

Single-Chamber SOFCs Using Hydrocarbons, Ethanol, and DME

Masaya Yano, Takanori Kawai, Kohsuke Okamoto, Atsuko Tomita* and Takashi Hibino

Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan

Fax: 81-52-789-4206, e-mail: hibino@urban.env.nagoya-u.ac.jp

*Material Research Institute for Sustainable Development, Advance Industrial Science and Technology, Nagoya 463-8560, Japan

Fax: 81-52-736-7406, e-mail: at-tomita@aist.go.jp

An anode-supported single-chamber solid oxide fuel cell (SC-SOFCs), which consisted of a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte, a $\text{Ni-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) cermet anode, and a $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 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 poorer performances for the DME and ethanol fuels than for the butane fuel, which resulted from low catalytic properties of the anode for the partial oxidation of DME and ethanol. An effective improvement was made 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.

Key words: single-chamber SOFC, DME, ethanol, intermediate temperature

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) have received much recent attention as next generation alternative energy sources because of their high overall efficiencies. However, the high temperature operation results in a number of challenges, such as mechanical stress, electrode sintering, and slow start-up time [1]. In particular, failure to obtain a gas-tight seal between chambers is very serious, causing gas leakage and eventually 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 towards 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 since no separation between fuel and air is required. In addition, 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:

- The mechanical and thermal resistance of SOFCs can be enhanced due to the simplified cell structure.
- The cell temperature can effectively be raised due to the fuel oxidation reaction.
- The solid electrolyte does not have to be pore-free, allowing for relatively low processing temperature of the electrolyte, thereby reducing manufacturing costs.

In SC-SOFCs, the two electrodes should meet the following criteria. 1) One electrode (anode) has to be electrochemically active for oxidation of the fuel but should be inert to oxygen reduction; 2) the other electrode (cathode) has to show the opposite properties. Consequently, the fuel cell generates the maximum open-circuit voltage (OCV) when each electrode is ideally selective to the corresponding electrode reaction.

One factor that lowers the OCV is when the target electrode reaction cannot overwhelm the counter electrode reaction in rate at the electrode, decreasing the potential for the target electrode reaction. Another factor is the direct chemical reaction of the fuel with the oxidant in the gas phase or on the electrode surface. This also causes an energy loss in the fuel cell.

We made the first application of this concept to SOFCs, 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. 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 OCV of about 350 mV and a peak power density of 2.3 mW cm^{-2} in the 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 (Fig. 1).

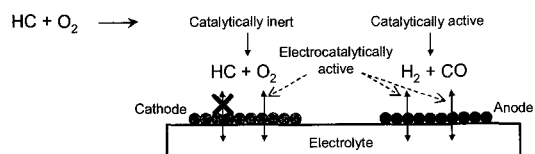
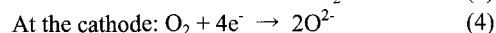
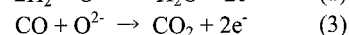
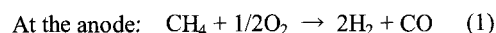


Fig. 1 Principle of SC-SOFCs.

Currently, attempts are under way by many researchers for improving SC-SOFCs using various innovative techniques [3-7]. As a result of their efforts, the power density increased significantly from 2.3 mW cm⁻² in 1993 to 760 mW cm⁻² at present. The temperature required for heating the SC-SOFCs was also reduced from 950 °C to room temperature by using the heating effect from the fuel oxidation reaction. It appears that the SC-SOFCs are equal to or better than conventional SOFCs on performance. Recent advances in SC-SOFC development has been reviewed in the literature [8].

In the above-related works, another important result is to make it possible to use different hydrocarbon fuels, including methane, ethane, propane, and butane, without serious carbon deposition, providing high flexibility of fuel used. On the other hand, environmental pollution and future energy supplies need to replace fossil fuels with renewable fuels. Dimethyl ether (DME) and ethanol are regarded as promising alternative fuels because not only fossil fuels but also biomass are the resources for their productions. While DME and ethanol were researched as fuels for conventional SOFCs [9,10], they are not still applied to SC-SOFCs. Since DME and ethanol are more reactive than hydrocarbons, the use of these fuels has the potential for improving the performance of SC-SOFCs, especially at low temperatures. In this study, we investigate the feasibility and efficacy of using DME and ethanol as fuels for SC-SOFCs. Comparative cell performances with DME, ethanol, and butane are measured in the temperature range of 250 to 350 °C. The anode catalysts are also optimized for reforming DME and ethanol.

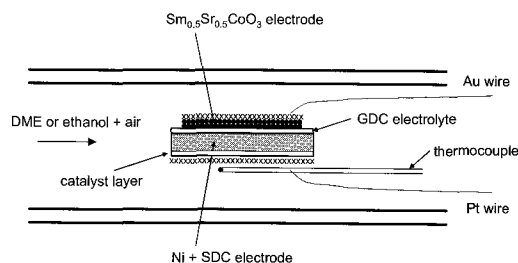


Fig. 2 A schematic illustration of a single-chamber SOFC supported by the anode.

2. EXPERIMENTAL

2.1 Fuel Cell Preparation

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 powder was ground in ethanol using a planetary ball mill for 1 hour, pressed into a pellet, and pre-sintered at 1400 °C for 5 hours in air. The surface of the pellet (diameter ca. 13.5 mm; thickness 0.95 mm) was spin-coated with a slurry of a GDC (Ce_{0.9}Gd_{0.1}O_{1.95}) electrolyte, which was prepared by mixing the corresponding powder with ethyl cellulose, terpineol and butyl carbitol. After drying at 90 °C in air, the pellet was sintered at 1500 °C for 10 hours in air. The electrolyte thickness, which was evaluated by scanning electron microscopy (SEM), was approximately 15 μm. A Sm_{0.5}Sr_{0.5}CoO₃ oxide (SSC) was used as the cathode (area 0.5 cm²). The preparation

and treatment of this electrode were described elsewhere [11].

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 percents of the metal oxide were in the range of 2 to 12. The Cu/Zn/Al catalyst was prepared by co-precipitation of the corresponding aqueous solution of nitrate (Cu(NO₃)₂, Zn(NO₃)₂, 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 hours in air. The metal/SDC/Ni and Cu/Zn/Al catalysts were ground in a similar manner as stated 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 posterior to the cathode deposition.

2.2 Fuel Cell Tests

The cell thus fabricated was set up in a ceramic tube (inner and outer diameters 13 and 17 mm, respectively) as shown in Fig. 2. A Pt wire and a Pt mesh were used as the output terminal and the electrical collector, respectively, for the anode, and an Au wire and an Au mesh were similarly used for the cathode. 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. Butane was used as the fuel for comparison, wherein the oxygen-to-butane 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 on the anode. The outlet gas from the cell having only the anode or cathode was analyzed on a dry basis using on-line gas chromatography (GC).

3. RESULTS AND DISCUSSION

3.1 Comparative Performances of SC-SOFC with Butane, DME and Ethanol Fuels

Since the operation of SC-SOFCs is based on the different catalytic properties of two electrodes for the partial oxidation of the fuel by oxygen, 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 the OCV measurements of an SC-SOFC without any catalyst layer in a DME- or ethanol-air mixture feed. These results are summarized as below:

- The optimal DME- and ethanol-to-oxygen molar ratios were found to be 1.8 and 0.6, respectively.
- The fuel cell showed the maximum OCVs for both the DME and ethanol fuels at a furnace temperature of 300 °C.
- The OCV increased with increasing flow rate and then approached an almost constant at more than 300 ml min⁻¹.

In the above-determined conditions, the cell performances using the DME and ethanol fuel were compared to the cell performance using the butane. It can be seen from Fig. 3 that the fuel cell revealed some

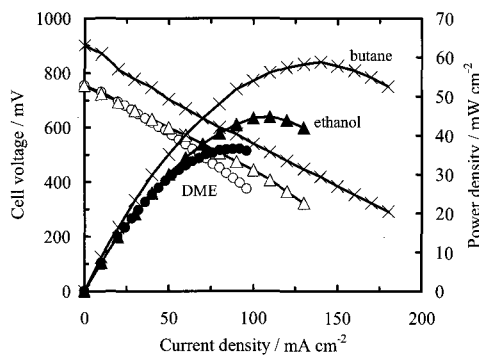


Fig. 3. Cell performances of SC-SOFC in mixture feeds of Various fuels and air at a furnace temperature of 300 °C.

similarities between the DME and ethanol fuels. Upon introducing the DME- or ethanol-air mixture, the cell temperature quickly rose to about 420 °C, and the fuel cell generated OCVs of about 755 mV. Also, in both cases, the cell voltage was very stable during the discharge, and no limiting current behavior was observed. However, the fuel cell using these fuels had obvious differences, especially in OCV, compared to the fuel cell using the butane fuel. The OCV values observed for DME and ethanol were lower by about 150 mV than the value observed for butane, although there was not a considerable difference in the current-voltage slope among the three fuels. 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).

As described earlier, the SC-SOFCs can generate high OCVs, when the anode is active to the partial oxidation of the fuel and the cathode is inert to such an oxidation. To understand the low OCVs observed for DME and ethanol in Fig. 3, the catalytic activities of the anode and cathode were measured at furnace temperatures around 300 °C. As shown in Fig. 4, all the tested fuels were partially oxidized to form hydrogen on the anode above 200 °C. The formation amount of hydrogen at 300 °C or more was in the order of butane > ethanol ≈ DME, which corresponds to the order of the OCV shown above. A similar order was observed for the formation amount of carbon monoxide. On the other hand, the partial oxidation of the three fuels proceeded at very slow rates on the cathode, indicating that SSC ideally functioned as a cathode in the DME-, ethanol- or butane-air mixture feed. Therefore, it is concluded that the catalytic activity of the anode for the partial oxidation of DME and ethanol plays a key role in the generation of the OCV

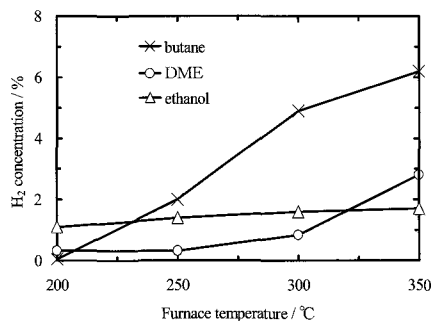


Fig. 4. Catalytic properties of Ni/SDC anode for partial oxidation of various fuels.

from the fuel cell.

3.2 Improvement of Cell Performance by 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 the cell performance. These results are summarized in Table 1 and 2. In the case of DME, the Ru/SDC/Ni catalyst layers provided the large positive effects on the OCV, with an optimal RuO₂ content of 5 wt.%. GC analysis of the outlet gas from the anode showed that the formation amount of hydrogen with the Ru/SDC/Ni catalyst layer was about 2 times higher than that without the catalyst layer. Zhang et al. reported that since a part of DME is decomposed into methane during the partial oxidation reaction, it is necessary to reform methane by using noble metal catalysts in order to enhance the hydrogen yield [12]. Indeed, we also observed the formation of methane in the GC analysis. Therefore, it seems that Ru functions as a promoter not only in the partial oxidation of DME but also in the steam reforming of methane. On the other hand, in the case of ethanol, the most significant improvement in the cell performance was achieved by using the Cu/Zn/Al catalyst layer. It was also confirmed that the formation amount of hydrogen with the Cu/Zn/Al catalyst layer was about 3 times increased compared to that without the catalyst layer. It is well known that Cu/Zn-based catalysts are active for the partial oxidation and steam reforming of alcohol [13].

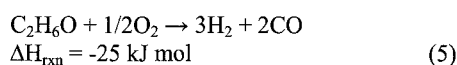
Another important result in Tables 1 and 2 is that both the catalyst layers improved the internal resistance as well as the OCV. This can be explained by the heating effect which is responsible for the catalyzed partial oxidation of DME and ethanol. These reactions evolve the following amounts of reaction heat [14]:

Table 1. Effect of various catalyst layers on cell performance in a mixture feed of DME and air.

	OCV [mV]	Ohmic resistance [Ω]	Electrode resistance [Ω]	Temperature rise [°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	-

Table 2. Effect of various catalyst layers on cell performance in a mixture feed of ethanol and air.

	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	-



Since the mixtures used in this study were slightly oxygen richer, larger amounts of reaction heat may be generated. These reaction heats resulted in a temperature rise of more than 100 °C at the anode, followed by thermal conduction to the cathode through the electrolyte (Tables 1 and 2). Similar heating effects were reported for hydrocarbon fuels by many research groups [3-5,7].

Figure 5 shows the performances 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 caused an enhanced OCV and a reduced the voltage drop. The resulting peak power density reached 64 mW cm⁻², which is about 1.8 times higher than that without the catalyst layer. Figure 6 shows the corresponding results for the ethanol-air mixture feed. 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.

It is worth noting that no carbon was observed on the surfaces of the Ru/SDC/Ni and Cu/Zn/Al catalyst layers after the test. This is indicative that carbon formation is suppressed by the presence of coexisting oxygen in the mixture feed, which is a large advantage over conventional SOFCs, as described earlier. Another worth noting is that the fuel-cell operation was also achieved at lower furnace temperatures: for example, in the case of ethanol, the fuel cell yielded a peak power

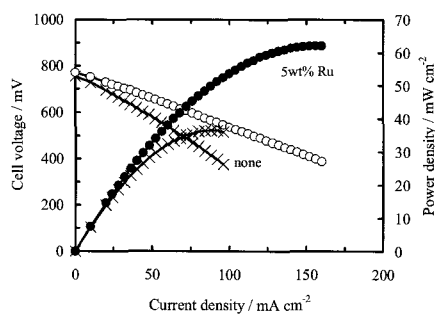


Fig. 5. Cell performances of SC-SOFC in a mixture feed of DME and air at a furnace temperature of 300 °C.

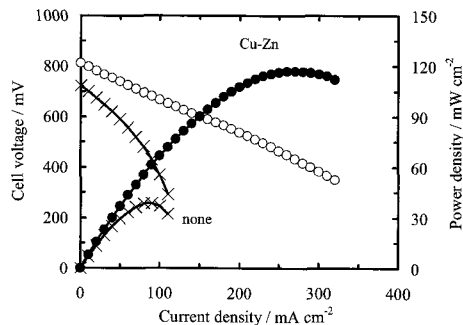


Fig. 6. Cell performances of SC-SOFC in a mixture feed of ethanol and air at a furnace temperature of 300 °C.

density of 59 mW cm⁻² at 250 °C.

4. CONCLUSION

SC-SOFCs operating in 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 the spin-coating technique. From the OCV measurements, the optimal operating conditions were experimentally determined. In addition, the OCV was found to be significantly influenced by the catalytic properties of the anode for the partial oxidation of the fuel. Ru/Ni/SDC and Cu/Zn/Al catalyst layers promoted the partial oxidation of DME and ethanol, respectively, resulting in an increase in the formation amount of hydrogen and carbon monoxide and a temperature rise of the cell. As a result, the peak power density reached 64 mW cm⁻² for DME and 117 mW cm⁻² for ethanol at a furnace temperature of 300 °C.

5. References

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