

Carbon deposition behaviour on Ni–ScSZ anodes for internal reforming solid oxide fuel cells

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Abstract

The operating properties of solid oxide fuel cells using Ni/scandia-stabilized zirconia (Ni–ScSZ) anodes under internal reforming conditions are investigated. A single-cell achieved a maximum power density of 0.64 W cm^{-2} at 900°C in $97\% \text{CH}_4/3\% \text{H}_2\text{O}$ mixture fuel. The cell voltage during the power generation at 0.5 A cm^{-2} is stable in $97\% \text{CH}_4/3\% \text{H}_2\text{O}$ mixture fuel at 900°C for at least 150 h. By contrast, degradation of anode performance and carbon deposition are found at 800°C under the same conditions. These results suggest that carbon deposition is hindered more effectively at higher temperature under operation at high current density.

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Keywords: Solid oxide fuel cell; ScSZ; Carbon deposition; Ni cermet; Power generation; Anode degradation

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much interest because of the possibility for internal reforming of hydrocarbon due to the high operating temperature of $800\text{--}1000^\circ\text{C}$. Carbon deposition by thermal cracking occurs simultaneously with the reforming reaction, and this results in deactivation of the anodes. To avoid carbon deposition, large quantities of steam (steam/carbon ratio, S/C, greater than 2) are added to the hydrocarbon fuels. This is, however, unattractive for fuel cells because steam dilution of the fuel lowers both the power density and the energy efficiency. Therefore, anode materials that can be used under low steam/carbon ratio conditions are required. Recently, the performance of SOFCs using a low steam/carbon ratio and methane have been reported [1–5]. Ni/scandia-stabilized zirconia (ScSZ) anodes have shown no degradation in current–voltage characteristics under operation conditions of a low S/C ratio at 1000°C [6]. Greater solubility of NiO in ScSZ has been found by calcination treatment than that in NiO–YSZ [7]. Moreover, Ni–ScSZ displays higher activity for steam reforming and thermal cracking reactions than

Ni–YSZ because of the smaller particles of Ni deposited on the surface of ScSZ after the reduction of NiO–ScSZ solid solution [7]. A detailed understanding of the reactions taking place on Ni–ScSZ during power generation are still to be obtained. This study examines the effects of current density and temperature on the catalytic properties of Ni–ScSZ anodes and their carbon deposition behaviour by analysis of the outlet fuel gas and stability tests.

2. Experimental

2.1. Preparation of test cells

$[(\text{Sc}_2\text{O}_3)_{0.11}(\text{ZrO}_2)_{0.78}]$ 99 wt.%– Al_2O_3 1 wt.% plates with a thickness of about $300 \mu\text{m}$ were used for the electrolyte. NiO and $10\text{Sc}1\text{CeSZ}$ $[(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.79}]$ were used for the anodes. NiO and $10\text{Sc}1\text{CeSZ}$ were mixed with ethanol for 24 h by means of ball milling and then dried to obtain the predetermined mass ratio of $\text{Ni}:\text{ZrO}_2 = 4:6$. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and 8YSZ $[(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.84}]$ were used for the cathode material. LSM and 8YSZ were mixed in the same way as the anode material to obtain the predetermined mass ratio of $\text{LSM}:8\text{YSZ} = 8:2$. The electrode materials and a polymer

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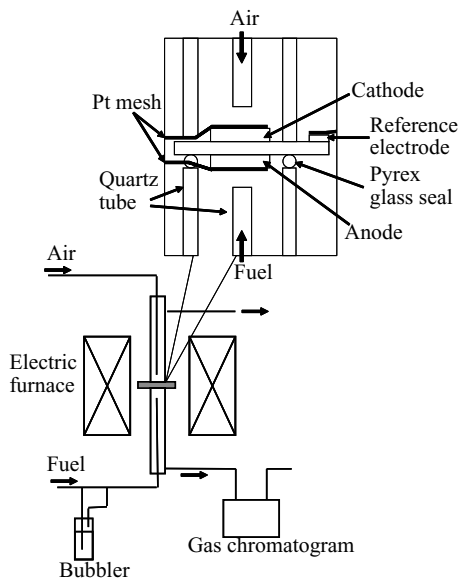


Fig. 1. Construction of apparatus.

binder were mixed and screen-printed on the electrolyte plates. The electrode surface area was 0.2 cm^2 . The reference electrode was fixed to the same surface along with the cathode material. Pt mesh current-collectors were attached to the electrodes. The gap between the Pt meshes and electrodes was filled with the electrode materials. The anodes were calcined at 1350°C and both cathodes and reference electrodes were calcined at 1150°C .

2.2. Apparatus for cell tests

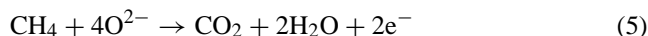
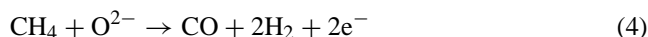
Construction of the apparatus is shown in Fig. 1. Gaseous mixtures of H_2 , CH_4 , and H_2O were supplied to the anode surface at a rate of 50 ml min^{-1} . Air was supplied to the cathode surface at a rate of 50 ml min^{-1} . Outlet fuel gases were analyzed with TCD-type gas-chromatography. Electrochemical measurements were conducted using a potenti/galvanostat.

2.3. Quantification of deposited carbon

After the test cells were heated at $800\text{--}1000^\circ\text{C}$, the anodes were reduced by H_2 . Using $\text{H}_2/3\%\text{H}_2\text{O}$ as fuel, current–voltage characteristics were monitored in order to check the anode performance and stability. After the voltage became stable at constant current, the fuel was switched from $\text{H}_2/3\%\text{H}_2\text{O}$ to $\text{CH}_4/3\%\text{H}_2\text{O}$ for measurements. After 10 h of operation, the cells were quenched. For evaluating the carbon deposited on the anode, the test cell was heated to 800°C in an argon flow. Then, the gas flow was switched from Ar to O_2 to oxidize the deposited carbon and the concentration and volume of carbon dioxide generated during oxidation were measured.

3. Results and discussion

Under the given operation conditions, whether carbon deposition occurs on anodes or not should be influenced by the electrochemical reactions as well as by the thermal reactions. Therefore, attention has been directed towards the electrochemical reactions and the thermal reactions. The possible reactions that can occur on the anode are as follows:



It is well known that the electrochemical reactions occur only at the triple-phase boundary (TPB; Ni-electrolyte-gas) [8] and thermal cracking occurs on the Ni surface [9]. To prevent deactivation of anodes, it is important to prevent the carbon deposition, not only at the TPB but also on other Ni surfaces.

The typical performance of a single cell with an Ni–ScSZ anode operating with a fuel of $\text{H}_2/3\%\text{H}_2\text{O}$ and $\text{CH}_4/3\%\text{H}_2\text{O}$ is shown in Fig. 2. The maximum power density is over 0.6 W cm^{-2} at 900°C using $\text{H}_2/3\%\text{H}_2\text{O}$ and $\text{CH}_4/3\%\text{H}_2\text{O}$ as fuel. At 800°C , the maximum power density is over 0.3 W cm^{-2} using $\text{H}_2/3\%\text{H}_2\text{O}$ as fuel.

The outlet gas when operating with $\text{CH}_4/3\%\text{H}_2\text{O}$ fuel is composed mainly of CH_4 , H_2 , CO and H_2O . The dependence

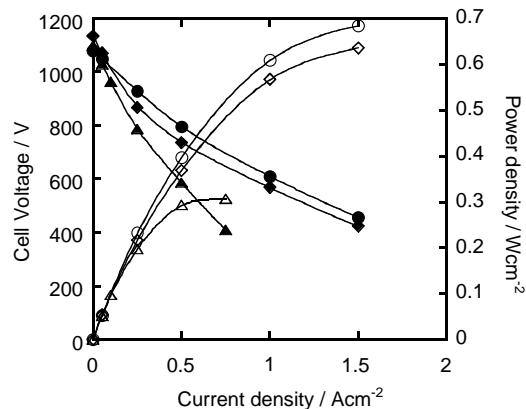


Fig. 2. Current–voltage characteristics: 900°C $\text{H}_2/3\%\text{H}_2\text{O}$: (●,○); $\text{CH}_4/3\%\text{H}_2\text{O}$: (◆,◇); 800°C $\text{H}_2/3\%\text{H}_2\text{O}$: (▲,△). Filled symbol: cell voltage; open symbol: power density.

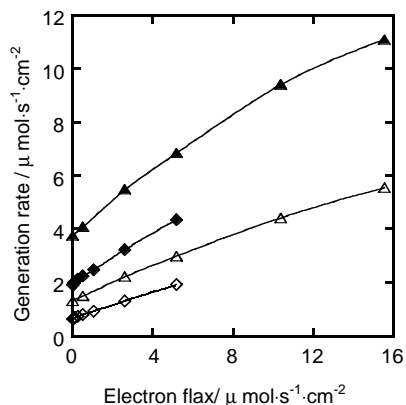


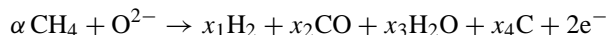
Fig. 3. Outlet gas analysis: CH₄/3% H₂O 900 °C, H₂: (▲); CO: (△); 800 °C, H₂: (◆); CO: (◇).

of H₂ and CO generation rates on current density is shown in Fig. 3. The H₂ and CO generation rates increase linearly with the current density. The slopes of these lines indicate the relationship of H₂ or CO generated versus electron flux. The slopes are as follows:

$$\text{H}_2 : 0.54, \text{CO} : 0.30 \text{ at } 900 \text{ }^\circ\text{C}$$

$$\text{H}_2 : 0.46, \text{CO} : 0.25 \text{ at } 800 \text{ }^\circ\text{C}.$$

These suggest that O²⁻ supplied to the anode by current flow activates both the reforming reaction and the partial oxidation of CH₄. Reactions 1–10 influence each other intricately on anodes. The overall anode reaction can be described as:



These coefficients are calculated by using the slopes of the lines described above and the results are as follows:

$$900 \text{ }^\circ\text{C} : \alpha = 0.75 \quad (\text{H}_2, \text{CO}, \text{H}_2\text{O}, \text{C}) \\ = (1.09, 0.60, 0.40, 0.15)$$

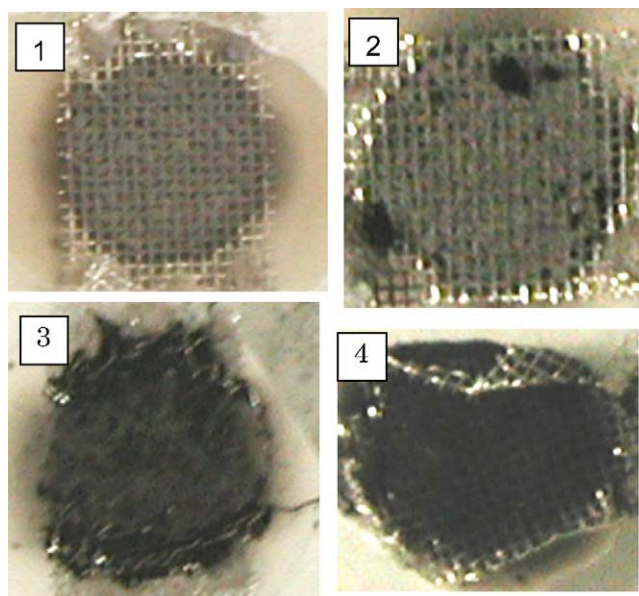


Fig. 5. Anode image before or after stability test (1) before; (2) 900 °C, 0.5 A cm⁻²; (3) 800 °C, 0.5 A cm⁻²; (4) 900 °C, 0 A cm⁻².

$$800 \text{ }^\circ\text{C} : \alpha = 0.71 \quad (\text{H}_2, \text{CO}, \text{H}_2\text{O}, \text{C}) \\ = (0.92, 0.50, 0.50, 0.21)$$

The data suggest that O²⁻ is more likely to react with C at 900 °C than at 800 °C, and less carbon deposition occurs at 900 °C than at 800 °C.

The stability of cells with Ni–ScSZ anodes using CH₄/3% H₂O as fuel was tested at a constant current density of 500 mA cm⁻² (Fig. 4). At 800 °C, cell voltage decreased and was unstable. By contrast, at 900 °C, cell performance increased during the first 70 h and become stable after that. The major reason for increase in cell voltage is the decrease of cathode overpotential by current flow [10]. After the stability tests, the anode were examined by optical microscopy (Fig. 5). After the stability test at 800 °C, a large amount

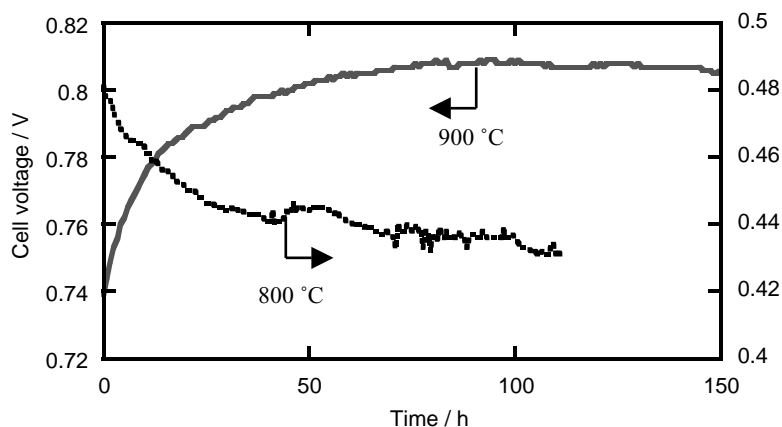


Fig. 4. Stability of cell voltage (CH₄/3% H₂O; 0.5 A cm⁻²).

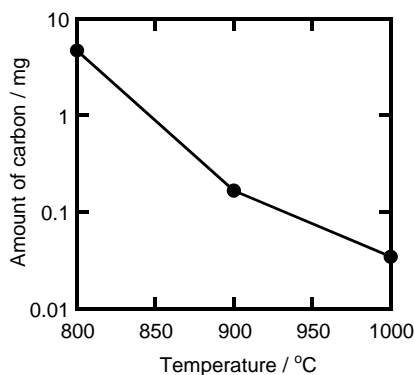


Fig. 6. Dependence of carbon amount on temperature ($\text{CH}_4/3\% \text{H}_2\text{O}$; 0.5 A cm^{-2}).

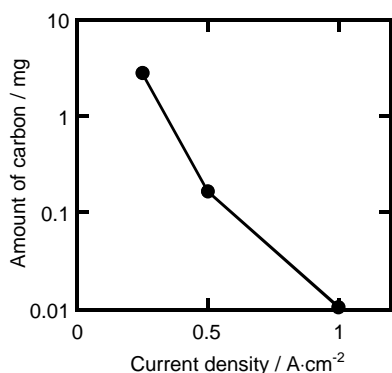


Fig. 7. Dependence of carbon amount on current density ($\text{CH}_4/3\% \text{H}_2\text{O}$; 900°C).

of carbon is found to have been deposited. Only, a small amount of carbon is observed on the anode operated at 900°C . These results suggest that difference in the stability at these temperatures is caused by a difference in the carbon deposition rate. Further, although a small amount of carbon is observed under the operation at 900°C , a large amount of carbon is observed at open-circuit. This can be explained by the fact that O^{2-} reacts with C and CH_4 (reactions 3 and 4), or H_2O generated electrochemically on anode reacts with C or CH_4 (reactions 1, 7, and 9). The fuel utilization is 0.04% in the stability test. These results suggest that current flow can prevent carbon deposition under a low S/C condition if there is sufficient current density.

The dependence of the deposited carbon on the operating temperature after 10 h of operation at 0.5 A cm^{-2} is shown in Fig. 6. The amount of deposited carbon decreases with increase in temperature. This result is consistent with opti-

cal microscopic observations of the anode after the stability test. Since it is well known that the thermal cracking rate increases with temperature [11] and the amount of carbon also increases with temperature in equilibrium, the present results indicate that reactions which remove C species are enhanced by raising the operation temperature and this overcomes the thermal cracking on the anode, i.e., the effect of current flow on preventing the carbon deposition increases with temperature. There are some possible explanations such as increase in the oxidation or the reforming rate with C or CH_4 , and increase in the diffusion rate of reactants on the anode with temperature.

The dependence of the amount of deposited carbon on the current density is presented in Fig. 7. The amount of deposited carbon increases with current density, and it is found that some level of current density (over 0.5 A cm^{-2}) is required to avoid carbon deposition.

4. Conclusions

Single cells with Ni–ScSZ anodes can be operated stably at 900°C using $\text{CH}_4/3\% \text{H}_2\text{O}$ as fuel for more than 150 h. Stable performance cannot, however, be achieved at 800°C . The amount of deposited carbon on Ni–ScSZ decreases with increase in temperature and current density. Carbon deposition on Ni–ScSZ can be prevented at high temperature and current density at a low steam/carbon ratio.

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