Full Paper

Solid oxide fuel cell using a H2 fuel/CO2 oxidant gas system

Yuta MIYAZAKI1, Taro SHIMONOSONO1, Yoshihiro HIRATA1,†, Soichiro SAMESHIMA1 and Katsuhiko YAMAJI2

1Department of Chemistry, Biotechnology, and Chemical Engineering, Kagoshima University, 1–21–40 Korimoto, Kagoshima 890–0065, Japan
2Fuel Cell Materials Group, Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 3, 1–1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan

This paper reports the performance of a solid oxide fuel cell with yttria-stabilized zirconia (YSZ) electrolyte, Ni–YSZ anode and (La0.8Sr0.2)0.95MnO3 (LSM) cathode or RuO2–YSZ cathode using air oxidant or a CO2 oxidant and a H2 fuel with 3% H2O at 600–800°C. The power density was higher for air oxidant than for a CO2 oxidant. The measured power density was associated with the reduction of CO2 gas to solid carbon for the RuO2–YSZ cathode. In the cell with the LSM cathode, a CO2 oxidant was reduced to the mixed state of CO molecules and solid carbon. The reactivity of O2 or CO2 molecules in their mixed oxidant gas system for the YSZ cell with the LSM cathode changed drastically at 50–70 vol% CO2 in the O2–N2–CO2 gas system. It is possible to produce an electric power and to reduce CO2 gas into solid carbon at the same time during the operation of a solid oxide fuel cells using a CO2 oxidant.

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Key-words: Solid oxide fuel cell, CO2 oxidant, Cathode, Yttria-stabilized zirconia, Strontium-doped lanthanum manganite

1. Introduction

Solid oxide fuel cells (SOFCs) can directly convert a chemical energy of a fuel into an electric power at a high conversion efficiency. The household SOFCs have been commercialized as a co-generation system of heat and electric power in Japan since 2011. The household SOFCs are operated with a H2 fuel produced by the reforming of CH4-rich city gas. The variety of fuels such as H2, CH4 or CO is one of the attractive feature of SOFCs. Air is easily available as an oxidant gas and suitable for the practical use for SOFCs. On the other hand, CO2 gas has been studied to be used as an oxidant for the fuel cell in a spacecraft. In a situation of a low concentration of O2 gas (e.g. outside the earth), such a power generation with a CO2 oxidant would be useful in future. On the other hand, in our life space, the applications of CO2 gas have become more important to decrease the CO2 concentration of the atmosphere. The fuel cell with a CO2 oxidant is one of the solutions for the above purposes. When the CO2 oxidant is electrochemically reduced at the cathode of SOFC to generate an electric power, the supplied CO2 gas is converted to CO gas or solid carbon. The separated CO gas or solid carbon is available as a fuel (source of thermal energy), a reductant or a chemical material. From the view point of storage of CO2 gas, the formation of solid carbon is attractive because of its stable and compact storage. That is, the SOFC with a CO2 oxidant is highly expected for both the generation of an electric power and the reduction of CO2 gas into CO gas or solid carbon.

In our previous study, CO2 gas was used as an oxidant of a SOFC to produce a CO fuel in the outlet gas of the cathode during the operation of a SOFC. The separated CO gas or solid carbon is reusable as a fresh fuel of a SOFC. When a CO2 oxidant and a H2–3% H2O fuel were supplied to the electrolyte-supported cell with an yttria-stabilized zirconia (YSZ) electrolyte (2 mm thickness), Ni–YSZ anode and RuO2–YSZ cathode, the measured open circuit voltage (0.79–0.92 V at 800°C) was close to the theoretical electromotive force by Nernst equation. The electric powers of 9.1–26.6 mW were measured at 14.4–41.0 mA of electric current at 800°C. In this study, the performance of the anode-supported YSZ cell with RuO2 cathode or lanthanum strontium manganite (LSM) cathode was examined for the H2–air gas system and the H2–CO2 gas system at 600–800°C. The RuO2 cathode was used in an electrochemical cell to promote a dry-reforming reaction of CH4. 

† 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

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with CO₂ gas (CH₄ + CO₂ → 2H₂ + 2CO) in our previous study.⁵ Since the RuO₂ cathode exhibited a high catalytic property for the electrochemical reduction reaction of CO₂ (CO₂ + 2e⁻ → CO + O²⁻), the RuO₂ cathode was employed in the SOFC with a CO₂ oxidant in this study. On the other hand, the LSM cathode is an established cathode because of the high chemical compatibility and a similar thermal expansion coefficient for a YSZ electrolyte as well as a high electrical conductivity and high catalytic performance. In addition, the LSM cathode is reported to be resistant to a strontium carbonate formation due to the reaction with CO₂ gas.⁷ Since the LSM cathode is a conventional cathode for the SOFC with air oxidant, the comparison of the SOFC performance between air and CO₂ oxidants was conducted in this study. To the authors' knowledge, such a comparison has not been reported yet.

2. Experimental procedure

2.1 Fabrication of anode-supported SOFC

In the fabrication of an anode powder, an YSZ powder (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 was stirred for 24 h and then freeze-dried. The freeze-dried powder was calcined at 600°C for 2 h in air. In the fabrication of a RuO₂–YSZ cathode, the YSZ powder was dispersed at 2.0 vol% solid in a 1.0 M RuCl₃ aqueous solution at a volume ratio of YSZ:Ru = 70:30. The pH value of the YSZ suspension was adjusted to 10 to precipitate Ru(OH)₃. After stirring for 24 h, the freeze-dried powder was calcined at 800°C for 1 h in air. In the fabrication of a RuO₂–YSZ cathode, the YSZ powder was dispersed at 5 vol% solid was stirred for 24 h and then freeze-dried. The freeze-dried powder was calcined at 600°C for 2 h in air. In the fabrication of a RuO₂–YSZ cathode, the YSZ powder was dispersed at 2.0 vol% solid in a 1.0 M RuCl₃ aqueous solution at a volume ratio of YSZ:Ru = 70:30. The pH value of the YSZ suspension 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. In the fabrication of (La₀.₈Sr₀.₂)₀.₉₅MnO₃ (LSM) cathode powder paste, the (La₀.₈Sr₀.₂)₀.₃MnO₃ powder. To fabricate an YSZ electrolyte film, the YSZ powder was dispersed at the solid content 25 vol% in a non-aqueous solution of 33 vol% isopropanol, 5 mass% of polyethylene glycol and 5 mass% of polyvinyl butyral against the mass of the YSZ powder. Nine mass% of polyethylene glycol and 5 mass% of polyvinyl butyral against the mass of the YSZ powder were added to the suspension as a humectant 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 100 MPa. The NiO–YSZ powder compact with the 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 RuO₂–YSZ or LSM cathode powder was dispersed at 15 vol% solid content in a solvent of 50 vol% ethanol–50 vol% polyethylene glycol. The prepared cathode powder paste 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 or heated at 1150°C for 2 h in air to form the LSM cathode. Then, 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 600–800°C by supplying a CO₂ or air oxidant at 100 ml/min and a H₂ fuel with 3% H₂O at 50 ml/min. The terminal voltage was controlled to measure the electric current by a potentiostat (HAL-3001, Hokuto Denko Corp., Japan). After the cell test, the elemental analysis of the cell was performed using an electron-probe microanalyzer (EPMA, JXA-8230, JEOL Ltd., Japan).

3. Results and discussion

3.1 Cell performance using the air oxidant/ H₂–3% H₂O fuel system

From the microstructural observation for the YSZ electrolyte film (Fig. 1), it was confirmed that YSZ grains of 2–7 µm sizes were completely densified and no pore remained in the YSZ film. Figures 2 and 3 show the cell performance using air oxidant and a H₂ fuel for the cells with RuO₂–YSZ cathode and (La₀.₈Sr₀.₂)₀.₉₅MnO₃ (LSM) cathode, respectively. The open circuit voltage (OCV) was almost the same for the RuO₂–YSZ cathode and LSM cathode, and as follows: 1.111–1.136 V at 600°C, 1.115–1.120 V at 700°C and 1.101–1.102 V at 800°C. The terminal voltage of both the YSZ cells decreased rapidly at a small current. The maximum power densities (MPD) for the cell with LSM cathode or YSZ cathode powder bed (10 mm diameter, 5 mm thickness) to press uniaxially at 80 MPa, followed by an isostatic pressing at 100 MPa. The NiO–YSZ powder compact with the 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 RuO₂–YSZ or LSM cathode powder was dispersed at 15 vol% solid content in a solvent of 50 vol% ethanol–50 vol% polyethylene glycol. The prepared cathode powder paste 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 or heated at 1150°C for 2 h in air to form the LSM cathode. Then, 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.

Fig. 1. Microstructure of the surface of YSZ electrolyte film sintered at 1400°C in air.
respectively. The measured OCV values were in good agreement with the Nernst voltages of 1.135 V at 600°C, 1.119 V at 700°C and 1.101 V at 800°C, which were calculated by Eq. (1),

\[
E = \frac{\Delta G}{2F} = \frac{1}{2F} \left[ \Delta G^\circ + RT \ln \frac{p_{\text{H}_2\text{O}}(\text{anode})}{p_{\text{H}_2}(\text{anode})p_{\text{O}_2}^{3/2}(\text{cathode})} \right] = E^\circ + \frac{RT}{2F} \ln \frac{p_{\text{H}_2\text{O}}(\text{a})}{p_{\text{H}_2}(\text{a})p_{\text{O}_2}^{3/2}(\text{c})}
\]  

(1)

where \(\Delta G\), \(F\), \(R\), \(T\) and \(p\) are the Gibbs free energy change, 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 \(\text{H}_2\), \(\text{H}_2\text{O}\) and \(\text{O}_2\) gases vary with the current density, and are expressed by Eqs. (2)–(4), respectively,

\[
p_{\text{H}_2}(a) = \frac{s_{\text{H}_2} - c_{\text{H}_2}}{s_{\text{H}_2} + s_{\text{H}_2\text{O}} - c_{\text{H}_2} + f_{\text{H}_2\text{O}}}
\]

(2)

\[
p_{\text{H}_2\text{O}}(a) = \frac{s_{\text{H}_2} + s_{\text{H}_2\text{O}} - c_{\text{H}_2} + f_{\text{H}_2\text{O}}}{c_{\text{H}_2}}
\]

(3)

\[
p_{\text{O}_2}(c) = \frac{s_{\text{O}_2} - c_{\text{O}_2}}{s_{\text{O}_2} + s_{\text{N}_2} - c_{\text{O}_2}}
\]

(4)

where \(s\), \(c\) and \(f\) are the mole numbers of supplied, consumed and formed gases per one second, respectively, in the oxidation of a \(\text{H}_2\) fuel \([\text{H}_2\text{ (anode)} + 0.5\text{O}_2\text{ (cathode)} \rightarrow \text{H}_2\text{O} \text{(anode)}]\). 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,

\[
c_{\text{H}_2}(or \ f_{\text{H}_2\text{O}}) = \frac{i}{nF}
\]

(5)

\[
c_{\text{O}_2} = \frac{1}{2} \frac{i}{nF}
\]

(6)

where \(i\) and \(n\) are the electric current and the number of electrons which contribute to the oxidation of 1 mol \(\text{H}_2\) fuel (i.e., \(n = 2\), respectively). The terminal voltage based on the Nernst equation was calculated by Eqs. (1)–(6) for the measured current density in Figs. 2 and 3. The \(f_{\text{H}_2\text{O}}\) value was calculated to be \(3.91 \times 10^{-7}\) mol/s at 75.4 mA (600 mA/cm², Fig. 3) and was 38.2% of the \(s_{\text{H}_2\text{O}}\) value (1.02 × 10⁻⁸ mol/s) for the \(\text{H}_2–3\text{vol}\% \text{H}_2\text{O}\) fuel at 50 ml/min. On the other hand, either \(c_{\text{H}_2}\) or \(c_{\text{O}_2}\) value was about 1% of \(s_{\text{H}_2}\) or \(s_{\text{O}_2}\) value, respectively, and was negligible in Eqs. (2)–(4). The terminal voltage was calculated by Eq. (1) using the partial pressures of inlet \(\text{H}_2\) and \(\text{O}_2\) gases and the partial pressure of \(\text{H}_2\text{O}\) by Eq. (3). The calculated terminal voltage and electric power were plotted in Figs. 2 and 3, and were significantly higher than the measured values. Therefore, the large measured voltage drop was due to the overpotential at the electrodes.

### 3.2 Cell performance using a \(\text{CO}_2\) oxidant/\(\text{H}_2–3\text{vol\% }\text{H}_2\text{O}\) fuel system

Figures 4 and 5 show the cell performance using a \(\text{CO}_2\) oxidant and a \(\text{H}_2\) fuel for the cells with RuO₂–YSZ cathode and LSM cathode, respectively. The OCV values of the cell with RuO₂–YSZ cathode were 0.036, 0.086 and 0.163 V at 600, 700 and 800°C, respectively, which were

![Fig. 2. (a) Terminal voltage and (b) power density of the YSZ cell with RuO₂–YSZ cathode at 600–800°C using air oxidant and a 97% \(\text{H}_2\)/3% \(\text{H}_2\text{O}\) fuel. The solid lines are the terminal voltages calculated by the Nernst equation.](image1)

![Fig. 3. (a) Terminal voltage and (b) power density of the YSZ cell with LSM cathode at 600–800°C using air oxidant and a 97% \(\text{H}_2\)/3% \(\text{H}_2\text{O}\) fuel. The solid lines are the terminal voltages calculated by the Nernst equation.](image2)
lower than those in the cell with LSM cathode (0.116 V at 600°C, 0.247 V at 700°C and 0.340 V at 800°C). While the terminal voltage in the cell with RuO2–YSZ cathode decreased linearly with increasing current density (Fig. 4), the cell with LSM cathode exhibited the nonlinear current–voltage curves at 700–800°C (Fig. 5). The MPD values of the cell with LSM cathode at 600, 700 and 800°C (Fig. 5) were 0.45 mW/cm² at 5.6 mA/cm², 1.8 mW/cm² at 22.3 mA/cm² and 8.2 mW/cm² at 82.0 mA/cm², respectively, which were two or three orders of magnitude larger than those of the RuO2–YSZ cathode.

Table 1 summarizes the cell resistance which was evaluated from the initial slope of current–voltage plot (Figs. 2–5). In both the oxidants, the cell resistance was significantly smaller for the cell with LSM cathode than for the cell with RuO2–YSZ cathode. While the cell resistance of CO2 oxidant was comparable to that of air oxidant for the LSM cathode, the cell resistance for the RuO2–YSZ cathode was larger for the CO2 oxidant than for air oxidant. According to the reported electrical conductivity of YSZ ceramics, the ohmic resistance of the present YSZ electrolyte of 30 μm thickness was calculated to be 0.67, 0.23 and 0.09 Ω·cm² at 600, 700 and 800°C, respectively, and were significantly smaller than the cell resistance in Table 1. That is, the polarization resistance of the electrodes determined the present cell performance with a CO2 oxidant or air oxidant.

The cell resistance was compared with the reported cell resistance of solid oxide electrolysis cell (SOEC). In the SOEC with a YSZ electrolyte, La0.8Sr0.2Cr0.5Mn0.5O3 cathode and La0.8Sr0.2FeO3 anode, 100% CO2 gas was supplied to the cathode side and the anode was exposed to the ambient air. The open circuit potential was close to zero V and the cell potential rose suddenly to ~0.8 V near 0 A of the supplied electric current. Then the cell potential increased gradually with increasing electric current and the corresponding cell resistance was 0.63 Ω·cm² at 700°C and 0.36 Ω·cm² at 800°C, which were about one order of magnitude smaller than those of the present cell with LSM cathode. In the SOEC with a YSZ electrolyte and Pt–YSZ electrodes, 99.9% CO2–1% CO gas and air were supplied to the cathode and anode, respectively. The cell resistance at the electric current of near 0 A was 120.4 Ω·cm² at 670°C and 70.0 Ω·cm² at 950°C, which were comparable to the resistance of the present cell with RuO2–YSZ cathode.

The measured OCV values were compared with the Nernst voltages for the following possible two reactions.

Table 1. Comparison of cell resistance between air and CO2 oxidants

| Cathode | Temp. (°C) | Air oxidant | CO2 oxidant |
|---------|------------|-------------|-------------|
|         |            | R (Ω·cm²)   | I range (mA/cm²) | R (Ω·cm²)   | I range (mA/cm²) |
| RuO2–YSZ | 600 | 737.3 | 0–1.3 | 1220.9 | 0–0.03 |
|         | 700 | 59.9 | 0–4.0 | 257.5 | 0–0.30 |
|         | 800 | 75.9 | 0–2.5 | 92.8 | 0–1.74 |
| LSM     | 600 | 27.8 | 0–19.9 | 12.1 | 0–10.4 |
|         | 700 | 8.6 | 0–59.7 | 9.1 | 0–11.9 |
|         | 800 | 7.1 | 0–53.3 | 5.9 | 0–45.4 |

R: evaluated from the initial slope of current–voltage plot (Figs. 2–5). The measured current range is shown in Table 1.
\[
\text{H}_2 \text{ (anode)} + \text{CO}_2 \text{ (cathode)} \rightarrow \text{H}_2\text{O} \text{ (anode)} + \text{CO} \text{ (cathode)} \tag{7}
\]
\[
2\text{H}_2 \text{ (anode)} + \text{CO}_2 \text{ (cathode)} \rightarrow \text{2H}_2\text{O} \text{ (anode)} + \text{C} \text{ (cathode)} \tag{8}
\]

The electromotive force for Eqs. (7) and (8) are calculated respectively by Eqs. (9) and (10), respectively,

\[
E = \frac{-\Delta G}{2F} = \frac{-1}{2F} \left[ \Delta G^\circ + RT \ln \frac{p_{\text{H}_2\text{O}}(\text{anode})p_{\text{CO}}(\text{cathode})}{p_{\text{H}_2}(\text{anode})p_{\text{CO}_2}(\text{cathode})} \right]
\]

\[
E = \frac{-\Delta G}{4F} = \frac{-1}{4F} \left[ \Delta G^\circ + RT \ln \frac{p_{\text{H}_2\text{O}}^2(\text{anode})a_C(\text{cathode})}{p_{\text{H}_2}(\text{anode})p_{\text{CO}_2}(\text{cathode})} \right]
\]

where \(a_c\) is the activity of solid carbon and is treated to be unity. Under the operation of the YSZ cell, the partial pressures of \(\text{H}_2\), \(\text{H}_2\text{O}\), \(\text{CO}_2\) and \(\text{CO}\) gases are expressed by Eqs. (11)–(14), respectively.

\[
p_{\text{H}_2}(a) = \frac{s_{\text{H}_2} - c_{\text{H}_2}}{s_{\text{H}_2} + s_{\text{H}_2\text{O}} - c_{\text{H}_2} + f_{\text{H}_2\text{O}}} \tag{11}
\]
\[
p_{\text{H}_2\text{O}}(a) = \frac{s_{\text{H}_2\text{O}} - c_{\text{H}_2\text{O}}}{s_{\text{H}_2\text{O}} + s_{\text{H}_2} - c_{\text{H}_2\text{O}} + f_{\text{H}_2}} \tag{12}
\]
\[
p_{\text{CO}_2}(c) = \frac{s_{\text{CO}_2} - c_{\text{CO}_2} + f_{\text{CO}}}{s_{\text{CO}_2}} \tag{13}
\]
\[
p_{\text{CO}}(c) = \frac{f_{\text{CO}}}{s_{\text{CO}} - c_{\text{CO}} + f_{\text{CO}}} \tag{14}
\]

The \(c_{\text{CO}_2}\) (or \(f_{\text{CO}}\)) is related to the electric current by Eq. (15),

\[
c_{\text{CO}_2}(\text{or } f_{\text{CO}}) = \frac{i}{nF} \tag{15}
\]

The \(n\) value is 2 for the reaction by Eq. (7) (i.e., \(c_{\text{CO}_2} = f_{\text{CO}} = i/2F\)) and 4 for the reaction by Eq. (8) (i.e., \(c_{\text{CO}_2} = i/4F\) and \(f_{\text{CO}} = 0\)). Both the \(c_{\text{H}_2}\) and \(c_{\text{CO}_2}\) values were calculated to be 9.76 \times 10^{-8} \text{ mol/s} at 18.8 \text{ mA} (150 \text{ mA/cm}^2) for the reaction by Eq. (7), which was less than 0.3% of the \(s_{\text{H}_2}\) value (50 ml/min of a \(\text{H}_2\)-3% \(\text{H}_2\text{O}\) fuel, supplied rate) or the \(s_{\text{CO}_2}\) value (100 ml/min of air, supplied rate), respectively. Then, the \(c_{\text{H}_2}\) and \(c_{\text{CO}_2}\) values were ignored in Eqs. (11)–(14). The terminal voltages were calculated by Eqs. (9) and (10) using the partial pressures of inlet \(\text{H}_2\) and \(\text{CO}_2\) gases and the partial pressures of \(\text{H}_2\text{O}\) and \(\text{CO}\) by Eqs. (12) and (14). The measured terminal voltage in Fig. 4(a) was close to the calculated value by Eq. (8). On the other hand, the terminal voltages measured in Fig. 5(a) were observed between the emf values by Eqs. (7) and (8), indicating the two reactions by Eqs. (7) and (8) proceeded simultaneously (e.g. \(3\text{H}_2 + 2\text{CO}_2 \rightarrow 3\text{H}_2\text{O} + \text{CO} + \text{C}\)).

The outlet gas from the cathode side was analyzed by gas chromatograph during the cell operation at a constant terminal voltage. As shown in Fig. 6(a), CO formation was observed at 800°C in both the cells with RuO\(_2\)–YSZ cathode and LSM cathode. In addition, it was confirmed that the amount of CO gas depended on the electric current. The cell with RuO\(_2\)–YSZ cathode at the constant terminal voltage of 0.08 V exhibited the decrease in the current density from 0.87 mA/cm\(^2\) at the starting point to 0.01 mA/cm\(^2\) for 80 min. However, the slight decrease of the current density from 35.8 mA/cm\(^2\) at the starting point to 28.6 mA/cm\(^2\) for 120 min was measured in the cell with LSM cathode at the constant terminal voltage of 0.11 V. However, CO concentration in Fig. 6(a) was larger than the calculated values based on the Faraday’s law. This discrepancy is attributed to the low concentration of CO gas and the measurement limit by the gas chromatograph used. The decrease in the CO concentration and electric current density in the cell with RuO\(_2\)–YSZ cathode is related to the severe carbon deposition at the cathode as described below. The elemental analysis by an energy (or wavelength) dispersive X-ray spectroscopy for the RuO\(_2\)–YSZ cathode and the LSM cathode was conducted after the cell operation at 800°C for 80–120 min. The exfoliation of the RuO\(_2\)–YSZ cathode from the YSZ electrolyte occurred unfortunately in the sample preparation for EPMA observation but 8.23 mass % carbon was detected at the RuO\(_2\)–YSZ cathode/YSZ electrolyte interface. On the other hand, only 0.57 mass % carbon was detected at the surface of the LSM cathode.

In our previous study, the electrochemical decomposition of CO\(_2\) gas (\(\text{CO}_2 \rightarrow \text{C} + \text{O}_2\)) was studied using the cell with a porous YSZ electrolyte, Ru–YSZ anode and Ni–YSZ cathode. When an electric field strength of 0.91
V/cm was applied to the cell at 400–800°C, the outlet gas contained 4–27% (average 15%) O2 gas and solid carbon was deposited in the Ni–YSZ cathode. The CO2 decomposition mechanism was proposed as follows. Ni metal at the cathode reacts with CO2 gas to form NiO and CO gas (Ni + CO2 → NiO + CO). The formed NiO is decomposed to Ni and O2− ions by reaction with the supplied electrons (NiO + 2e− → Ni + O2−). Ni metal and CO gas react further to form NiO and solid C (Ni + CO → NiO + C). The produced O2− ions are transported to the anode by surface diffusion and bulk diffusion through the porous YSZ electrolyte (oxide ion conductor) and converted to O2 gas in the anode (O2− → 0.5O2 + 2e−). In addition, a part of CO gas formed in the cathode reacts with O2− ions in the anode to form again CO2 and electrons (O2− + CO → CO2 + 2e−). Furthermore, the decomposition of CO gas was observed over the porous YSZ electrolyte. The substitution of Zr4+ ions for Y3+ ions produces the positively charged oxygen vacancy (2Y2O3 → 4e− + 4Y2O2 + 2V2O7). The supplied CO gas reacts with the oxygen vacancy to form solid C and positively charged holes (2V2O7 + 2CO → 2O2 + 2C + 4h+). However, little hole conduction occurs in the YSZ electrolyte under a low oxygen partial pressure. The produced holes react quickly with O2− ions transported by surface diffusion and bulk diffusion through YSZ grains from the cathode (4h+ + 2O2− → O2). As a result, O2 gas is produced over YSZ grains through the interaction among oxygen vacancy, CO gas and diffusion O2− ions. In the present study, CO2 decomposition into solid carbon and O2− ions proceeded in the cathode by the reaction of CO2 molecules with electrons supplied from the anode (CO2 + 4e− → C + 2O2−). The above-mentioned CO2 decomposition occurred more easily in the RuO2–YSZ cathode than in the LSM cathode. RuO2 in the cathode may be reduced to Ru metal by the reaction with electrons supplied from the anode (RuO2 + 4e− → Ru + 2O2−). The formed O2− ions are transported through the YSZ electrolyte to the anode side to react with a H2 fuel (H2 + O2− → H2O + 2e−). The Ru metal in the cathode reacts with CO2 molecules to form again RuO2 and solid carbon (Ru + CO2 → RuO2 + C). The YSZ cell with the RuO2–YSZ cathode possesses the two kind of performance producing an electric power and reducing CO2 molecules to solid carbon and O2− ions during the operation of the cell.

### 3.3 Influence of air addition to CO2 oxidant on cell performance

The performance of the cell with LSM cathode was measured using an air–CO2 mixed oxidant (O2–N2–CO2 gas system) and a H2 fuel with 3% H2O at 800°C (Fig. 7). The Nernst voltages for Eq. (1) (H2 + 0.5O2 → H2O) and Eq. (8) (2H2 + CO2 → 2H2O + C) were also plotted in Fig. 7. The partial pressures of O2 and CO2 at the cathode were evaluated from the mixing fraction of air and CO2 gases. Since CO gas did not exist in the inlet air–CO2 mixed gas, the Nernst voltage for Eq. (7) (H2 + CO2 → H2O + CO) could not be calculated. The measured OCV values increased at a higher O2 gas concentration and were about 1 V at 12.6–20.9% O2, which were close to the Nernst voltages by Eq. (1). However, the OCV values decreased rapidly below 10.5% O2, and approached the emf values by Eq. (8). The above result indicates that the reactivity of O2 or CO2 molecules in the mixed oxidant gas is affected by the gas fraction and changes drastically in the range of 6.3–10.5 vol % O2 (70–50% CO2). The OCV value was almost constant above 10.5% O2 but the MPD value increased significantly from 3.4 mW/cm2 for a 10.5% O2 (50% CO2) oxidant to 134.5 mW/cm2 for 20.9% O2 oxidant. This result indicates the addition of air to CO2 decreases the resistance (overpotential) for formation of O2− ions at the cathode, resulting in the increase in the MPD values.

### 4. Conclusions

The performance of a SOFC with 8 mol % YSZ electrolyte, Ni–YSZ anode and LSM cathode or RuO2–YSZ cathode was examined using a CO2 oxidant or air oxidant and a H2 fuel with 3% H2O at 600–800°C. The power density was higher for air oxidant than for a CO2 oxidant. The electromotive force (emf) for a CO2 oxidant depended on the kind of cathodes and close to the emf by the reaction of 2H2 (anode) + CO2 (cathode) → 2H2O (anode) + C (cathode) for the RuO2–YSZ cathode. In the cell with the LSM cathode, the emf values were observed between two Nernst equations for 2H2 + CO2 → 2H2O + C and H2 + CO2 → H2O + CO. The maximum power densities for the LSM cathode at 600, 700 and 800°C were two or three orders of magnitude larger than those for the RuO2–
YSZ cathode. The reactivity of O₂ or CO₂ molecules in the mixed oxidant was dominated by the gas fraction and changed drastically in the range of 50–70 vol% CO₂. The YSZ cell using a CO₂ oxidant possesses two kinds of performance producing an electric power and reducing CO₂ molecules to solid carbon at the same time during the operation of the cell.

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