PERFORMANCE OF ANODE SUPPORTED CELLS WITH Ni-ScSZ ANODE FOR LOW S/C METHANE AND ETHANE FUELS

Katsuhiko Yamaji, Haruo Kishimoto, Yueping Xiong, Teruhisa Horita, Natsuko Sakai
Manuel E. Brito, and Harumi Yokokawa
National Institute of Advanced Industrial Science and Technology (AIST)
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

ABSTRACT

Possibility of stable operation of SOFCs with methane and ethane fuels at a low steam/carbon (S/C) ratio (containing 1.2 mol% H2O) was investigated for anode supported SOFCs with a scandia stabilized zirconia (ScSZ) electrolyte and a Ni-ScSZ anode. For methane, severe carbon deposition was observed around the anode after cell tests at T = 1073 K. The effect of carbon deposition became smaller with decreasing operation temperature, and a stable cell operation was achieved without severe carbon deposition for 88 h at higher fuel utilization rate around 50%. For ethane, nickel was heavily disintegrated accompanied with severe carbon deposition even at T = 973 K. With decreasing operation temperature, the disintegration became less. As a result, a stable cell operation was achieved only with a slight amount of deposited carbon at the fuel injection part for over a week at \( U_f = 54 - 46\% \) at \( T = 826 \) K.

INTRODUCTION

Efficient power generation is expected for solid oxide fuel cells (SOFCs) because SOFCs can directly utilize many kinds of hydrocarbon (HC) fuels without any external reformers, and many researchers are actively studying direct utilization of HC fuels (1-11). In order to realize direct feeding of HC fuels into SOFCs, there are some problems to be overcome, and the most important one is to suppress severe carbon deposition on and around Ni component in anodes, which sometimes spoils the framework of the anode. Normally, a large amount of water is fed with HC fuels at a high ratio of steam to carbon (S/C) > 2 to avoid carbon deposition, which needs a large water feeding equipment. If the S/C ratio can be reduced to the level of room temperature humidity, the complicated water supplying equipment will not be necessary for the SOFC system. However, with decreasing S/C ratio, carbon deposition becomes more severe.

To suppress carbon deposition at low S/C fueling conditions, we considered two attractive approaches. The first is the utilization of scandia stabilized zirconia (ScSZ) for the electrolyte and anode cermet. Ukai et. al. reported a Ni-ScSZ cermet anode had a lower overpotential and higher stability than conventional Ni-YSZ cermet anode for low S/C methane (S/C = 3/97) at 1273 K (5). The second is to decrease the operation temperature of SOFCs. Murray et. al. reported that the carbon deposition could be suppressed by decreasing operation temperature with GDC for electrolyte and/or anode

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cermet (3,4). In view of these two approaches, we expected that lowering the operation temperature of SOFCs utilizing a ScSZ electrolyte and Ni-ScSZ cermet anode will be effective in eliminating carbon deposition on and around the anode fed with HC fuels at low S/C ratios. In addition, the effect of cell operation at high fuel utilization rates was also considered. With increasing fuel utilization rate, a larger amount of H$_2$O and CO$_2$ is electrochemically produced; H$_2$O and CO$_2$ are expected to oxidize deposited carbon.

The aim of this study is to investigate the conditions of stable operation of SOFCs for methane and ethane fuels at low S/C ratio (containing 1.2 mol% H$_2$O) in anode supported cells; the anode supported structure was selected to obtain suitable cell performance at lower temperatures. To improve cell performance for HC fuels, Ni-ScSZ and ScSZ were chosen as the anode and the electrolyte, respectively. We mainly focused on the effects of increasing fuel utilization rate and decreasing operation temperature on suppressing carbon deposition.

**EXPERIMENTAL**

**Cells**

A scandia stabilized zirconia (1 mol% CeO$_2$ – 10 mol% Sc$_2$O$_3$ – 89 mol% ZrO$_2$, Daiichi Kigenso Kagaku Kogyo Co., Ltd., hereafter ScSZ) was adopted for the electrolyte and cermet anode of anode supported cells. The weight ratio of ScSZ to NiO in the anode was fixed at 40/60.

Two kinds of anode supported electrolyte cells were utilized in this study. One kind of cell is fabricated by electrophoretic deposition (EPD) technique. The details of the fabrication conditions were shown in our previous report (12,13). The thickness of the anode substrates and the electrolytes were about 1 mm and 5 µm, respectively. The other kind of cell is fabricated by Japan Fine Ceramics Co., Ltd., by screen printing method. The thickness of the anode substrate and the electrolyte were about 1 mm and 30 µm, respectively. Hereafter, the former cell is abbreviated as EPD cell and the latter cell is abbreviated as JFC cell.

A strontium-doped lanthanum manganite (La$_{0.85}$Sr$_{0.15}$)$_{0.95}$MnO$_3$ or an Ag-Pt-ScSZ cermet (14) (fabricated by Tanakakikinzoku K. K., the weight ratio of Ag/Pt/ScSZ = 5/5/7) was adopted for the cathode. It should be noted that Ag-Pt-ScSZ cathode was selected only for a test use and not for a practical use. The LSM cathode was sintered on the electrolyte at $T = 1473$ K and the Ag-Pt-ScSZ cathode was fired on the electrolyte at 1173 K. The diameter of cathodes was fixed at 24 mm.

**Testing**

A hard glass (Pyrex glass) and a soft glass were used as gas sealants for fuels at higher temperatures above $T = 973$ K and at lower temperatures below 923 K, respectively. A platinum mesh with platinum leads was attached with a platinum paste (Tanakakikinzoku K. K., TR-7907) on the LSM cathode surface as the current collector and fired at $T = 1273$ K in air. For Ag-Pt-ScSZ cathode, a platinum mesh with platinum leads was pushed onto it during the measurement as a current collector. For anodes, a
metal (nickel or gold) mesh attached with gold leads was pushed onto the anode surface as the current collector at higher temperatures above $T = 1023$ K.

Schematic view of single cell test equipment is shown in Fig. 1. The single cell tests were operated with a potenio/galvanostat (Electrochemical Interface, Solartron Analytical, SI-1287) and an impedance analyzer (Impedance/Gain-Faze Analyzer, Solartron Analytical, SI-1260). As the oxidant, 100 cm$^3$min$^{-1}$ of air was fed to the cathode. All fuels ($H_2$, $CH_4$ and $C_2H_6$) were humidified with water at $T = 283$ K, which means the fuel gas contains 1.2% of $H_2O$. Before feeding $CH_4$ or $C_2H_6$, the cell was operated with humidified $H_2$. After the current density became steady at a fixed terminal voltage, $H_2$ was changed into $CH_4$ or $C_2H_6$. The flow rates of $CH_4$ and $C_2H_6$ were usually set 1/4 and 1/7 of the flow rate of $H_2$, respectively, according to the chemical equivalent in the reaction with oxygen.

RESULTS AND DISCUSSION

Methane Fuel

Single cell tests for methane fuel were carried out with the EPD cells with attached LSM cathode. The SEM image of a fractured surface of an EPD cell is shown in Fig. 2. A thin and dense ScSZ electrolyte is sandwiched by adequately porous electrodes. A typical result of power generation tests with $H_2$ fuel at a flow rate of 30 cm$^3$min$^{-1}$ at $T = 973$ K is shown in Fig. 3. The current density ($j$) was quite low at earlier stage of the cell tests and increased with operation time due to the improvement of the interfacial conductivity at the interface between LSM and ScSZ (12). The $I-V$ data were collected after the
performance became stable. The open circuit voltage was 1.10 V at 973 K, which was close to the theoretical value. The power density at the terminal voltage of 0.7 V was more than 200 mWcm$^{-2}$ at $T = 973$ K.

After the fuel was changed from hydrogen to methane at $T = 1073$ K, the cell performance gradually decreased with time. Furthermore, a large amount of carbon was deposited on the Ni mesh current collector and the anode surface after the cell test. In addition, the anode and Ni mesh were damaged and pulverized due to severe carbon deposition especially at the fuel injection part. The results of single cell tests at $T = 1023$ K were similar to the results at $T = 1073$ K. The rate and the amount of carbon deposition were reduced by decreasing operation temperature, but the anode and the Ni mesh current collector were also damaged by methane fuel around at methane injection part.

Figure 3. $I-V$ and $I-P$ curves at $T = 973$ K with $H_2$ fuel for a typical EPD cell with an LSM cathode.
Figure 4. Time dependency of $j$ after fueling methane for an EPD cell with an LSM cathode at a fixed terminal voltage of 0.7 V at $T = 973$ K.

When the operation temperature was decreased from $T = 1023$ K to 973 K, the effect of carbon deposition became extremely mild. Figure 4 shows a result of power generation test at a fixed terminal voltage of 0.7 V at $T = 973$ K. After 8 hours of operation, fuel was changed from H$_2$ to CH$_4$, and the flow rate of CH$_4$ was kept at 2.5 cm$^3$min$^{-1}$. Just after the fuel was changed, the current and $U_f$ were 0.72 A and 50%, respectively. After 88 hours operation with methane fuel, the cell performance slightly decreased with time and the current and $U_f$ became 0.64 A and 45%, respectively. After the cell test, no visible deposited carbon existed around the anode including the Ni mesh current collector. The stable operation was reproducibly achieved under high $U_f$ conditions at $T = 973$ K. However, under low $U_f$ conditions and OCV conditions, carbon was easily deposited on the anode and Ni mesh even at $T = 973$ K. It is believed that the removal of deposited carbon immediately occurred on the anode and around the nickel mesh under high $U_f$ conditions. Under high $U_f$ conditions, it is expected that large amounts of CO$_2$ and H$_2$O are produced and they suppress carbon deposition. At any rate, a stable cell operation with slightly humidified methane fuel was achieved for 88 h without severe carbon deposition.

**Ethane fuel**

The single cell test with ethane fuel was started with the EPD cells with attached LSM cathode at $T = 973$ K($U_f = 24\%$). The cell performance rapidly decreased after ethane injection and the cell was finally broken. After the cell test, a large amount of carbon was found deposited on and in the anode. The Ni mesh current corrector was also covered with deposited carbon, and furthermore, was partly consumed near the fuel injection part. According to the results at $T = 973$ K, lowering of the operation temperature is required to prevent the hard attack on Ni from ethane fuel, which means the cell performance should be improved at lower temperatures. In order to improve the cell performance at
lower temperatures, a Pt-Ag-ScSZ cermet electrode was applied for the test cathode. A typical result in power generation tests with H₂ fuel at \( T = 973 \text{ K} \) and 873 K is shown in Fig. 5. The flow rate of H₂ was 30 cm³min⁻¹. The open circuit voltages were 1.12 and 1.13 V at \( T = 973 \text{ K} \) and 873 K, respectively, which were close to the theoretical values. The power density at the terminal voltage of 0.7 V was about 300 mWcm⁻² and 100 mWcm⁻² at \( T = 973 \text{ K} \) and 873 K, respectively.

Cell tests with ethane fuel were continued with the EPD cells with attached Pt-Ag-ScSZ cathode. At \( T = 923 \text{ K} \) (\( U_f = 38\% \)) and 873 K(\( U_f = 25\% \)), power generation tests were continuously carried out only for several hours, and the cells were easily broken during

Figure 5. \( I-V \) and \( I-P \) curves at \( T = 973 \text{ K} \) with H₂ fuel for a typical JFC cell with a Pt-Ag-ScSZ cathode.

![Graph showing \( I-V \) and \( I-P \) curves](image)

Figure 6. Photographs of the (a)Ni current collector and (b)anode surface after a single cell test at \( T = 923 \text{ K} \) with ethane fuel for 88 h. The middles of the mesh and anode were blackened by deposited carbon, near the fuel injection part.
the tests. After cell tests, a large amount of carbon was found deposited on the Ni mesh current collector and anode, and a part of Ni mesh near the fuel injection part was consumed after the cell test as shown in Fig. 6. The severe carbon deposition on the anode near the fuel injection part is also shown in the same figure. Cracks crossed the severe carbon deposition part of the anode, which suggests that the break in the cell occurred due to stress by the deposited carbon at the fuel injection part. In addition, the carbon deposited area in the anode was expanded due to the significantly deposited carbon at open pores of the anode, which caused pulverization of the anode after oxidation reaction at the anode.

Cell tests with ethane fuel were continued with the JFC cell and Pt-Ag-ScSZ cathode at $T = 873$ K. Power generation tests were carried out at higher $U_f$ condition of 36-43%. Although the cell performance decreased with operation time, the power generation test was continuously conducted for about a hundred hours without break in the cell at following test conditions; terminal voltage 0.5 V, flow rate of ethane 1.3 cm$^3$min$^{-1}$, and total currents 0.56 A (as started) and 0.465 A (as stopped), respectively. However, the anode and the Ni current corrector near the fuel injection part were fully covered by deposited carbon after the cell test. Therefore, the cell test was next done by lowering the operation temperature at $T = 826$ K. In addition, the current collector was changed from Ni to Au in addition to eliminate carbon deposition on it.

Figure 7 shows the results of power generation test at a fixed terminal voltage of 0.5 V. After four hours operation, fuel was changed from H$_2$ to C$_2$H$_6$. The flow rate of C$_2$H$_6$ was 1.3 cm$^3$min$^{-1}$. When the fuel was changed, the current and $U_f$ were 0.705 A and 54%, respectively. The cell performance gradually decreased with time, and the current and $U_f$ became 0.595 A and 46%, respectively, after 163 hours operation with low S/C ethane. The current density decreased gradually with operation time. After the cell test, a slight amount of visible carbon was deposited near the fuel injection point as shown in figure 8. There is no visible carbon deposition on the Au mesh current collector and alumina components. Figure 9 shows the SEM photographs of the anode surface. In the

![Figure 7](image_url)

**Figure 7.** Time dependency of $j$ after fueling ethane for a JFC with a Pt-AG-ScSZ cathode at a fixed terminal voltage of 0.5 V at $T = 826$ K.
vicinity of the ethane injection part, the porous Ni-ScSZ anode was fully surrounded by the deposited carbon, and the deposited carbon filled the pores in. On the contrary, there was no visible carbon on the anode surface away from the fuel injection part. Although a small amount of carbon was partly deposited on the anode and the current density decreased gradually with operation time, a stable cell operation with slightly humidified ethane fuel was achieved for over a week.

**DISCUSSION**

By utilizing a ScSZ electrolyte for Ni cermet anodes and electrolytes, availability of anode supported SOFCs for stable power generation with low S/C methane and ethane was confirmed. In this study, two important facts which are effective in suppressing carbon deposition were confirmed:

1. Decreasing operation temperature of SOFCs to decrease the carbon deposition rate (as reported by E. Murray et. al. (4),
2. Increasing fuel utilization rate to increase the ratio of oxidants in the anode.

With increasing fuel utilization rate, larger amounts CO₂ and H₂O are produced by electrochemical oxidation of methane or ethane; CO₂ and H₂O are expected to suppress carbon deposition by acting as oxidant. Near the fuel injection part, the probability of

![Figure 8](image_url)

*Figure 8. Photographs of (a) anode surface and (b) Au current collector after a single cell test at T = 826 K with ethane fuel for 163 h.*

![Figure 9](image_url)

*Figure 9. SEM images of the anode surface after cell test at T = 826 K with ethane fuel for 163 h; (a) fuel injection part and (b) away from fuel injection part.*
H₂O and CO₂ diffusion from the reaction part of the anode increases with fuel utilization rate and decreases with fueling rate; it should be noted that the increase of the fuel utilization rate also leads to a decrease in the fuelling rate at the same time. As a result, the oxygen partial pressure around the fuel injection part increases with fuel utilization rate, and therefore, deposited carbon is removed by diffusing H₂O and CO₂.

In this study, anode supported structure was selected to improve the cell performance at lowered temperatures. However, the thick anode structure is not suitable to consume the deposited carbon by oxide gases produced at anode/electrolyte interface because the fuel injection part, where the severest carbon deposition takes place for Ni-based anode, is far from the anode/electrolyte interface. Thus, it is suggested that thin anode structures supported by electrolyte, cathode, or conductive powder should be more effective to suppress carbon deposition around a fuel injection part.

In spite of the disadvantages described above, stable operation with low S/C methane and ethane was achieved with anode supported cells in this study, which suggests that application of a ScSZ to the cermet anode and electrolyte of SOFCs is effective in suppressing carbon deposition for low S/C ethane and methane fuels. However, no comparison between ScSZ and other materials was carried out in this study. This work will be carried out in the near future.

CONCLUSIONS

The stable operation conditions of SOFCs for methane and ethane fuels at low steam/carbon (S/C) ratio (containing 1.2 mol% H₂O) were investigated for anode supported SOFCs using scandia stabilized zirconia (ScSZ) electrolyte and Ni-ScSZ anode. Stable cell operations were achieved at T = 973 K for methane fuel and at T = 826 K for ethane fuel, respectively. In order to eliminate severe carbon deposition, the effectiveness of decreasing operation temperature and increasing fuel utilization rate was reconfirmed. In addition, it is suggested that application of a ScSZ to the cermet anode and electrolyte of SOFCs is effective in suppressing carbon deposition.

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