



Single-Chamber SOFCs Using Dimethyl Ether and Ethanol

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An anode-supported single-chamber solid oxide fuel cell (SC-SOFC), consisting of a Ce_{0.9}Gd_{0.1}O_{1.9} electrolyte, a Ni-Ce_{0.8}Sm_{0.2}O_{1.8} (SDC) cermet anode, and a Sm_{0.5}Sr_{0.5}CoO₃ cathode, was operated in a mixture feed of dimethyl ether (DME), ethanol or butane, and air at a furnace temperature of 300°C. This SC-SOFC showed comparatively poor performance for DME and ethanol fuels when compared to the performance for butane fuel, resulting from the relatively small difference in catalytic activity for DME and ethanol oxidation between the anode and the cathode. An effective improvement was achieved by attaching Ru/SDC/Ni and Cu/Zn/Al catalyst layers for DME and ethanol, respectively, on the anode surface. As a result, peak power densities of 64 and 117 mW cm⁻² were obtained for DME and ethanol, respectively.

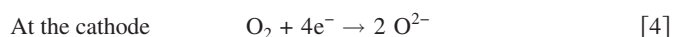
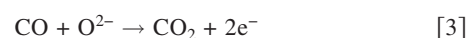
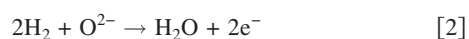
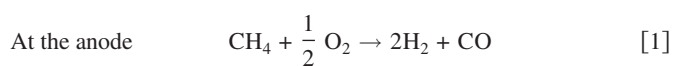
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Manuscript submitted January 4, 2007; revised manuscript received April 20, 2007. Available electronically June 22, 2007.

Solid oxide fuel cells (SOFCs) have received much recent attention as next-generation alternative energy sources because of their high overall efficiencies and good fuel flexibility. However, the high-temperature operation results in a number of challenges that need to be overcome, including interfacial diffusion between cell components, mechanical stress due to their different thermal expansion coefficients, and electrode deactivation by poisoning and sintering.¹ In particular, failure to obtain a gastight seal between chambers is a very serious problem, causing gas leakage and eventual destruction of the stacked cells. Moreover, the addition of a large amount of steam to hydrocarbon fuels is needed to avoid carbon formation on the anode surface, requiring complicated water management in SOFC systems.

One approach toward addressing the above challenges is to design an SOFC with only one gas chamber. This type of SOFC is named "single-chamber SOFC" (SC-SOFC), wherein both the anode and cathode are exposed to the same mixture of fuel and oxidant gas. As a result, the gas-sealing problem can be inherently avoided as no separation of fuel and air is required. Furthermore, carbon deposition is less of a problem due to the presence of a large amount of oxygen in the mixture. SC-SOFCs have several additional benefits: (i) the mechanical and thermal resistance of SOFCs can be enhanced due to the simplified cell structure, (ii) the cell temperature can effectively be raised due to the fuel oxidation reaction, and (iii) the solid electrolyte does not have to be pore-free, allowing for relatively low processing temperature of the electrolyte, thereby reducing manufacturing costs.

We applied this concept to SOFCs for the first time, wherein an SC-SOFC was operated with a mixture feed of methane and air at a furnace temperature of 950°C.² Ytria-stabilized zirconia (YSZ), Ni-YSZ cermet (or Pt), and Au were used as the electrolyte, anode, and cathode, respectively. It was seen that partial oxidation of methane by oxygen proceeded at a very fast rate on the anode, while no significant reaction between methane and oxygen was observed on the cathode. The resulting SOFC generated an open-circuit-voltage (OCV) of about 350 mV and a peak power density of 2.3 mW cm⁻² for a methane and air mixture feed. The observed OCV was considered to be due to the local oxygen concentration gradient, resulting from the difference in catalytic activity for the partial oxidation of methane by oxygen between the two electrodes.



One reason for the low OCV observed is that each electrode was not ideally selective to the corresponding electrode reaction. Another reason is the direct chemical reaction of the fuel with the oxidant in the gas phase or on the electrode surface. These also caused an energy loss in the fuel cell.

Currently, attempts are under way by a number of researchers to improve SC-SOFCs using various innovative techniques.³⁻⁷ Consequently, the power density has been increased significantly from 2.3 to 760 mW cm⁻². The furnace temperature required for operating the SC-SOFCs has also been reduced from 950 to 200°C. More recently, a thermally self-sustained SC-SOFC was developed using the heating effect from the fuel oxidation reaction. It appears that the SC-SOFCs are equal to or better than conventional SOFCs in terms of performance. Advances in SC-SOFC development have been reviewed in a recent publication.⁸

In these recent studies, another important result makes it possible to use different hydrocarbon fuels, including methane, ethane, propane, and butane, without significant carbon deposition, providing high flexibility in terms of the fuel used. Environmental pollution and future energy supplies necessitate the replacement of fossil fuels with renewable fuels. Dimethyl ether (DME) and ethanol are regarded as promising alternate fuels because not only fossil fuels but also biomass are resources for their production. DME and ethanol have been subjected to research as fuels for conventional SOFCs.⁹⁻¹¹ However, these fuels have not been investigated in detail for SC-SOFCs, although ethanol has been previously used as a test fuel.¹² Because DME and ethanol are more reactive than hydrocarbons, the use of these fuels shows the potential for improving the performance of SC-SOFCs, especially at low temperatures, but their use also makes it hard to handle the cell operation. In this study, we investigated the feasibility and efficacy of using DME and ethanol as fuels for SC-SOFCs. Comparative cell performance using DME, ethanol, and butane are measured in the temperature range of 250–350°C. The anode catalysts have also been optimized for reforming DME and ethanol.

Experimental

The anode material was prepared from a mixture of 50 wt % Ce_{0.8}Sm_{0.2}O_{1.9} (SDC), 5 wt % acetylene black, and NiO for the rest. The mixed powders were ground in ethanol using a planetary ball mill for 1 h, pressed into pellets, and presintered at 1400°C for 5 h in air. The surface of the pellet (diameter ca. 13.5 mm, thickness 0.95 mm) was spin-coated with a slurry of Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) electrolyte, which was prepared by mixing the corresponding powders with ethyl cellulose, terpineol, and butyl carbitol. After drying

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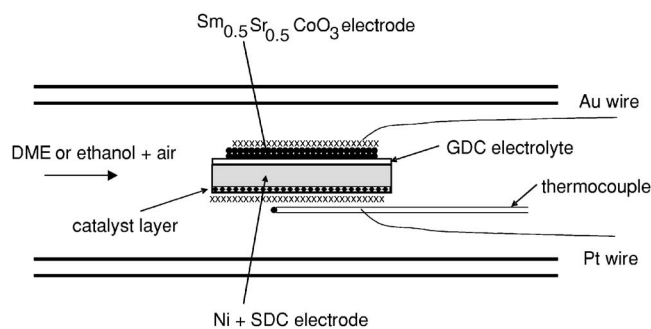


Figure 1. Schematic illustration of a single-chamber SOFC supported by the anode.

at 90°C in air, the pellet was sintered at 1500°C for 10 h in air. The electrolyte thickness, which was evaluated using scanning electron microscopy (SEM), was approximately 15 μm. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ oxide (SSC) was used as the cathode (area 0.5 cm²). The preparation and treatment of this electrode have been described elsewhere.¹³

Various metal/SDC/Ni and Cu/Zn/Al catalyst layers were also deposited on the anode surface opposite to the electrolyte surface. The metal/SDC/Ni catalysts were prepared by mixing the desired amounts of metal oxide (PdO, PtO₂, Rh₂O₃, or RuO₂), SDC, and NiO powders, wherein the weight percent of the metal oxide was in the range of 2–12. The Cu/Zn/Al catalyst was prepared by coprecipitation of the corresponding aqueous solution of nitrates [Cu(NO₃)₂, Zn(NO₃)₂, and Al(NO₃)₃] with sodium carbonate solution at approximately 60°C. After washing with distilled water and drying at 105°C in air, the precipitate was calcined at 500°C for 5 h in air. The metal/SDC/Ni and Cu/Zn/Al catalysts were ground in a similar manner as above and then smeared on the anode surface as thinly as possible with a brush. The metal/SDC/Ni catalysts were baked at 1380°C prior to the cathode deposition, while the Cu/Zn/Al catalyst was baked at 500°C subsequent to cathode deposition.

The cell thus fabricated was set up in a ceramic tube (inner and outer diameter of 13 and 17 mm, respectively) as shown in Fig. 1. A DME- or ethanol-air mixture with various DME- or ethanol-to-oxygen molar ratios was supplied to the cell at flow rates between 200 and 350 mL min⁻¹. For the ethanol-air mixture, air was bubbled through ethanol in a vessel maintained at the desired temperatures and then introduced through a gas line heated at a higher temperature into the ceramic tube. Butane was used as the fuel for comparison, wherein the butane-to-oxygen molar ratio was maintained at a stoichiometric value of 0.5 for the partial oxidation of butane. The cell temperature was measured by attaching a thermocouple to the anode. The outlet gas from the anode-supported cell having only the anode or the electrolyte-supported cell having only the cathode was analyzed on a dry basis using on-line gas chromatography (GC).

Results and Discussion

Comparative performance of SC-SOFC with butane, DME, and ethanol fuels.— Because the operation of SC-SOFCs is based on the different catalytic properties of the two electrodes for partial oxidation of the fuel, the cell performance is strongly dependent on experimental parameters, such as the fuel-to-oxygen molar ratio, the operating temperature, and the total flow rate. We first determined the optimal operating conditions from OCV measurements of an SC-SOFC without any catalyst layer in mixture feeds of DME or ethanol and air. Figure 2 shows the changes in OCV with fuel-to-oxygen molar ratio in the DME- or ethanol-air mixture feeds. At fuel-to-oxygen molar ratios near the stoichiometric value of 2 for the partial oxidation of DME and ethanol, the fuel cell with DME generated OCVs above 700 mV, whereas the fuel cell with ethanol showed nonreproductive OCVs ranging from positive to negative

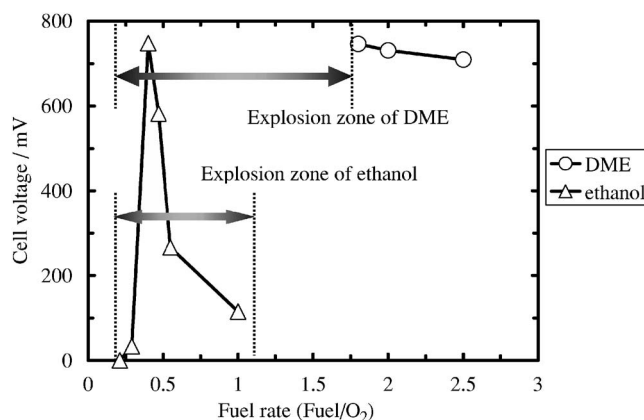


Figure 2. OCVs of SC-SOFC in mixture feeds of DME or ethanol and air with fuel-to-oxygen molar ratios.

values. This result indicates that ethanol is not an easily available fuel under the present conditions. GC analysis of the outlet gas from the electrodes revealed that reactions between ethanol and oxygen, including partial and deep oxidations, took place at the cathode as well as at the anode. Consequently, there seems to be an insignificant local oxygen concentration gradient between the two electrodes in the ethanol-air mixture feeds. However, Fig. 2 also shows relatively high OCVs above 500 mV in a narrow range of the ethanol-to-oxygen molar ratio (0.4–0.5). This narrow window can be explained by assuming that the reaction rate of ethanol oxidation is decreased at each anode and cathode to a different degree as oxygen is rich, resulting in a slight difference in the catalytic properties between them under limited conditions. Ethanol-to-oxygen molar ratios between 0.4 and 0.5 are within the explosion limit of ethanol in air (3.3–19 vol %). This again indicates that it is difficult to use ethanol as a fuel in the present SC-SOFC. Nevertheless, we continue to investigate the SC-SOFCs with ethanol as well as DME from the viewpoint of scientific interest.

Figure 3 shows the changes in OCV with furnace temperature in the DME- or ethanol-air mixture feeds. The dependence of the OCV on furnace temperature was relatively small for DME at all the tested temperatures but was significantly large for ethanol, 715–746 mV for DME and 503–748 mV for ethanol. The large temperature dependence observed for ethanol is also attributable to the limited difference in catalytic properties for ethanol oxidation between the anode and cathode, which is sensitive not only to the fuel-to-oxygen molar ratio but also to the temperature. Figure 4 shows changes in OCV with gas flow rate in the DME- or ethanol-

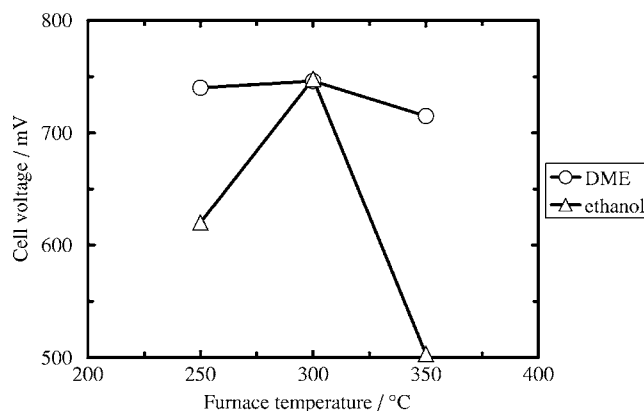


Figure 3. OCVs of SC-SOFC in mixture feeds of DME or ethanol and air at various furnace temperatures.

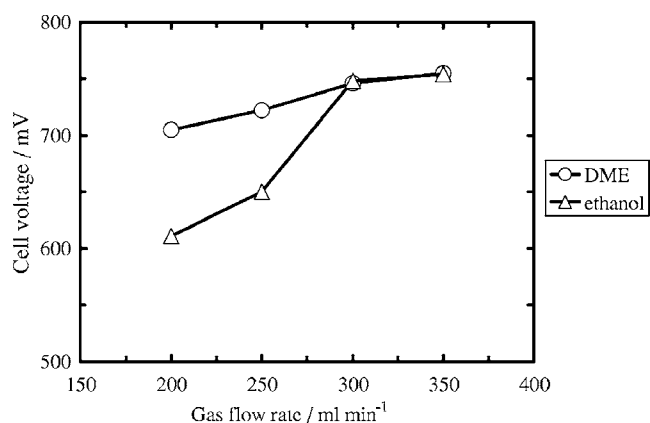


Figure 4. OCVs of SC-SOFC in mixture feeds of DME or ethanol and air at various gas-flow rates.

air mixture feeds. Both the OCVs increased with increasing gas flow rate and attained an almost constant value at a flow rate of more than 300 mL min^{-1} . Similar dependence on the gas-flow rate has been reported for hydrocarbon-air mixtures by many researchers,^{3-6,8} who interpreted the heat evolved by fuel oxidation at the anode to be proportional to the gas-flow rate, causing an increase in the cell temperature with increasing gas-flow rate. Based on the above results, subsequent experiments were carried out at DME-to-oxygen and ethanol-to-oxygen molar ratios of 1.8 and 0.4, respectively, and at a furnace temperature of 300°C and a flow rate of 350 mL min^{-1} , unless otherwise specified.

For these conditions, the cell performance using DME and ethanol was compared to the cell performance using butane. It can be seen from Fig. 5 that the fuel cell revealed some similarities between the DME and ethanol fuels. Upon introducing the DME- or ethanol-air mixture, the cell temperature quickly rose to about 400°C , and the fuel cell generated an OCV of about 755 mV . Also, in both cases, the cell voltage was stable during discharge, and no limiting current behavior was observed. However, the fuel cells using these fuels had obvious differences, especially for the OCV, compared to the fuel cell using the butane fuel. The OCVs observed for DME and ethanol were lower by about 150 mV when compared to the value observed for butane. As a result, the peak power density was lower with DME (37 mW cm^{-2}) and ethanol (44 mW cm^{-2}) than with butane (59 mW cm^{-2}).

To understand the low OCVs of the SC-SOFC with DME and ethanol shown in Fig. 5, the catalytic activities of the anode and

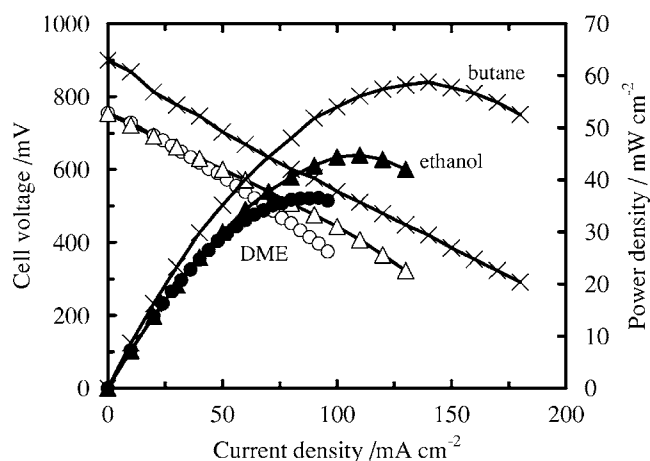
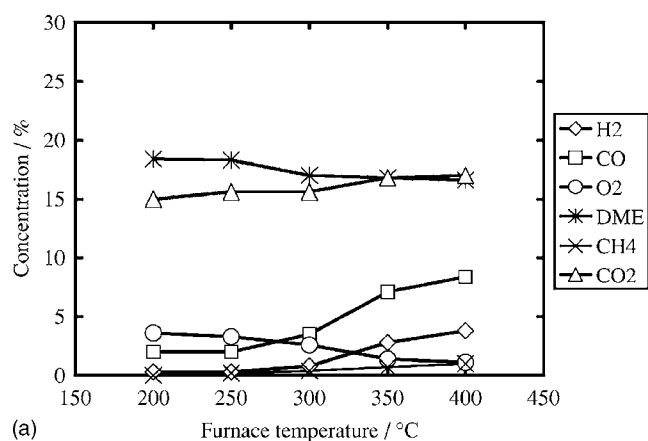
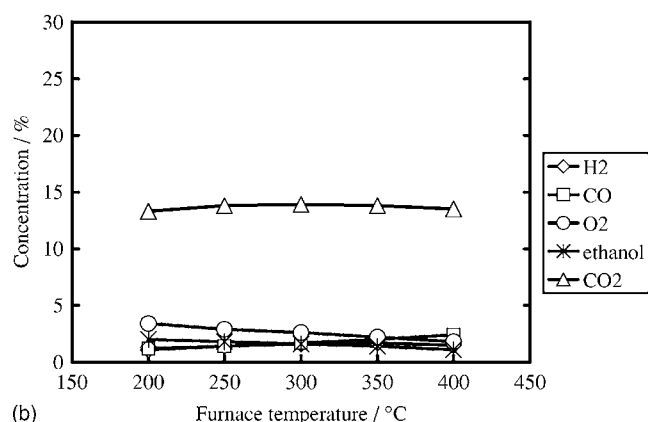


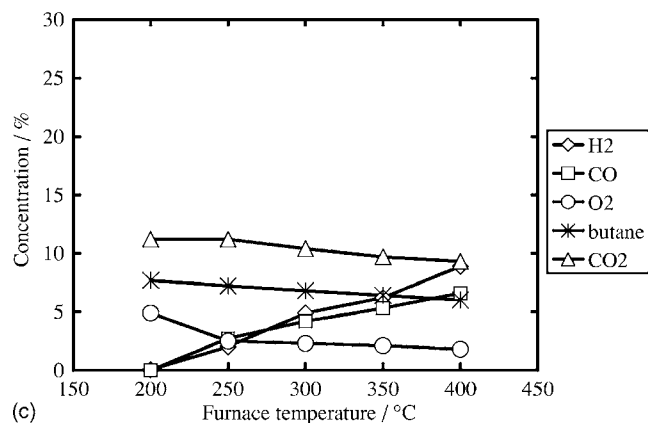
Figure 5. Cell performance of SC-SOFC in mixture feeds of various fuels and air at a furnace temperature of 300°C .



(a)



(b)



(c)

Figure 6. Catalytic properties of Ni/SDC anode for partial oxidation of (a) DME, (b) ethanol, and (c) butane.

cathode were measured at furnace temperatures between 200 and 400°C . As can be seen from Fig. 6, all the tested fuels were not only partially but also completely oxidized at the anode above 200°C . The proportion of partial oxidation of the three fuels was significantly lower for ethanol than for butane and DME, which can be understood in terms of the low ethanol-to-oxygen molar ratio. Moreover, the formation amount of hydrogen was lower for DME and ethanol than for butane, which can account for the low OCVs observed for DME and ethanol. However, there was no systematic relationship between OCV and formation amount of other products. This higher sensitivity of the OCV to hydrogen compared to carbon monoxide and carbon dioxide may be due to the low-temperature operation. Miura et al. showed a similar effect of temperature on the mixed potential for hydrogen.¹⁴ Figure 7 shows that both partial and deep oxidations of the three fuels proceed with slow rates on the

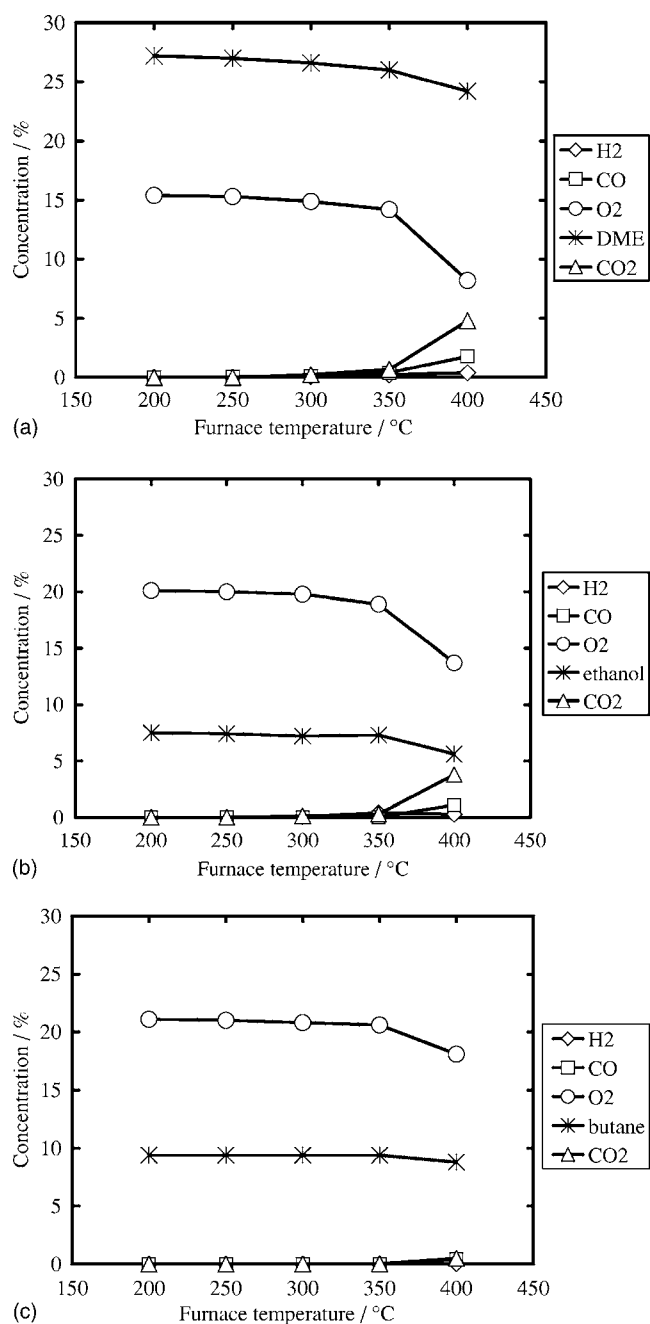


Figure 7. Catalytic properties of SSC cathode for partial oxidation of (a) DME, (b) ethanol, and (c) butane.

cathode, indicating that the cathode is more inert to the oxidation of the three fuels compared to the anode. However, the cathode became active to some extent at 400°C, which is close to the actual cell temperature under the present fuel cell conditions. This degree of activity for fuel oxidation was more remarkable for DME and ethanol than for butane, which may also be responsible for the low OCVs observed for DME and ethanol. Thus, it is concluded that the generation of the OCV from the fuel cell with DME and ethanol is competitively affected by the catalytic properties of the anode and cathode, which is more complicated when compared to the behavior of the fuel cell with butane.

The use of the Pt electric collector can affect the catalytic properties of the anode and the resulting cell performance of SC-SOFCs. Indeed, Napporn et al. have reported that the Pt electric collector used at the anode in their experiment exerted a strong effect on the

Table I. Effects of various catalyst layers on cell performance in a mixture feed of DME and air at 300°C.

	OCV (mV)	Ohmic resistance (Ω)	Electrode resistance (Ω)	Temperature rise ($^{\circ}\text{C}$)
None	755	1.79	4.83	103
5 wt % Ru	771	1.54	2.79	131
5 wt % Rh	760	1.9	2.8	–
5 wt % Pd	729	1.16	2.91	–
5 wt % Pt	766	1.09	3.12	–
Cu–Zn	672	2.32	9.28	–
2 wt % Ru	770	1.74	4.46	–
5 wt % Ru	771	1.54	2.79	131
9 wt % Ru	766	1.4	2.54	–
12 wt % Ru	760	1.65	3.98	–

cell temperature; the temperature rise was larger with the Pt electric collector than without.¹⁵ We also observed DME and ethanol oxidation products in the outlet gas from the Pt electric collector. However, the gas concentrations of hydrogen, carbon monoxide, and carbon dioxide observed for the Pt electric collector were 0.1, 1.1, and 3.5%, respectively, at 300°C, which are much lower than the corresponding gas concentrations shown in Fig. 6. Thus, we presumed that fuel oxidation mainly proceeded on the anode.

Improvement in cell performance using catalyst layers.— The above results suggest that the performance of the SC-SOFC would be further improved by enhancing the catalytic activity of the anode for the partial oxidation of DME and ethanol. For this purpose, we attached various catalyst layers on the anode surface and then evaluated their effects on cell performance. In the case of DME, the Ru/SDC/Ni catalyst layers yielded a positive effect on the OCV, with an optimal RuO₂ content of 5 wt %, as shown in Table I. Figure 8 shows the gas composition of the outlet gas from the anode with the Ru/SDC/Ni catalyst layer for the same conditions as in Fig. 6. While the formation amounts of hydrogen and carbon monoxide were increased about two- or threefold, the formation amount of carbon dioxide was slightly decreased, depending on the temperature. This result is indicative that the Ru/SDC/Ni catalyst layer enhanced partial oxidation rather than the deep oxidation. As described earlier, the enhanced hydrogen formation is considered to contribute to the improvement of OCV of the fuel cell. Table I also shows that the Ru/SDC/Ni catalyst layers improved the internal resistance as well as the OCV. This result can be explained by the heating effect resulting from the catalyzed partial oxidation. This reaction yields the following amount of reaction heat¹⁶

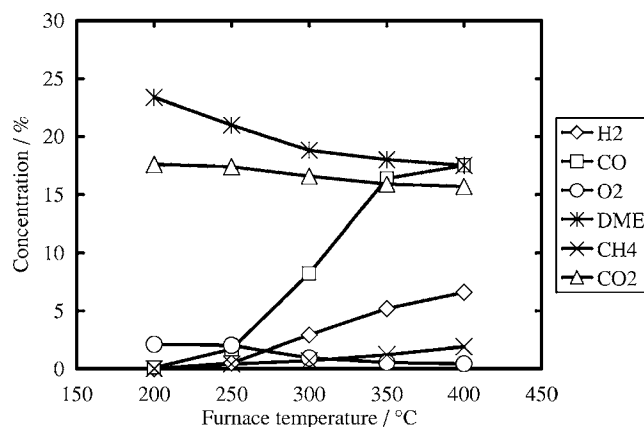


Figure 8. Catalytic properties of Ni/SDC anode with Ru/SDC/Ni catalyst layer for partial oxidation of DME.

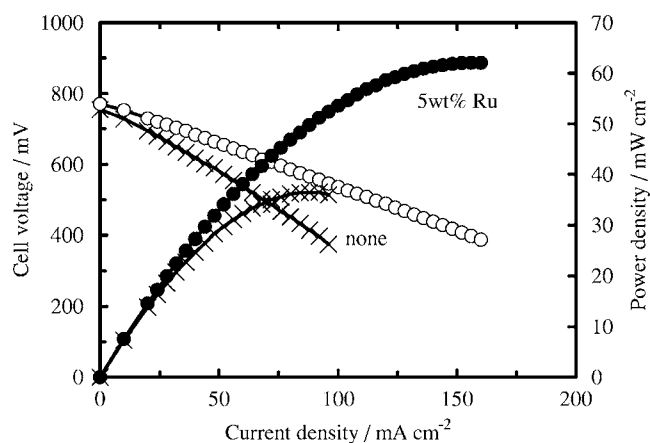
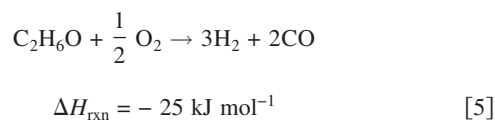


Figure 9. Cell performances of SC-SOFCs with and without Ru/SDC/Ni catalyst layer in a mixture feed of DME and air at a furnace temperature of 300°C.



The released heat resulted in an additional temperature rise of about 30°C at the anode, followed by thermal conduction to the cathode through the electrolyte. As a result, the internal resistance of the fuel cell was effectively reduced.

Figure 9 shows the performance of the SC-SOFCs with and without the Ru/SDC/Ni catalyst layer in the DME–air mixture feed at a furnace temperature of 300°C. The use of the catalyst layer resulted in enhanced OCV and a reduced voltage drop. The resulting peak power density reached 64 mW cm⁻², which is about 1.8 times higher than without the catalyst layer.

In the case of ethanol, the most significant improvement in cell performance was achieved by using the Cu/Zn/Al catalyst layer, as shown in Table II. In particular, the increase in OCV and cell temperature was greater than that observed for the SC-SOFC with the Ru/SDC/Ni catalyst layer in the DME–air mixture feed. Figure 10 shows the gas composition of the outlet gas from the anode with the Cu/Zn/Al catalyst layer for the same conditions as in Fig. 6. It was confirmed that the formation amounts of hydrogen and carbon monoxide with the Cu/Zn/Al catalyst layer were increased a maximum threefold compared to the amounts formed without the catalyst layer. It is well known that Cu/Zn-based catalysts are active for the partial oxidation and steam reforming of alcohol.¹⁷ This result can be related to the increase in OCV but cannot explain the higher OCV for ethanol than the value for DME. Note that the ethanol–air mixture used in this study was considerably oxygen-rich, as shown in Fig. 7. The oxygen-rich environment is a favorable condition for the cathode because a relatively large amount of oxygen still remains even if fuel oxidation takes place. Consequently, the cathode

Table II. Effects of various catalyst layers on cell performance in a mixture feed of ethanol and air at 300°C.

	OCV (mV)	Ohmic resistance (Ω)	Electrode resistance (Ω)	Temperature rise (°C)
None	754	1.52	3.59	122
Cu–Zn	811	1.41	1.44	189
5 wt % Ru	794	1.48	3.19	–
5 wt % Rh	702	1.5	3.01	–
5 wt % Pd	740	2.04	2.58	–
5 wt % Pt	763	3.84	16.71	–

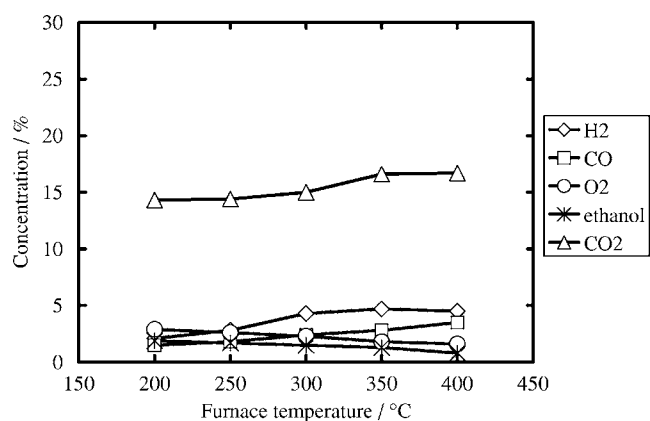
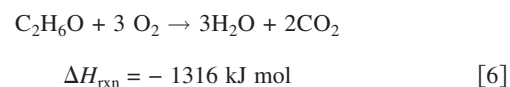


Figure 10. Catalytic properties of Ni/SDC anode with Cu/Zn/Al catalyst layer for partial oxidation of ethanol.

potential is insensitive to the fuel oxidation at the cathode, so that the anode potential mainly determines the OCV of the fuel cell. We presume that this situation leads to the higher OCV for ethanol than for DME. Another important result in Fig. 10 is that the deep oxidation of ethanol was also catalyzed by using the Cu/Zn/Al catalyst layer, which is different from the behavior of the Ru/SDC/Ni catalyst layer. More important is that this reaction yields a larger amount of reaction heat than that of Reaction 5¹⁶



Thus, it is suggested that the temperature rise observed using ethanol was higher by about 50°C when compared to the value observed using DME, as shown in Table II.

Figure 11 shows the performance of the SC-SOFCs with and without the Cu/Zn/Al catalyst layer in the ethanol–air mixture feed at a furnace temperature of 300°C. The enhancement in performance was more remarkable for ethanol than for DME. In particular, the voltage drop was significantly reduced by using the Cu/Zn/Al catalyst layer. Consequently, the highest peak power density of 117 mW cm⁻² could be obtained in this study.

No carbon was observed on the surface of the Ru/SDC/Ni and Cu/Zn/Al catalyst layers after the test. This implies that carbon formation is suppressed by the presence of the coexisting oxygen in the mixture feed, which is a significant advantage over conventional SOFCs. Another point worth noting is that fuel-cell operation was

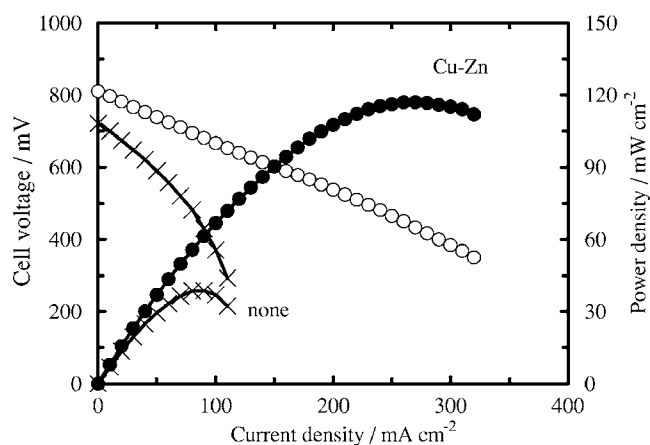


Figure 11. Cell performance of SC-SOFCs with and without Cu/Zn/Al catalyst layer in a mixture feed of ethanol and air at a furnace temperature of 300°C.

also achieved at a lower furnace temperature; for example, in the case of ethanol, the fuel cell yielded a peak power density of 59 mW cm^{-2} at 250°C . However, challenges still remain for further improvements in the present SC-SOFCs, especially in terms of fuel utilization. The fuel utilization was estimated to be less than 2% because a large amount of DME and especially ethanol was subjected to deep oxidation in the fuel cells. The development of more ideally selective anode and cathode materials for fuel oxidation and oxygen reduction are required to solve this challenge.

Conclusions

SC-SOFCs operating with a DME- or ethanol-air mixture feed were proposed in the present study. An anode-supported fuel cell, Ni-SDC|GDC|SSC, was fabricated by spin-coating. From OCV measurements, the optimal operating conditions were experimentally determined: DME- and ethanol-to-air molar ratios of 1.8 and 0.4, respectively, a furnace temperature of 300°C , and a gas-flow rate of 350 mL min^{-1} . In addition, the OCV was found to be competitively influenced by the catalytic properties of the anode and cathode for fuel oxidation, including partial- and deep-oxidation reactions. This behavior was in contrast to the behavior of an SC-SOFC in a butane-air mixture feed. Ru/Ni/SDC and Cu/Zn/Al catalyst layers mainly promoted the partial oxidation of DME and ethanol, respectively, resulting in an increase in the OCV of the fuel cell. Furthermore, the Cu/Zn/Al catalyst layer also catalyzed the

deep oxidation of ethanol, providing a large temperature rise in the cell. As a result, the peak power density reached 64 mW cm^{-2} for DME and 117 mW cm^{-2} for ethanol.

Nagoya University assisted in meeting the publication costs of this article.

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