



Single-Chamber SOFCs with a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ Electrolyte Film for Low-Temperature Operation

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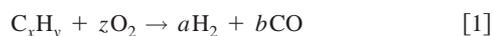
Single-chamber solid oxide fuel cells (SOFCs) with an anode-supported $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte were operated in a mixture of butane and air at furnace temperatures of 200–300°C. The electromotive force (emf) of the cell and the voltage drop were strongly influenced by the catalytic activity of the anode for the partial oxidation of butane. The promotion of hydrogen formation by the addition of Ru to the anode caused an increase in the emf and a reduction in the voltage drop. As a result, stable power densities of 44 and 176 mW cm^{-2} were obtained at 200 and 300°C, respectively.

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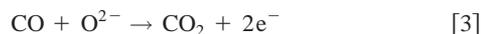
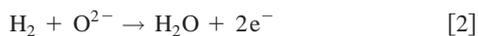
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Conventional solid oxide fuel cells (SOFCs) using yttria-stabilized zirconia (YSZ) as the electrolyte are operated in the temperature range of 700–1000°C to achieve sufficient ion conduction in the electrolyte.¹ This limits applications of SOFCs to power sources for electric vehicles and portable devices. Accordingly, considerable research efforts have recently been devoted to developing SOFCs capable of starting up at low temperatures by using highly ion-conducting electrolytes. Ceria-based oxides, notably Gd^{3+} - or Sm^{3+} -doped ceria (GDC or SDC), are promising electrolytes, because they show much higher ion conductivities than YSZ. For example, Doshi *et al.* reported a peak power density of 140 mW cm^{-2} at 500°C for a hydrogen-air fuel cell with an anode-supported GDC electrolyte.² However, it is difficult for these materials to have low ohmic resistances below 300°C: even a 5 μm GDC electrolyte is calculated to show a large ohmic resistance of 7 $\Omega \text{ cm}^2$ at 300°C from its conductivity.

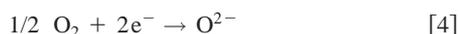
We have proposed a novel single-chamber SOFC to meet rapid low-temperature startup criteria for mobile and portable power generation systems.^{3,4} More recently, similar investigations and characterizations have been carried out by many research groups.^{5–8} This type of SOFC consists of only one gas chamber, where the anode and the cathode are exposed to the same mixture of a hydrocarbon and air. The partial oxidation of hydrocarbons proceeds to form hydrogen and carbon monoxide over a Ni-based electrode, whereas such an oxidation proceeds at a very slow rate over a perovskite-type oxide electrode



This allows the Ni-based electrode to work as the anode for the following reactions



On the other hand, the perovskite-type oxide electrode acts as the cathode for the following reaction



As a result, the SOFC generates a large electromotive force (emf) in the gas mixture. Furthermore, this cell evolves reaction heat, because Reaction 1 is exothermic, thus allowing an additional temperature rise in the neighborhood of the anode. A previous study showed that the resulting power density reached 38 mW cm^{-2} at a furnace temperatures of 300°C in a butane-air mixture.⁴ Here, it

should be noted that the thickness of the used ceria-based electrolyte, which supports itself in the cell, was still 150 μm . There is the possibility that a further reduction in the electrolyte thickness provides a higher performance at 300°C or less.

In this study, we demonstrate this possibility by fabricating an anode-supported GDC electrolyte. This paper shows that the single-chamber SOFC thus fabricated can operate in the furnace-temperature range of 200–300°C. An improvement of the performance by the addition of a noble metal to the anode is also reported.

Experimental

The anode material was prepared from a mixture of 50 wt % SDC ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$), 0 or 1 wt % RuO_2 , 0 or 1 wt % PdO , 5 wt % acetylene black, and NiO for the rest. The mixed powder was ground in ethanol using a planetary ball mill for 14 h, pressed into a pellet, and pre-sintered at 1425°C for 5 h in air. The surface of the pellet (*ca.* 10 mm diam, 1 mm thick) was spin-coated with a slurry of a GDC ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) electrolyte, which was prepared by mixing the corresponding powder with polyacrylic acid and ethyl carbite. After drying at 90°C in air, the pellet was sintered at 1500°C for 10 h in air. The electrolyte thickness, which was evaluated by scanning electron microscopy (SEM), was $\sim 15 \mu\text{m}$. A $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ oxide (area 0.5 cm^2) was used as the cathode. The preparation and treatment of this electrode were described elsewhere.^{3,4}

The cell thus fabricated was set up in a ceramic tube (inner and outer diameters 13 and 17 mm, respectively) as shown in Fig. 1. 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 butane-air mixture with an oxygen-to-butane molar ratio of 2 was supplied to the cell at a flow rate of 300 mL min^{-1} . Methane, ethane, and propane, which were also mixed with air with their stoichiometric molar ratios for Reaction 1, were used as the fuels for comparison. The cell temperature was measured by attaching a thermocouple on the anode. The outlet gas from the cell having only the anode was analyzed on a dry basis using on-line gas chromatography.

Results and Discussion

Different hydrocarbon-air mixtures were supplied to the single-chamber SOFC at furnace temperatures of 200 to 300°C. The cell generated emfs between 16 and 920 mV, where the potentials of the Ni-SDC electrode were always negative vs. the $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode (Fig. 2). The observed emfs were strongly dependent on the hydrocarbon species and the furnace temperature. In all the tested temperature range, the cell showed large emfs around 900 mV with butane, while showing very small emfs with methane. The emfs with ethane and propane suddenly decreased when the furnace temperature changed from 250 to 225°C, above which they were kept at ~ 900 mV. More important was the order of the emf observed

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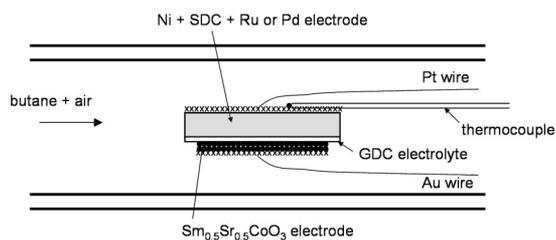


Figure 1. A schematic illustration of a single-chamber SOFC supported by the anode.

at furnace temperatures below 250°C, butane > propane > ethane > methane, which may be related to their reactivity for Reaction 1.

Evidence for the above relation is provided by the analysis of the outlet gas from the cell having only the anode (Fig. 3). At a furnace temperature of 300°C, the hydrocarbons other than methane were partially oxidized to form hydrogen according to Reaction 1. With decreasing furnace temperature, the formation amount of hydrogen decreased in the order of butane > propane > ethane > methane, which well corresponds to the order of the emf shown above. A similar order was observed for the formation amount of carbon monoxide over the anode, although its amount was smaller than that of hydrogen. Therefore, it is concluded that the catalytic activity of the Ni-SDC anode for Reaction 1 plays a key role in the generation of the emf.

Fuel-cell tests were carried out with butane at furnace temperatures of 200–300°C (Fig. 4). Current could be drawn from the cell at all the tested temperatures. The current density–cell voltage curves

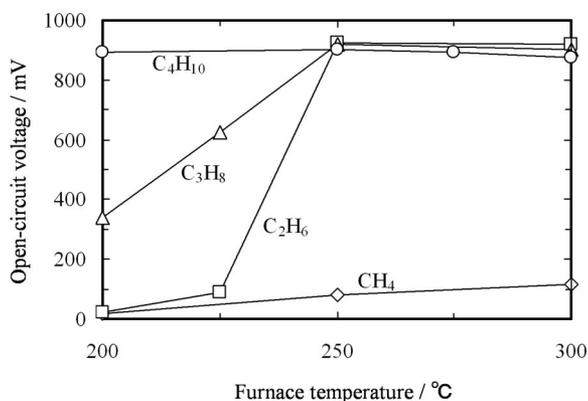


Figure 2. Dependence of emf on furnace temperature. $O_2/CH_4 = 0.5$, $O_2/C_2H_6 = 1$, $O_2/C_3H_8 = 1.5$, $O_2/C_4H_{10} = 2$; flow rate 300 mL/min⁻¹.

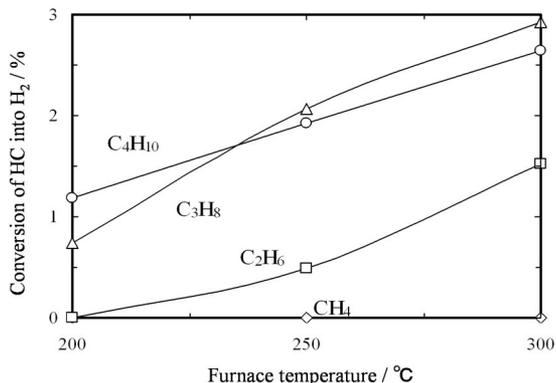


Figure 3. Dependence of formation amount of hydrogen on furnace temperature. The experimental conditions are the same as those in Fig. 2.

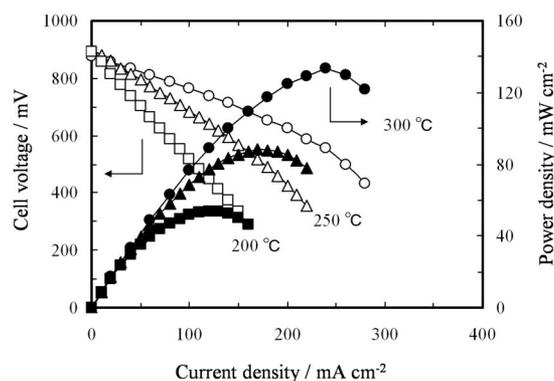


Figure 4. Cell voltage and power density vs. current density for a single-chamber SOFC, Ni-SDC|GDC|Sm_{0.5}Sr_{0.5}CoO₃, in a butane-air mixture: $O_2/C_4H_{10} = 2$; flow rate 300 mL/min⁻¹. The temperature shown in the figure means the furnace temperature.

were almost linear at low current densities, where the voltage drops were approximately 55, 110, and 180 mV per 50 mA cm⁻² at furnace temperatures of 300, 250, and 200°C, respectively. However, the voltage drop tended to increase at high current densities. This can be explained by both the dilute hydrogen produced over the anode and the thick anode thickness of 1 mm. It is likely that a further increase in the current density may cause a limiting current behavior. Nonetheless, the peak power density ranged from 53 mW cm⁻² at a furnace temperature of 200°C to 133 mW cm⁻² at a furnace temperature of 300°C. The impedance spectra at the open-circuit voltage showed very small ohmic resistances of 1.1 Ω cm² at a furnace temperature of 200°C and 0.5 Ω cm² at a furnace temperature of 300°C. Note that these resistances were much lower than those calculated from the ion conductivities of GDC, which suggests a temperature rise in the cell due to reaction heat produced by Reaction 1. Indeed, we confirmed large temperature increases of about 110 and 140°C at furnace temperatures of 200 and 300°C, respectively, by attaching a thermocouple on the anode. The ohmic resistance of GDC predicted by the conductivity at 450°C is 0.56 Ω cm², which is roughly in agreement with the result observed above. We also found that such a temperature rise was significantly influenced by the flow rate of the gas mixture and the oxygen-to-butane molar ratio in the gas mixture: the heating effect was enhanced by increasing the flow rate and the molar ratio. Similar tendencies are observed by Napporn *et al.* with methane⁷ and by Barnett *et al.* with propane.⁹ A possible explanation for this influence is the notion that Reaction 1 consists of a complex set of elementary steps: decomposition, dehydrogenation, complete oxidation, and reforming reactions. Only complete oxidation of butane or lower hydrocarbons is largely exothermic. It seems that the proportion of this step in the overall steps become larger as the flow rate and the oxygen-to-butane molar ratio increase.

The above results suggest that the performance of the SOFC would be further improved by increasing the rate of hydrogen formation, which may prevent the limiting current behavior at high current densities, as well as increasing the cell temperature. These can be achieved by addition of catalysts in the anode. A reforming catalyst such as Ru can be useful for increasing the rate of hydrogen formation. An addition of an oxidation catalyst such as Pd can promote complete oxidation of hydrocarbons and generate more heat to increase the cell temperature.

Figure 5 shows the performances of the SOFCs with different anodes in the butane-air mixture at a furnace temperature of 300°C: the used anodes are Ni-50 wt % SDC, Ni-50 wt % SDC-1 wt % RuO₂, and Ni-50 wt % SDC-1 wt % PdO. As can be seen, the addition of 1 wt % PdO to the anode caused a reduced emf and an enhanced voltage drop. In addition, the cell voltage was very unstable during discharging the cell. The actual cell temperature

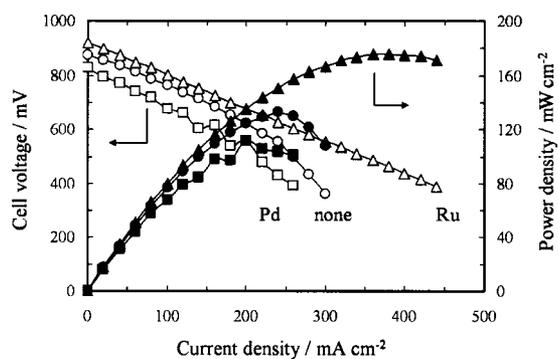


Figure 5. Cell voltage and power density vs. current density for three single-chamber SOFCs, Ni-SDC, Ni-SDC-Ru, and Ni-SDC-Pd[GDC] $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, in a butane-air mixture at a furnace temperature of 300°C: $\text{O}_2/\text{C}_4\text{H}_{10} = 2$; flow rate 300 mL/min⁻¹. The RuO₂ and PdO contents in the anode were 1 wt %.

reached ~450°C, which was slightly higher than that of the cell with the parent anode. However, the hydrogen concentration in the outlet gas was reduced to less one-half that of the cell with the parent anode (Fig. 6). On the other hand, a significant improvement in the performance was achieved by the addition of 1 wt % RuO₂ to the anode. There were two effects on the performance: an increase in the emf from 875 to 921 mV and a linear relationship between the current density and the cell voltage over a wide current range. As a result, the peak power density reached 176 mW cm⁻², which is 1.3 times higher than that of the cell with the parent anode. The addition of Ru to the anode increased the hydrogen concentration in the

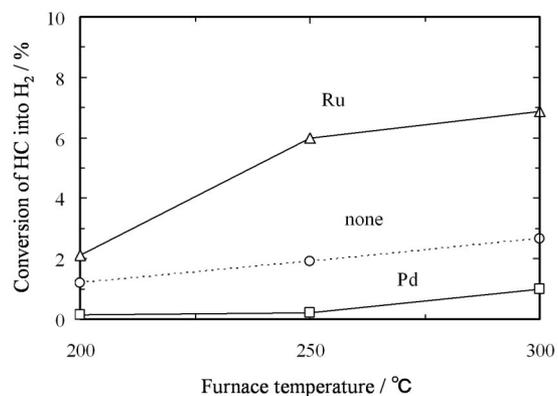
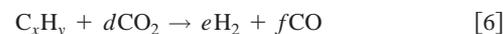
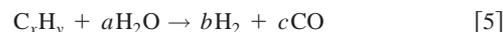


Figure 6. Dependence of formation amount of hydrogen on furnace temperature. The experimental conditions except the temperature are the same as those in Fig. 5.

outlet gas by a factor of 1.8 (Fig. 6), which suggests that Ru catalyzed the reforming of butane or lower hydrocarbons according to the following reactions



However, these effects were degraded by decreasing the temperature: the peak power densities were 93 mW cm⁻² at a furnace temperature of 250°C and 44 mW cm⁻² at a furnace temperature of 200°C. This is due to a deterioration in the catalytic activity of Ru with decreasing temperature (Fig. 6). It is necessary to optimize the Ru content and particle size in more details.

We finally describe information regarding carbon deposition on the anode surface. No carbon was observed for at least 10 h at any temperatures. This is in agreement with the result reported for the other single-chamber SOFCs in various hydrocarbon-air mixtures.⁵⁻⁸ Because the coking is predicted thermodynamically possible under the present conditions, such a deviation from equilibrium would be due to kinetic reasons: for example, the decomposition of butane, which causes carbon deposition, proceeds at very slow rate in the low-temperature range. In addition, the effects of the applied current¹⁰ and the added Ru¹¹ may contribute to a reduction of carbon deposition.

Conclusion

The present results showed the feasibility of a single-chamber SOFC capable of starting up at low furnace temperatures of 200-300°C. This was achieved by the fabrication of an anode-supported GDC electrolyte and by the addition of Ru to the anode. As shown in this study, the use of a more optimized anode material is important in operating the SOFC at lower temperatures. Further work is in progress regarding the improvement of the anode material.

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