Cell performance of strontium ruthenium oxide cathode/Gd-doped ceria (GDC) electrolyte/nickel-GDC anode system

Yoshihiro HIRATA,† Kenshi MATSUMOTO, SoichiRO SAMESHIMA, Naoki MATSUNAGA, Minako NAGAMORI and Taro SHIMONOSONO

Department of Chemistry, Biotechnology, and Chemical Engineering, Kagoshima University, 1–21–10 Korimoto, Kagoshima 890–0065
†Fine Particle Processing Group, Nano Ceramics Center, National Institute for Materials Science, 1–2–1 Sengen, Tsukuba, Ibaraki 305–0047

Cell performance was measured at 773–1073 K for Ni–GDC(Gd-doped ceria) anode-supported GDC film (60 μm thickness) with SrRuO3 cathode using a 3 vol% H2O-containing H2 fuel. Reduction of particle size (< 1 μm) of SrRuO3 cathode was effective to decrease the voltage drop at the cathode because of the increased length of triple phase boundary (GDC electrolyte-SrRuO3 cathode-O2 gas). Open circuit voltage (OCV) of GDC electrolyte in an anode atmosphere without H2 fuel was close to the value calculated by Nernst equation for no electronic conduction. However, the OCV in a H2-containing atmosphere decreased from the values by Nernst equation owing to the increased electronic conduction in a GDC film. This tendency of decrease in OCV became significant for thinner GDC film. This result was interpreted by the dissolution and dissociation of H2 fuel in a GDC film to form protons and electrons (H2 → 2H+ + 2e−).

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to form a SrRuO$_3$ cathode powder. The freeze-dried powder was heated at 1073–1273 K for 2–4 h in air. The heated SrRuO$_3$ was milled with alpha-alumina ball (3 mm diameter) for 24 h. The size and phase of milled powder were investigated by X-ray diffraction (RINT 2200, Rigaku Denki Corp., Ltd., Japan) and scanning electron microscope (SM–300, Topcon Corp.).

2.2. Fabrication of anode-supported SOFC

GDC suspensions of 15–25 vol% solids were prepared using a mixed solution of toluene (33 vol%) and isopropanol (67 vol%). Polyethylene glycol of 9 mass% and polyvinyl butyral of 5 mass% were added to the non-aqueous GDC suspensions. The suspensions were stirred for 24 h and then consolidated on polyester sheet by doctor blade (DP–100, Tsugawa Seiki Seikosakusho, Tokyo) at a transfer rate of 15 cm·min$^{-1}$. The front and back blade clearance was 170 and 250 μm, respectively. The formed film was left at room temperature for 24 h. The dried film was cut and shaped into a circle of 22 mm diameter. The GDC film was placed on a NiO–GDC powder bed (22 mm diameter, 2 mm thickness) to form a porous structure and copressed uniaxially at 50 MPa, followed by isostatic pressing at 294 Pa. The copressed compacts were heated at 1673–1773 K for 4 h in air. The bulk density and microstructure of the cosintered laminate were investigated by the Archimedes method using distilled water and scanning electron microscope. The SrRuO$_3$ powders before and after the milling were dispersed, respectively, at 15 vol% solid in a mixed solution of 90 vol% ethanol – 10 vol% ethylene glycol. This suspension was spread on the GDC electrolyte over NiO–GDC anode by screen printing (mesh 70μm, diameter 4 mm), and heated at 1173–1273 K for 1 h in air. The thickness of the attached layer was 80–100 μm.

2.3. Measurement of cell performance

A Pt wire reference electrode was fixed on the surface of GDC film with Pt paste at 1173 K. A Pt mesh was also attached to the each electrode with Pt paste. The anode-supported GDC cell was set to an alumina holder and sealed at 1173 K using a glass O-ring. The cell performance was measured by feeding air (100 ml·min$^{-1}$) and 3 vol% H$_2$O-containing H$_2$ fuel (100 ml·min$^{-1}$) into the cathode and anode, respectively. The NiO of the anode was reduced to Ni by heating at 1073 K in a H$_2$ fuel before the measurement of cell performance (NiO + H$_2$ → Ni + H$_2$O). A direct current-voltage relation was measured at 773–1073 K (As–510, NF Kairosekkei Block Co., Japan). The oxygen partial pressure of the fuel was monitored by yttria-stabilized zirconia oxygen gas sensor operated at 973 K. The OCV of the anode-supported GDC cell was compared with OCV values of the cells with thick GDC electrolyte (500 and 700μm thickness) and Ni–YSZ anode-supported YSZ cell (40μm thickness) with Pt cathode. The thick GDC electrolytes were prepared by pressing a raw GDC powder isostatically at 294 MPa into a disk of 22 mm diameter and 2 mm thickness and by subsequent sintering at 1773 K for 4 h in air. The NiO–GDC suspension (anode) and SrRuO$_3$ suspension (cathode) were spread on the polished surfaces of thick GDC electrolyte of 15 mm diameter. A NiO–YSZ anode-supported YSZ electrolyte was formed by dry pressing and doctor blade processing as described in section 2.2. The green cell was sintered at 1623 K in air. The relative density of NiO–YSZ anode with dense YSZ film was 85.4%. A high purity commercial YSZ powder (13.4 mass% Y$_2$O$_3$, 86.6 mass% ZrO$_2$, TZ–8Y, Tosoh Corp.) was used as a raw powder.

3. Results and discussion

3.1 Microstructures of cell and cathode particles

Figure 1 shows the cross section and surface structure of dense GDC film (60 μm thickness) supported by NiO–GDC anode after cosintering in air at 1673 K for 4 h. Little pores were observed on the GDC film and the grain size ranged from 1.0 to 3.7 μm. The GDC film was tightly adhered to the thick NiO–GDC anode. No warp of the laminate (anode-supported GDC film) was observed after the cosintering. In previous paper, the following important results and analysis were reported for the sintering of the laminate: (1) the laminate using a thin anode layer warped after the sintering because of the difference in the shrinkage of electrolyte and electrode layers, (2) a larger shrinkage was measured for the electrode at 1373–1473 K and for the electrolyte at 1573–1773 K, and (3) the increase of the thickness of anode was effective to decrease the warp and to increase the bulk density of the laminate. Based on the above understanding, the thickness of the NiO–GDC anode was adjusted to 2 mm in this paper and as a result no warp was achieved after the sintering.

On the other hand, SrRuO$_3$ cathode has a high electronic conductivity and high chemical compatibility with GDC electrolyte but shows a rapid grain growth during the heating of precursor (mixture of RuCl$_3$ and Sr(NO$_3$)$_2$). The suppression of grain growth of SrRuO$_3$ particles is desired to maintain the effective length of triple phase boundary (GDC electrolyte–SrRuO$_3$ cathode–O$_2$ gas). Figure 2 shows the SrRuO$_3$ particles formed by heating at 1173–1273 K (a,c) and by subsequent milling with Al$_2$O$_3$ ball (3 mm diameter) for 24 h (b, d). The average particle size was 13 and 19μm for the heating at 1173 K for 4 h and 1273 K.

Fig. 1. Cross section (a) and surface (b) of gadolinium-doped ceria (GDC) film supported by NiO–GDC anode.

Fig. 2. SrRuO$_3$ cathode particles formed by heating at 1173 K for 4 h (a) and 1273 K for 2 h (c). The produced particles (a) and (c) were subsequently milled with Al$_2$O$_3$ ball for 24 h to form particles (b) and (d), respectively.
K for 2 h, respectively. When the SrRuO₃ precursor was heated at 1273 K for 4 h, the particle size increased more to 30 μm. That is, the size of SrRuO₃ is sensitive to the heating condition. After the ball milling, little change was observed for the SrRuO₃ formed at 1273 K (c,d). However, the average size of particles formed at 1173 K decreased drastically to 0.9 μm by the milling. In this paper, the milled fine SrRuO₃ particles were printed on the surface of GDC film. Fortunately, no significant change was observed for the cathode particles after the measurement of cell performance at 773–1073 K.

3.2 Measurement of cell performance with dense thin GDC film

The cell performance of 60 μm thin GDC film covered with 0.9 μm SrRuO₃ particles (cell 1) was measured using a H₂–H₂O fuel and compared with the cell performance of 90 μm GDC film covered with 19 μm SrRuO₃ particles (cell 2), reported in our previous paper. Figure 3 shows the terminal voltage (a) and electric power density (b) as a function of current density at 773–1073 K for cell 1. The OCV was 0.294, 0.434, 0.471 and 0.484 V at 773, 873, 973 and 1073 K, respectively. The oxygen partial pressure at the anode was measured to be 2.00 × 10⁻²³ and 3.48 × 10⁻¹⁷ Pa at 873 and 1073 K, respectively. These values were used to calculate the OCV by Nernst equation. The calculated OCV was 1.17 and 1.11 V at 873 and 1073 K, respectively. The measured OCV deviated from the calculated OCV. This result is discussed more in a latter part and indicates the increased electronic conduction of the GDC film in the H₂–H₂O fuel. The maximum power density was 33, 113, 219 and 348 mW/cm² at 773, 873, 973 and 1073 K, respectively.

Figure 4 shows the performance of cell 2. The oxygen partial pressures measured at the anode were similar to those in Fig. 3. The OCV for cell 2 was also lower than that calculated by Nernst equation. The maximum power density was 34, 100, 150 and 244 mW/cm² at 773, 873, 973 and 1073 K, respectively. The power density between cells 1 and 2 was similar at the low temperatures (< 873 K). However, cell 1 showed a higher power density than cell 2 at the high temperatures (> 973 K). This enhanced power density in cell 1 resulted from the decreased thickness of GDC film and the increased length of triple phase boundary at the cathode.

Figure 5 shows the voltage drop between SrRuO₃ cathode and reference Pt cathode at 973–1073 K for cells 1 and 2. The voltage drop became apparently smaller for cell 1 than for cell 2. The reduction of particle size (< 1 μm) of SrRuO₃ cathode was effective to increase the length of triple phase boundary. As a result, overpotential at the cathode was reduced. The higher operation temperature decreases efficiently the voltage drop at the cathode because of the higher reaction rate between electrons and oxygen molecules at the cathode.

An interesting measurement in cell 1 was the decrease of OCV with time as shown in Fig. 6. Basically, no oxide ions are transported in a solid electrolyte with no electronic conduction at 0
A/cm² of current density. That is, the OCV of electrolyte with unity of transference number of oxide ions is independent of the flow rate of air. This discussion is carried out in section 3.3. The decrease of OCV is related to the decrease of oxygen partial pressure in the cathode layer, as presented by Eq. (5) or (6) in a latter part. The GDC film is a mixed conductor of oxide ions and electrons at a given oxygen pressure of anode. Under the OCV condition, the current densities of oxide ions and electrons are same in the magnitude as shown in Fig. 7. The oxygen molecules in the cathode layer are transported as oxide ions to the anode side through GDC layer. The electrons produced at the anode move to the cathode side. This transport phenomena proceed under the OCV condition. When the rate of supply of oxygen molecules into the cathode layer is smaller than the flow rate of air, the oxygen partial pressure inside of the cathode layer decreases as compared with the oxygen partial pressure of air, causing the decrease of OCV. The fine SrRuO₃ particles (< 1 μm) were used to make the cathode in cell 1. The decreased particle size leads to the formation of hierarchical structure of small pores in the cathode layers. This makes the difficulty of diffusion of air into the cathode layer. As seen in Fig. 6, the OCV of cell 2 using the cathode with large SrRuO₃ particles (19 μm) was stable at the small flow rate (100 ml/min) of air. This result is due to the formation of large open spaces in the cathode layer. The smooth migration of air and fuel inside the electrode layers provides the stable OCV. A similar transport mechanism of oxygen molecules was measured in the thermal decomposition of ammonia over nickel/Gd-doped ceria cermet which separated ammonia gas from air. Although the pyrolysis of ammonia proceeded over a dense GDC electrolyte, no H₂ was detected in the outlet gas. This result was explained by the formation of H₂O from H₂ and O₂ transported through a GDC mixed conductor from anode.

### 3.3 Open circuit voltage and internal short circuit current

Figure 7 shows the flux (J) of O²⁻ ions and electrons in a mixed conductor with thickness L facing both air (cathode) and fuel (anode).

\[
J(O²⁻) = \frac{\sigma(O²⁻) \left(\frac{1}{2} RT \ln \frac{P_{O₂(c)}}{P_{O₂(a)}} + \frac{2}{\sigma} \frac{\partial \eta(c)}{\partial x} \right)}{2F} \tag{1}
\]

where \( \sigma(O²⁻) \) is the conductivity of oxide ions, R the gas constant, F the Faraday constant, T the temperature, and \( \eta \) the electrochemical potential of electron. The J(e) is represented by Eq. (2).

\[
J(e) = \frac{\sigma(e) \frac{\partial \eta}{\partial x}}{F} = -\sigma(e) \frac{\partial \varphi}{\partial x} \tag{2}
\]

where \( \varphi \) is the electric potential. The electronic conductivity \( \sigma(e) \) is expressed by Eq. (3).

\[
\sigma(e) = K \frac{P_{O₂(c)}}{\sigma} \tag{3}
\]

where K and n are constants. Under an open circuit, the summation of \( J(O²⁻) \) and \( J(e) \) is 0. This condition leads to an internal short circuit current by Eq. (4) and open circuit voltage \( (E) \) by Eq. (5).

\[
\left[J(O²⁻)\right] = \left[J(e)\right] = \frac{nRT}{4FL} \sigma(O²⁻) \ln \left[\frac{\sigma(O²⁻) + K P_{O₂(c)}}{\sigma(O²⁻) + K P_{O₂(a)}}\right] \tag{4}
\]

\[
E = \eta(c) - \eta(a) = \frac{nRT}{4F} \ln \left[\frac{P_{O₂(c)}}{P_{O₂(a)}}\right] + \left\{\frac{K}{\sigma(O²⁻)}\right\} \tag{5}
\]

Figure 8 shows the OCV measured for GDC and YSZ electrolyte at 873 and 1073 K as a function of oxygen partial pressure at the anode. The dotted lines express \( E_s \) by Eq. (6). The solid lines represent Eq. (5) for GDC electrolyte, where n and K were determined by Hebb-Wagner ion blocking cell in previous papers.12,13 These solid lines deviated from the Nernst equation at lower \( P_{O₂(c)} \) range because of the increased electronic conduction of GDC electrolyte at the anode.

The formation of \( O²⁻ \) at the anode side of GDC electrolyte is closely related to the reduction of \( Ce^{4+} \) to \( Ce^{3+} \). The difference of OCV between Eqs. (5) and (6) is due to the above electronic conduction and becomes negligible at a lower temperature (Fig. 8(a)). That is, GDC may be used as an electrolyte of intermediate temperature SOFC. The OCV (1.08 V) of YSZ at 1073 K lies on the dotted line by Eq. (6). A slight deviation was observed at 873 K between Eq. (6) (1.13 V) and OCV (1.05 V) of YSZ. The above result is associated with the significantly high chemical stability of YSZ and the high transference number of oxide ions in a H₂-rich atmosphere. As seen in Figs. 3 and 4, the OCV measured for GDC films facing air and \( H₂–H₂O \) fuel deviated from Eq. (5) and showed apparently a tendency of decrease with decreasing thickness of GDC film. The \( H₂ \) atmosphere reduces the OCV of GDC film as compared with the atmosphere without \( H₂ \) molecules (Eq. (5), Hebb-Wagner method) at a similar \( P_{O₂(a)} \). This result is important for use of GDC film as an electrolyte of SOFC and is discussed more.

Figure 9 shows the J–L relation of Eqs. (4) and (7) for GDC.
films. It is found that the internal short circuit current increases as the GDC film becomes thinner. This increased J causes the decrease in OCV. As seen in Fig. 9, the influence of atmosphere at the anode is significant at a thin GDC film. In the thick GDC electrolyte (~1 mm), the difference of J between the two atmospheres with (Eq. (7)) and without H2 fuel (Eq. (4), Hebb-Wagner method) is negligible, suggesting little difference of OCV values. However, the J value in a H2 fuel (Eq. (7)) is larger than that in a reduced atmosphere without H2 molecules (Eq. (4)) for a thinner GDC film. As seen in Fig. 9, the J value for YSZ film in the H2–H2O atmosphere is very small as compared with the GDC films, supporting the high chemical stability in a H2-rich atmosphere.

3.4 Influence of H2 at anode

In previous study, we measured the hydrogen solubility in RDC and YSZ.23) The following solubility of hydrogen was measured by SIMS analyses: 8 mol% YSZ – 1 × 1018 atom/cm3 at 1160 K, CeO2 – 1 × 1018 atom/cm3 at 1153 K, Ce0.8La0.2O1.9 – 7 × 1018 atom/cm3 at 1123 K, Ce0.8Yb0.2O1.9 – 1 × 1020 atom/cm3 at 1153 K. RDC has much higher hydrogen solubility than CeO2 or YSZ. When the size of doped rare earth element becomes smaller, the hydrogen solubility increases. This result indicates the oxygen vacancy of RDC may enhance the hydrogen solubility. The dissolved hydrogen may react with positively charged oxygen vacancy by Eq. (8),

\[ \text{H}_2 + V_{\text{O}}^\ast \rightarrow 2\text{H}^+ + V_{\text{O}}^\cdot \]  

The neutral oxygen vacancy changes to positively charged oxygen vacancy and electrons by Eq. (9).

\[ V_{\text{O}}^\cdot \rightarrow V_{\text{O}}^\ast + 2e^- \]  

The summation of Eqs. (8) and (9) provides Eq. (10), which corresponds to the formation of protons and electrons from the dissociated H2 molecules.

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]  

As a result, protons and electrons are formed in GDC film, which increases J value in an open circuit (Fig. 9). When the anode atmosphere contains H2 molecules, electrons are produced through two mechanisms: (1) reduction of Ce4+ to Ce3+ as discussed previously, (2) dissociation of H2 molecules by Eq. (10). These two mechanisms may couple to give electron conduction and proton conduction in GDC film:12)

\[ \text{Ce}_x\text{O}_y + \text{H}_2 \rightarrow \text{Ce}_x\text{O}_y + 3e^- + 2\text{H}^+ + V_{\text{O}}^\ast + \frac{1}{2}\text{O}_2 \]  

\[ \text{Ce}_x\text{O}_y + 2\text{O}_2 + \text{H}_2 \rightarrow \text{Ce}_x\text{O}_y + 5e^- + 2\text{H}^+ + 2V_{\text{O}}^\ast + \text{O}_2 \]  

The concentration of electrons is greatly increased under the H2-containing atmosphere as compared with the case without H2 (Fig. 9, Eq. (4)). The important result is the low hydrogen solubility in CeO2 and YSZ, indicating that (1) the interaction between oxygen vacancy in YSZ and hydrogen is small and (2) pure CeO2 without oxygen vacancy by doping of rare earth element has little interaction with hydrogen. This fact concludes that the coupling of the reduction of Ce4+ to Ce3+ and the accompanied formation of oxygen vacancy is responsible for the interaction with H2, producing electron conduction and formation of proton.23) As a result, the OCV is reduced. The prevention of dissolution of hydrogen in a GDC film should be planned to increase the OCV and resultant power density.

The decrease of overpotential at the cathode may be an effective strategy to maintain a high terminal voltage during the operation of SOFC. The overpotential at the anode is usually lower than that of cathode.24,25) The decrease of overpotential enhances the oxide ion current (flux of oxide ions). When the flux of oxide ions in the GDC film is significantly higher than the flux of hydrogen dissolved, the diffusing oxide ions react with hydrogen molecules at the anode triple phase boundary over the surface of GDC film. This surface reaction is favorable to maintain a high terminal voltage, contributing to a high power density.

Another strategy is the coating of surface (anode side) of GDC...
film with thin YSZ film to prevent the dissolution of H₂ fuel. The solubility of H₂ in YSZ is much lower than that of GDC. In addition the good adhesion of very thin YSZ film suppresses the diffusion of O₂ gas formed by the reaction of Ce⁴⁺ and lattice O⁻ ions in a GDC film at the anode. The above effects contribute to the suppression of formation of electrons and protons and to the resultant increase of OCV or terminal voltage. These effects are studied experimentally in future.

4. Conclusions

(1) Reduction of the particle size (<1 μm) of SrRuO₃ cathode was effective to decrease the voltage drop at the cathode of Ni–GDC anode-supported GDC film cell because the length of triple phase boundary at the cathode was increased.

(2) The following maximum power density was measured for the anode-supported cell of 60 μm GDC film using a 3 vol% H₂O–H₂ fuel: 33 mW/cm² at 773 K, 113 mW/cm² at 873 K, 219 mW/cm² at 973 K, and 348 mW/cm² at 1073 K.

(3) The OCV of thin GDC electrolytes below 1073 K in the atmosphere without H₂ molecules was close to the values calculated by Nernst equation for no electronic conduction by 10⁻¹⁵ Pa of anode oxygen pressure.

(4) However, the OCV of GDC electrolyte in an atmosphere with H₂ molecules deviated from the values by the Nernst equation. Hydrogen molecules dissolve greatly in the GDC films to form protons and electrons in the film, leading to the increase in internal short circuit current. This phenomenon causes the decrease in OCV and resultant power density.

(5) The OCV of thin YSZ electrolyte was very close to the theoretical values calculated by Nernst equation. This result is due to the significantly high chemical stability of YSZ in a H₂ atmosphere.

(6) Although YSZ contains positively charged oxygen vacancy, the interaction between oxygen vacancy and hydrogen is negligible, leading to the low hydrogen solubility. This result also contributes to the little formation of electrons and protons in YSZ.

References