conductivity (3.16×10^{-2} S/cm at 800°C for YSZ,⁹⁾ 2.9×10^4 S/cm at room temperature for RuO₂,⁵⁾ 10^3 S/cm at 800°C for Ni–YSZ¹⁰⁾). Then the IR drop of the cell was evaluated to be 0.01 V at 60 mA/cm² and 0.03 V at 200 mA/cm² by the Nernst Eq. (1). Therefore, the large measured voltage drop was due to the overpotential at the electrodes. In addition, since the cell performances in the H₂/air, CO/air and CO–H₂O/air systems were compared using the identical cell, the difference of the cell performance is attributed to the overpotential at the anode.

Although the Pt metal may exhibit a higher catalytic property than the Ni metal, both the amount and the specific surface area of Pt mesh or Pt paste are significantly smaller than that of Ni particles in the anode as described below, which decreases the catalytic activity of Pt. The weight of 80 meshes Pt with the area of $5 \times 5 \text{ mm}^2$ was 0.0162 g and smaller than 0.4339 g Ni in the anode in this experiment. The specific surface area of Pt mesh with 0.076 mm diameter was calculated to be $2.4 \times 10^{-3} \text{ m}^2/\text{g}$ which was significantly smaller than $34 \text{ m}^2/\text{g}$ of Ni particles with the particle size of 20 nm.¹¹⁾ In addition, the Pt mesh and Pt paste were placed 5 mm away from the anode/electrolyte interface, and would be no longer available as an electrochemical reaction site. The effect of Pt on the anode reaction may not be dominant in this experiment.

3.2 CO–O₂ gas system

Figure 3 shows the terminal voltage and power density of the SOFC with a CO fuel and air oxidant at 600–800°C. The electrochemical reactions at the cathode and the anode are expressed as $0.5\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ and $\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{e}^-$, respectively, and the total reaction is represented by $\text{CO (anode)} + 0.5\text{O}_2 \text{ (cathode)} \rightarrow \text{CO}_2 \text{ (anode)}$. The Nernst voltage is expressed by Eq. (7),

$$\begin{aligned} E &= -\frac{\Delta G}{2F} \\ &= -\frac{1}{2F} \left[\Delta G^\circ + RT \ln \frac{P_{\text{CO}_2}(\text{anode})}{P_{\text{CO}}(\text{anode}) P_{\text{O}_2}^{1/2}(\text{cathode})} \right] \\ &= E^\circ - \frac{RT}{2F} \ln \frac{P_{\text{CO}_2}(\text{a})}{P_{\text{CO}}(\text{a}) P_{\text{O}_2}^{1/2}(\text{c})} \end{aligned} \quad (7)$$

Fig. 3. (a) Terminal voltage and (b) power density of the YSZ fuel cell using a gas system of CO fuel/air oxidant at 600–800°C.

where ΔG is the Gibbs free energy change for CO_2 formation from CO and O_2 . Under the operation of the YSZ cell, the partial pressures of CO, CO_2 and O_2 gases are expressed by Eqs. (8)–(10), respectively. The dominator for Eqs. (8) and (9) represents the total mole number of the anode outlet gas including an Ar gas.

$$P_{\text{CO}}(\text{a}) = \frac{s_{\text{CO}} - c_{\text{CO}}}{s_{\text{CO}} + s_{\text{Ar}} - c_{\text{CO}} + f_{\text{CO}_2}} \quad (8)$$

$$P_{\text{CO}_2}(\text{a}) = \frac{f_{\text{CO}_2}}{s_{\text{CO}} + s_{\text{Ar}} - c_{\text{CO}} + f_{\text{CO}_2}} \quad (9)$$

$$P_{\text{O}_2}(\text{c}) = \frac{s_{\text{O}_2} - c_{\text{O}_2}}{s_{\text{O}_2} + s_{\text{N}_2} - c_{\text{O}_2}} \quad (10)$$

The c_{CO} (or f_{CO_2}) and c_{O_2} are related to the electric current by Eqs. (11) and (12), respectively,

$$c_{\text{CO}} \text{ (or } f_{\text{CO}_2}) = \frac{i}{nF} \quad (11)$$

$$c_{\text{O}_2} = \frac{1}{2} \frac{i}{nF} \quad (12)$$

The n value is 2 for the reaction of CO (anode) + 0.5O_2 (cathode) $\rightarrow \text{CO}_2$ (anode). The c_{CO} and c_{O_2} values were calculated to be 8.49×10^{-8} and 4.25×10^{-8} mol/s, respectively, at 16.4 mA (58.0 mA/cm^2), which were 2.5% of the s_{CO} value (50 ml/min of 10% CO–90% Ar fuel, supplied rate) and 0.3% of the s_{O_2} value (100 ml/min of air, supplied rate), respectively. Then, the c_{CO} and c_{O_2} values were ignored in Eqs. (8)–(10). The terminal voltage was calculated by Eq. (7) using the partial pressures of inlet CO and O_2 gases and the partial pressure of CO_2 by Eq. (9). The opposite temperature dependences of first and second terms in Eq. (7) compensate the temperature de-

pendence of Nernst voltage in Fig. 3(a) [$\Delta G^\circ(600^\circ\text{C}) = -206.7$, $\Delta G^\circ(700^\circ\text{C}) = -198.0$, $\Delta G^\circ(800^\circ\text{C}) = -189.3$ kJ/mol, based on the thermodynamic database¹²⁾]. Since the calculated voltage drop by Nernst equation is negligible in Fig. 3, the measured decrease in the terminal voltage and power density is also due to the overpotential at the electrodes. The measured open circuit voltage decreased with decreasing heating temperature, and was 0.972, 0.560 and 0.471 V at 800, 700 and 600°C, respectively. The reported OCV value for the 50% CO–50% N_2 gas system in Cu–ceria–YSZ anode is 1.2 V at 700°C.¹⁾ One of the reasons for the low OCV value in the present YSZ cell may be the disproportionation reaction of CO fuel ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) and discussed in a later part. The disproportionation of CO gas is accelerated thermodynamically at a lower heating temperature⁷⁾ and the anode surface is covered with the deposited carbon. Cu catalyst may suppress the formation of carbon from CO gas.

Figure 4 shows the CO utilization rate for the outlet gas (i.e. ratio of CO_2 concentration with respect to the summation of CO and CO_2 concentrations), which was compared with the values calculated by Eq. (13) based on the Faraday's law.

$$U_{\text{CO}} = \frac{f_{\text{CO}_2}}{s_{\text{CO}} - c_{\text{CO}} + f_{\text{CO}_2}} = \frac{f_{\text{CO}_2}}{s_{\text{CO}}} \quad (c_{\text{CO}} = f_{\text{CO}_2}) \quad (13)$$

The measured CO utilization rates were larger than the calculated values, indicating that the CO gas was not only consumed electrochemically but also converted to CO_2 and solid carbon by CO disproportionation. The difference of CO utilization rates between the measurement and

Fig. 4. Current density and gas fraction of the outlet gas for a CO fuel.

Fig. 5. (a) Terminal voltage and (b) power density of the fuel cell using a gas system of CO–H₂O mixed fuel/air oxidant at 500–800°C.

calculation corresponds to the CO₂ fraction from the CO disproportionation. Since the cell test in the CO/O₂ gas system was followed by the cell test in the CO–H₂O/O₂ gas system, the carbon deposition could not be analyzed after the cell test in the CO/O₂ gas system.

3.3 CO–H₂O/O₂ gas system

Figure 5 shows the terminal voltage and power density for a gas system of CO–H₂O fuel/air oxidant at 500–800°C. At 800°C, the OCV value decreased from 0.972 V for a CO fuel (Fig. 3) to 0.737 V for a CO–H₂O fuel. At 600°C, the H₂O addition appeared to increase the OCV value for a CO fuel. These electric powers are discussed in Fig. 6. Figure 6 shows the comparison of the electric

Fig. 6. Ratios of electric powers of (a) a CO fuel or (b) CO–H₂O fuel to a H₂ fuel.

powers between CO fuel or CO–H₂O fuel and H₂ fuel as a function of current density. The electric powers for a CO fuel and a CO–H₂O fuel were low as compared with the electric power for a H₂ fuel. The addition of H₂O vapor in a CO fuel narrows the difference in the electric powers at 600–800°C and provides a larger electric power at a large current density. The carbon deposited due to the CO disproportionation at a lower temperature (Fig. 3) may be eliminated as a CO gas by the reaction with H₂O vapor ($C + H_2O \rightarrow CO + H_2$), contributing to the stable electric power at a given operation temperature. After the cell test, the carbon deposition was analyzed by EPMA. As shown in Fig. 7, the carbon element was observed at both the anode and the electrolyte. Since the carbon at the electrolyte is attributed to the contamination during the preparation of the sample for the EPMA observation, the amount of carbon actually deposited at the anode during

Fig. 7. (a) Microstructure and (b)–(f) elemental distributions of (b) Zr, (c) Y, (d) O, (e) Ni and (f) C of the cross section of YSZ electrolyte supported by Ni-YSZ anode after the cell test in the CO–H₂O/O₂ gas system.

Fig. 8. Volume ratio of (A) CO₂(outlet gas)/CO(inlet gas) and (B) H₂(outlet gas)/CO(inlet gas).

the cell test would be significantly small. Unfortunately, the cell test in the CO–H₂O/air system was conducted continuously after the cell test in the CO/air system. Then the carbon deposition in the CO/air system could not be analyzed by EPMA. However, the carbon deposition would be one of the possible explanation for the deviation of the measured CO₂ concentration from the calculated values based on the Faraday's law in Fig. 4. The deposited carbon was eliminated by the reaction with H₂O gas during the cell test in the CO–H₂O/air system.

Figure 8 shows the volume ratio of the outlet CO₂ gas or outlet H₂ gas to the inlet CO gas as a function of current density. The H₂/CO ratio is related to the shift reaction of CO gas with H₂O gas ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) and oxi-

dation of carbon with H₂O vapor ($\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$). The CO₂/CO ratio includes the information from the electrochemical oxidation of CO gas ($\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$), the conversion of CO gas by shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$), the CO disproportionation ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) and oxidation of carbon with H₂O gas ($\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$). The H₂/CO ratio was independent of the current density but the CO₂/CO ratio increased with increasing current density of 26–71 mA/cm². The information of current density dependence of CO₂/CO ratio is related to the electrochemical oxidation of a CO fuel. The H₂/CO ratio and the CO₂/CO ratio, which are independent of the current density, are closely related to the shift reaction, CO disproportionation and oxidation of deposited carbon. As

seen in Figs. 6 and 8, it is possible to produce an electric power and a H₂ fuel at the same time during the operation of a SOFC at 500–800°C using the gas system of a CO–H₂O fuel/air oxidant. The future work is to increase both the electric power and the amount of H₂ gas during the SOFC operation.

4. Conclusions

A SOFC with an YSZ electrolyte, Ni–YSZ anode and Ru–YSZ cathode was operated using H₂, CO and CO–H₂O fuels at 500–800°C. The terminal voltage drop and the decrease in the electric power at a larger current density were due to the overpotential at the electrodes. The CO fuel is not only consumed electrochemically but also converted to CO₂ gas and solid carbon by CO disproportionation. The addition of H₂O vapor in a CO fuel narrowed the difference in the electric powers at 600–800°C and provided a larger electric power at a larger current density. It is possible to produce an electric power and a H₂ fuel at the same time during the operation of a SOFC using the CO–H₂O fuel/air oxidant gas system.

References

- 1) O. Costa-Nunes, R. J. Gorte and J. M. Vohs, *J. Power Sources*, **141**, 241–249 (2005).
- 2) A. M. Sukeshini, B. Habibzadeh, B. P. Becker, C. A. Stoltz, B. W. Eichhorn and G. S. Jackson, *J. Electrochem. Soc.*, **153**, A705–A715 (2006).
- 3) V. Alzate-Restrepo and J. M. Hill, *J. Power Sources*, **195**, 1344–1351 (2010).
- 4) Y. Hirata, S. Daio, A. Kai, T. Shimonosono, R. Yano, S. Sameshima and K. Yamaji, *Ceram. Int.*, **42**, 18373–18379 (2016).
- 5) W. D. Ryden and A. W. Lawson, *Phys. Rev. B*, **1**, 1494–1500 (1970).
- 6) S. Matayoshi, Y. Hirata, S. Sameshima, N. Matsunaga and Y. Terasawa, *J. Ceram. Soc. Jpn.*, **117**, 1147–1152 (2009).
- 7) Y. Hirata, T. Shimonosono, K. Ueda, S. Sameshima and K. Yamaji, *Ceram. Int.*, **43**, 3639–3646 (2017).
- 8) T. Shimonosono, G. Hiramatsu, Y. Hirata, S. Sameshima, N. Matsunaga, T. Doi and T. Horita, *Adv. Mat. Res.*, **26–28**, 275–278 (2007).
- 9) J.-H. Park and R. N. Blumenthal, *J. Electrochem. Soc.*, **136**, 2867–2876 (1989).
- 10) S. T. Aruna, M. Muthuraman and K. C. Patil, *Solid State Ionics*, **111**, 45–51 (1998).
- 11) Y. Okawa and Y. Hirata, *J. Eur. Ceram. Soc.*, **25**, 473–480 (2005).
- 12) NIST-JANAF Thermochemical Tables, <http://kinetics.nist.gov/janaf/>.