

# Improvement of anode performance by surface modification for solid oxide fuel cell running on hydrocarbon fuel

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## Abstract

A Ni/yttria-stabilized zirconia (YSZ) cermet anode was modified by coating with samaria-doped ceria (SDC,  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_2$ ) sol within the pores of the anode for a solid oxide fuel cell (SOFC) running on hydrocarbon fuel. The surface modification of Ni/YSZ anode resulted in an increase of structural stability and enlargement of the triple phase boundary (TPB), which can serve as a catalytic reaction site for oxidation of carbon or carbon monoxide. Consequently, the SDC coating on the pores of anode made it possible to have good stability for long-term operation due to low carbon deposition and nickel sintering.

The maximum power density of an anode-supported cell (electrolyte; 8 mol% YSZ and thickness of 30  $\mu\text{m}$ , and cathode;  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ ) with the modified anode was about 0.3  $\text{W}/\text{cm}^2$  at 700 °C in the mixture of methane (25%) and air (75%) as the fuel and air as the oxidant. The cell was operated for 500 h without significant degradation of cell performance.

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## 1. Introduction

Recently, much effort has been devoted in developing reduced-temperature solid oxide fuel cells (SOFCs) running on hydrocarbon fuels instead of hydrogen [1–4]. This type of SOFC is more suitable for the residential power generation (RPG) or auxiliary power units (APU) than other types of fuel cells due to the simplicity of fuel processing [5]. Moreover, decreasing the operating temperature of SOFC to around 700 °C offers the potential to reduce the system costs and increase long-term stability of the cell components. However, the low operating temperature decreases the cell performance because of low ionic conductivity of yttria-stabilized zirconia (YSZ) and the high overpotential at the electrodes. In addition, when hydrocarbon fuels are directly inserted into the anode, the Ni-based anode is rapidly deactivated because nickel catalyzes carbon deposition [6]. Nowadays, to minimize resistive loss across the electrolyte, many researchers have developed anode-supported SOFCs based on a thin-film electrolyte [7,8]. Finally the electrode overpotentials and carbon deposition have remained major

problems for reduced-temperature SOFCs running on hydrocarbon fuels.

We reported a new method of improving electrode performance by coating thin films of YSZ or samaria-doped ceria (SDC) within the pores of electrode by a sol–gel coating technique [9–11]. In the previous papers, we demonstrated that the YSZ or SDC layers deposited within the cathode can provide paths for oxide ions and expand the reaction zone into the new triple phase boundary (TPB). In this study, we have focused on the development of a new anode having high performance and good stability with hydrocarbon fuels. Therefore, the effect of the SDC coating on the Ni/YSZ anode was extensively investigated by ac impedance spectroscopy and dc polarization methods.

## 2. Experimental

### 2.1. Preparation of the SDC sol

The SDC sol was made of a commercial  $\text{CeO}_2$  colloidal dispersion (0.01–0.02  $\mu\text{m}$  particles in  $\text{H}_2\text{O}$ ) supplied from Alfa Aesar. The commercial  $\text{CeO}_2$  sol was diluted with distilled water and Sm nitrate ( $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.9%, Aldrich) in distilled water was added to the dilute  $\text{CeO}_2$  sol

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while stirring the solution in order to make 20 mol% Sm doped ceria sol.

## 2.2. Preparation of Ni/YSZ powder and the anode substrate

In order to prepare suitable anode powders for anode-supported type cells, NiO powder (Alfa Aesar) and YSZ powder (Tosoh Co. Ltd., TZ-8Y) were mixed and milled together in a weight ratio of 50:50. For the anode substrates, the starting powder mixture was compacted and pre-sintered to prepare an anode substrate at 1400 °C for 1 h. A disk-shaped anode substrate, or a fuel electrode, having a diameter of about 2.5 cm, a thickness of about 1 mm, and a porosity of 40%, was then produced. Thereafter, YSZ was coated on the substrate by a slurry coating method and sintered at 1500 °C for 2 h to make a dense electrolyte layer with a thickness of about 30 μm.

The green layers of cathodes with 1 cm × 1 cm area were formed on the YSZ electrolyte by slurry coating of the cathode material and drying. The slurry was prepared by mixing La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> powders (praxair) with methyl cellulose and water. The LSM cathode was sintered at 1100 °C for 2 h.

## 2.3. Sol–gel coating

Sol–gel coating was carried out through the dip coating method. The anode-supported cells were completely dipped into the SDC sols for several seconds and dried at room temperature, followed by calcination at 600 °C for 2 h. In order to increase the amount of SDC coating within the electrodes, dip coating and calcination cycles were repeated several times.

## 2.4. Measurement of anode performance and single cell performance

Impedance measurements were conducted with a Solartron 1260 frequency analyzer and 1287 electrochemical interface. The ac impedance spectra in the frequency range of 0.01 Hz–10<sup>3</sup> kHz, with an excitation voltage of 10 mV, were taken to ensure a linear response. The *I*–*V* characterization and ac impedance analyses on the anode-supported cells modified by sol–gel coating were also performed at the temperature of 700 °C in the mixture of methane (25%) and air (75%) as the fuel and air as the oxidant.

## 3. Results and discussion

### 3.1. Effect of sol–gel coating on anode performance

Samaria-doped ceria xerogels were prepared to characterize the crystalline phases of SDC coating film. In the XRD patterns (Fig. 1) of the xerogel calcined at various temperatures, distinctive cubic peaks appeared above the temperature of 400 °C. From the XRD results, it is presumed that the SDC coating film can serve as the path of oxygen ion conduction at over 400 °C. In previous papers [9–11], we have reported that the YSZ or SDC coating in the vicinity of TPB lead to an increase in the electrochemical reaction sites (ERS). The microporous YSZ or SDC layers can provide an ionic conduction path from the additional TPB area to the electrolyte. Consequently, the electrode reaction zone can be broadened to the region that ionic conduction can take place without significant increase of electrolyte resistance [10]. In the case of the SDC coating on the anode microstructure,

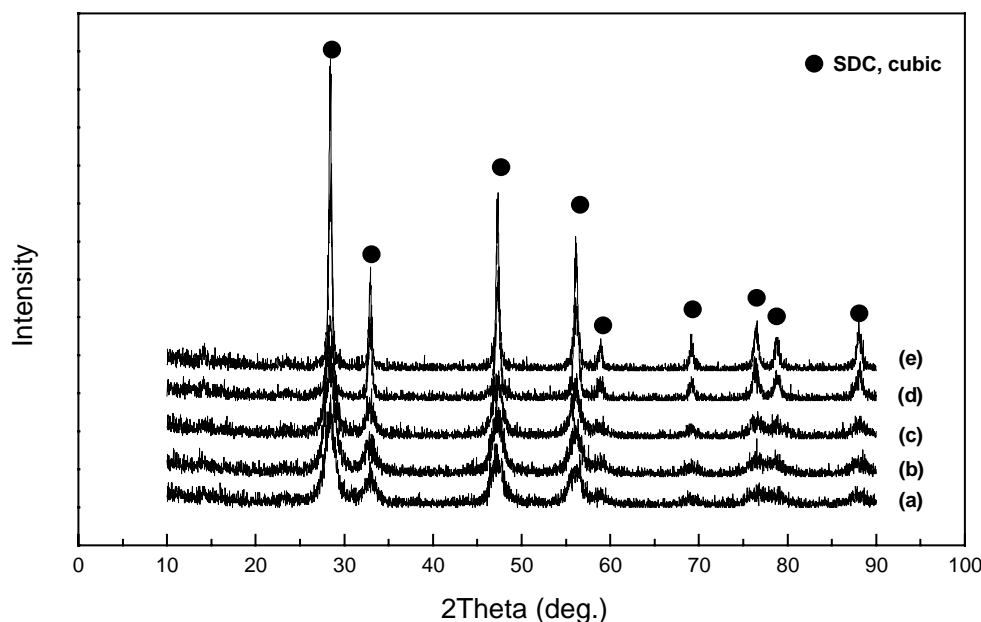


Fig. 1. XRD patterns of SDC xerogel as a function of heat-treatment temperature; (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 800 °C.

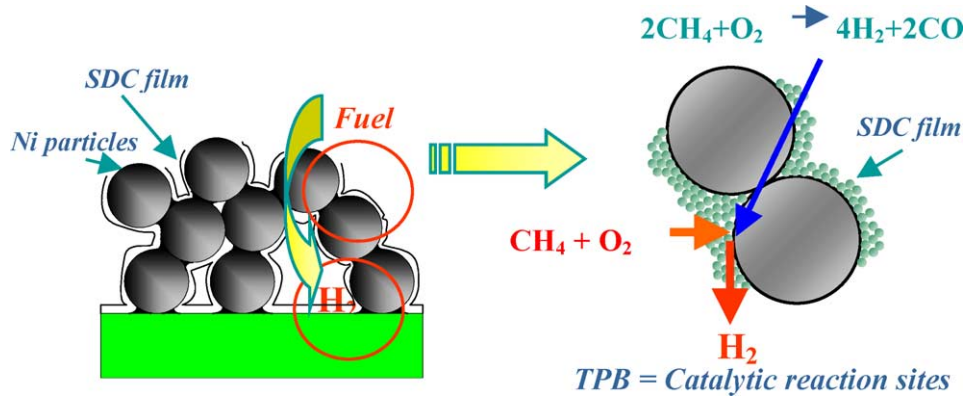


Fig. 2. Schematic illustration of an anode microstructure coated with SDC sol.

also it can be expected that sintering of Ni particles can be prevented from occurring during the cell operation and also carbon deposition can be reduced by the re-oxidizing mechanism of ceria [12]. For example, the fine SDC particles can impede the surface diffusion of Ni by a pinning effect. Moreover, the additional TPB sites can play an important role in catalyzing the partial oxidation of methane, as illustrated in Fig. 2.

It is well known that the ceria provides a high catalytic activity to hydrocarbon oxidation because of its oxygen storage capacity [4,12,13]. The ceria having an oxygen storage property can lead to suppression of carbon deposition on the Ni-based catalyst in a methane-rich atmosphere.

Fig. 3 shows the decrease of electrode polarization ( $R_p$ ) according to the SDC coating on a symmetric anode cell. Note that the symmetric cell yields an impedance spectrum including the ohmic contribution of the electrolyte and interface, as well as the double contribution of the electrode polarization [14]. The electrolyte resistance ( $R_{\text{electrolyte}}$ ) was almost the same but the  $R_p$  was four-times lower than that

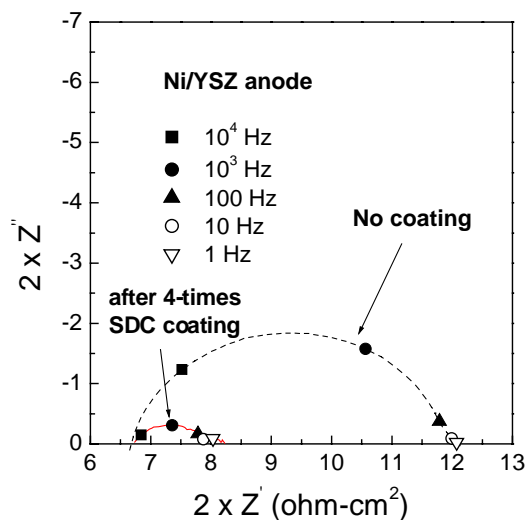


Fig. 3. Impedance spectra of a symmetric anode cell measured at 700 °C in 97% H<sub>2</sub>+3% H<sub>2</sub>O atmosphere.

of the unmodified anode. This is attributed to an increase in ERS, resulting from the microporous SDC thin-film deposited in the vicinity of TPB by sol-gel coating. Consequently, it is clear that SDC coating on anode microstructure increased the anode performance in the same manner of the coating on the cathode [9–11].

### 3.2. Effect of sol-gel coating on anode stability

The state-of-the-art SOFC anode consists of nickel and YSZ cermet. In general, the nickel offers the catalytic activity for the anode reactions and electronic conductivity, while the YSZ particle hinders the coarsening of the Ni network during cell operation and provides an oxygen ion path to expand the reaction zone over the TPB [15]. In order to increase the anode performance, fine particles of YSZ and Ni would be more desirable. However, if the particle size of Ni becomes smaller than that of YSZ, spontaneous sintering of Ni particles may occur and then the electron-conducting path may be broken. In this regard, if we can control the anode microstructure as in Fig. 2, the structural stability of the anode will greatly increase regardless of the particle size of Ni. In order to investigate the effect of the sol-gel coating on structural stability of an anode, linear shrinkage and porosity of porous Ni plates coated with SDC sol were measured (Table 1). The Porosity of the non-coated Ni plate was 27.2% after sintering at 1000 °C for 3 h, while the Ni plate coated in amount of 1.5 wt.% SDC exhibited a high porosity of 77.8%. This means that sol-gel coating on the anode can effectively prevent sintering of Ni particles, as depicted in Fig. 2.

Table 1

Linear shrinkage and porosity of Ni plate coated with SDC sol after sintering at 1000 °C for 3 h

Coating amount (wt.%)	Linear shrinkage (%)	Porosity (%)
0	28.7	27.2
0.3	4.7	70.7
1.5	2.6	77.8

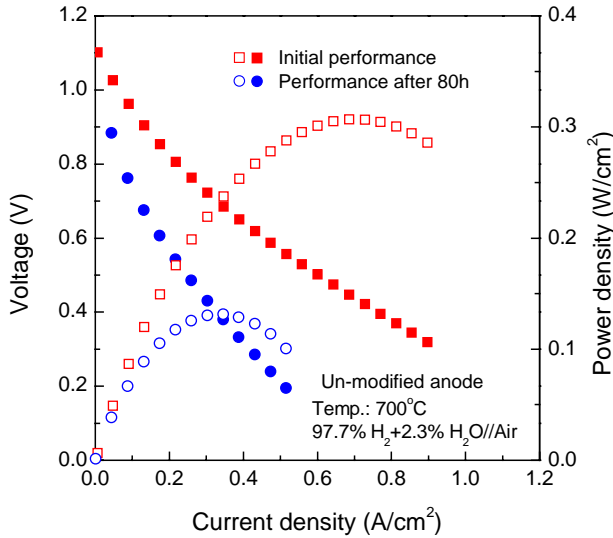


Fig. 4. Performance change of the single cell with unmodified anode measured at 700 °C in 97% H<sub>2</sub>+3% H<sub>2</sub>O atmosphere.

For example, when the anode microstructure is not optimized in terms of stability, performance of the cell will decrease during the operation, as shown in Fig. 4. In general, the anodes for SOFC are made with NiO and YSZ but NiO in the anode is reduced to Ni in the operating condition. Therefore, if the anode microstructure is not controlled well, the metal phase, Ni, will be easily sintered together due to the high operating temperature. The cell performance with poor anode microstructure decreased rapidly after the operation of only 80h, as shown in Fig. 4. Fig. 5 shows impedance spectra of the cell with poor anode microstructure measured at different operating times. The cell was operated at 700 °C with humidified hydrogen as the fuel and air as the oxidant.

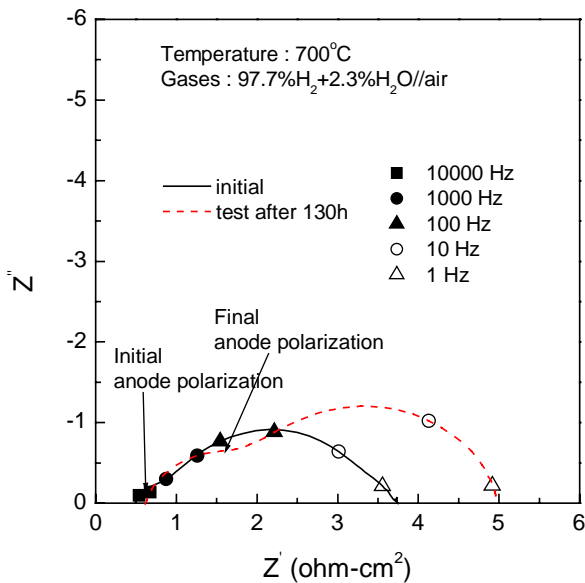


Fig. 5. Changes of impedance spectra of a single cell with unmodified anode.

From Fig. 5, it appears that each impedance spectra consists of at least three semi-circles. As reported in our previous paper and other literature [9,16], the semi-circle at the highest frequency region represents the anode polarization in the single cell impedance. Therefore, the increase of the semi-circle at the highest frequency region shows the rapid degradation of cell performance in Fig. 4. Even though the operating temperature was as low as 700 °C, the anode polarization in the high frequency region increased from 0.49 to 1.27 Ω cm<sup>2</sup> due to sintering of the Ni particles. Evolution of the maximum power densities of single cells with operating time are summarized in Table 2. For the cells with unmodified anodes, the maximum power densities decreased during the cell operation. On the other hand, the cell coated with SDC sol both electrodes exhibited little decrease in maxi-

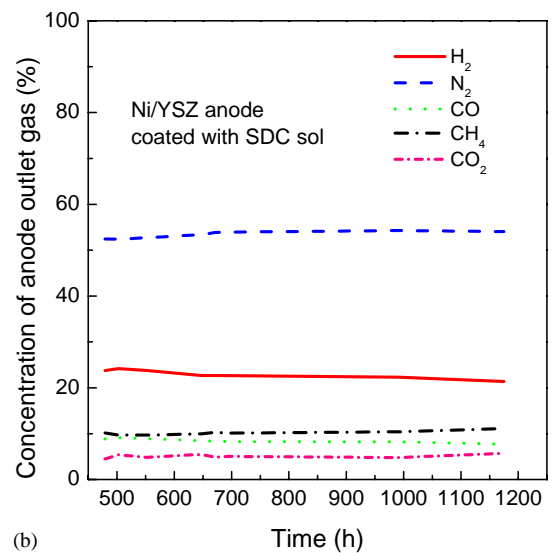
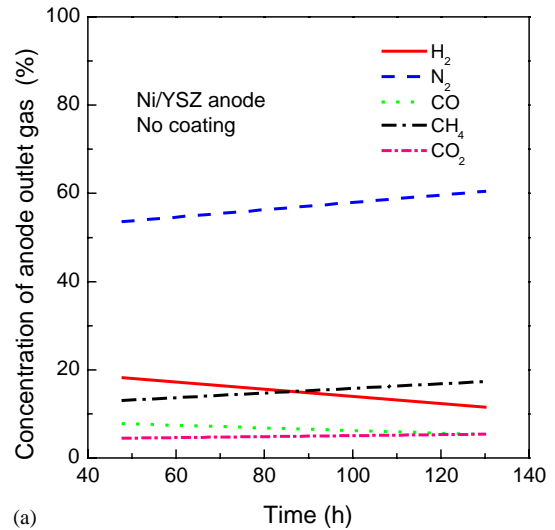


Fig. 6. Compositions of the outlet gases from anodes measured at 700 °C with the mixture of methane (25%) and air (75%) as the fuel under open-circuit conditions.

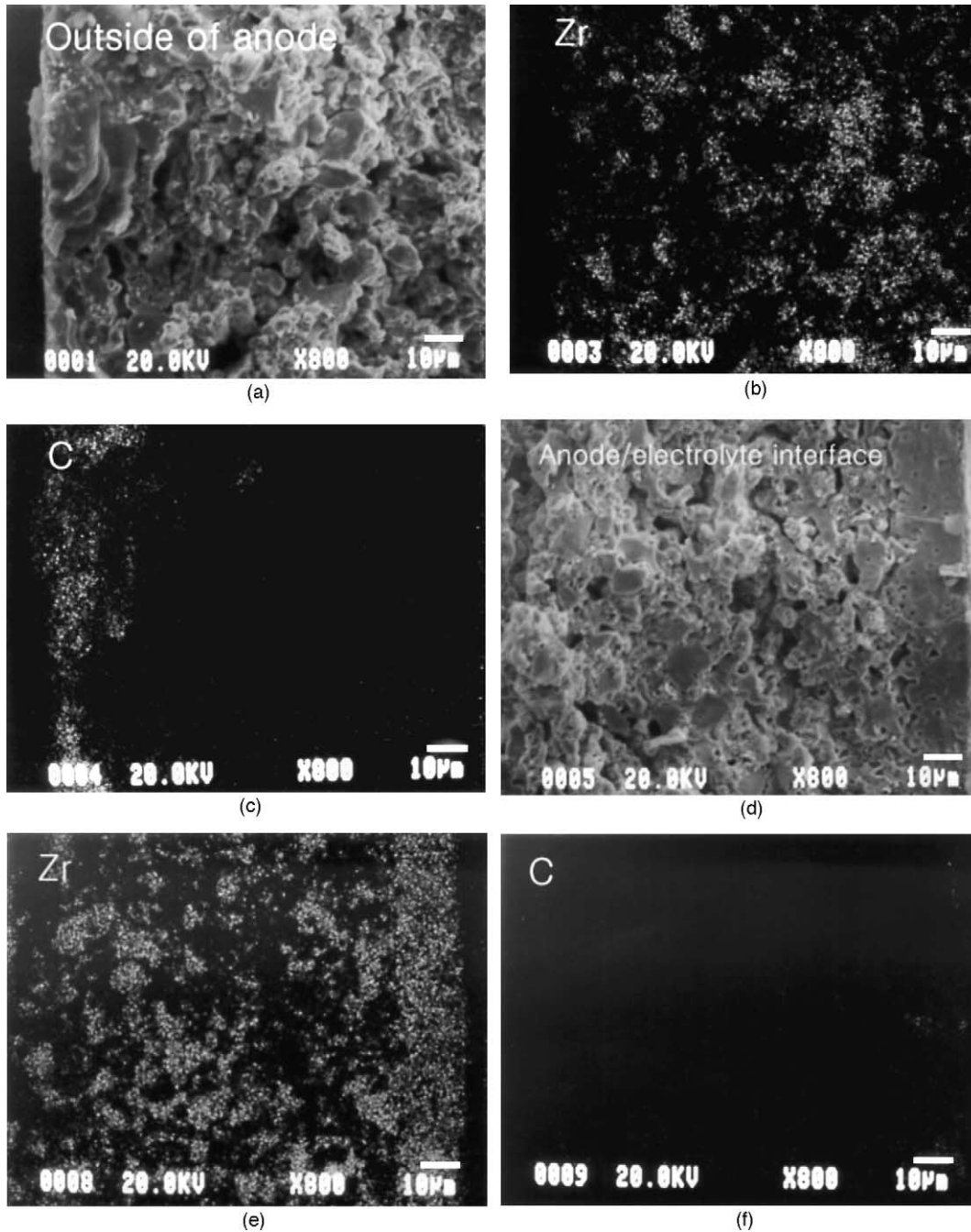


Fig. 7. Electron probe microscopic analysis (EPMA) of the modified anode operated at 700 °C with 25% methane in air under open-circuit condition for 500 h: (a) SEM image of outside anode; (b) Zr mapping of outside anode; (c) C mapping of outside anode; (d) SEM image of anode/electrolyte interface; (e) Zr mapping of interface and (f) C mapping of interface.

mum power density even though it was operated for longer times (500 h) than the other cells.

### 3.3. Effect of sol-gel coating on partial oxidation of methane

As mentioned above, one of the most critical issues in the SOFC running on hydrocarbon fuels is the risk of carbon formation from the fuel gas. For example, methane will de-

compose when heated in the absence of air or steam at the temperatures above about 650 °C via pyrolysis reactions:



Another source of carbon formation is from the disproportionation of carbon monoxide via the so-called Boudouard reaction [6]:



Table 2  
Changes of maximum power densities with the operating time measured at 700 °C with humidified hydrogen (97%) as the fuel and air as the oxidant

Coating part	Coating material	Maximum power density (W/cm <sup>2</sup> )		Operating time (h)
		Initial	Final	
Cathode and anode	SDC sol	0.45	0.42	500
Cathode only	SDC sol	0.43	0.29	50

Especially, this reaction (2) can be catalyzed by metal such as nickel and therefore there is a high risk of carbon deposition occurring on the anode for SOFC which contains nickel. A particular type of carbon formation occurs on the surface of nickel, known as carburization, leading to spalling of the nickel known as “metal dusting”. One of the simple methods to reduce the risk of carbon formation from the reactions (1) and (2) is to add steam to the fuel stream, leading to the carbon gasification reaction:



However, the addition of steam to fuel is not appropriate for the APU and portable power generation (PPG) systems due to an increase of complexity and bulkiness. In this regard, many researchers have focused on so-called “direct methane” operation of SOFC, which works with dry methane without coking [1–4]. However, coking can be suppressed only by the operation with a high current density [3], which may be a drawback especially for the APU and PPG systems. In this study, we are interested in partial oxidation of hydrocarbon fuels, which have the advantage of compactness for the APU and PPG systems.

Fig. 6 shows the compositions of the outlet gases from the anodes measured at 700 °C under open-circuit conditions, when methane and air were introduced into the anodes. Total flow rate of the fuel was 600 cm<sup>3</sup>/min (STP) and a volume ratio of methane to oxygen was 1.59:1. As shown in Fig. 6(a), the hydrogen concentration of the outlet gas decreases with increase of operating time. For the cell coated with SDC coating on the anode, however, there is no significant change in the composition of the outlet gases during the operation of 700 h (Fig. 6(b)). As a result of the gas chromatography analysis, oxygen was found to be almost completely consumed by reacting with methane to form hydrogen, carbon monoxide, and carbon dioxide. The SDC-coated anode shows stable production of the hydrogen and carbon monoxide compared to the unmodified anode. Qualitative analysis of carbon deposition was performed by electron probe microscopic technique. Fig. 7 shows secondary electron microscopic (SEM) images and carbon mapping images of the anode modified by SDC coating, which was operated at 700 °C with 25% methane in air under open-circuit condition for 500 h. As can be seen from the pictures, there is no carbon deposition in the region of the anode/electrolyte interfaces (Fig. 7f) in contrast with the carbon mapping at the outside of anode (Fig. 7c). From the results, it seems that the

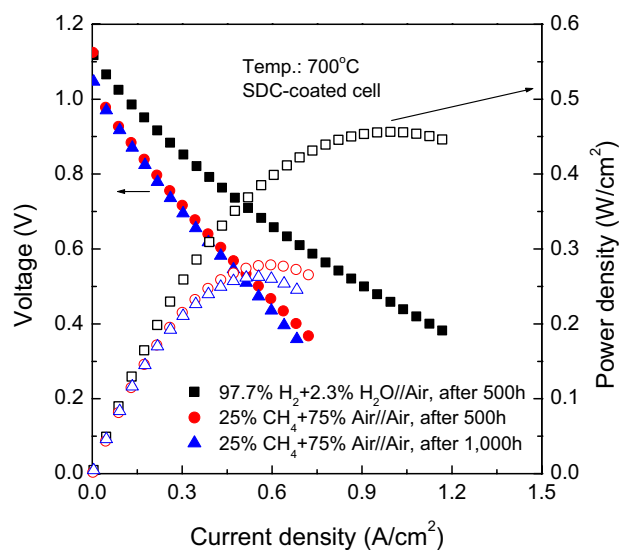


Fig. 8. Performance of a single cell coated with SDC sol under various operating conditions.

differences between the modified and unmodified anodes in hydrogen production and carbon deposition were attributed to the structural and catalytic stabilities of the anodes. Namely, sintering of Ni particles in the non-coated anode reduced the surface area of the catalyst, resulting in a decrease of the hydrogen and carbon monoxide production. In addition, the SDC coating reduced carbon deposition in the anode by oxidation of CO molecules adsorbed on the Ni surface through reaction with oxygen transported to the Ni-SDC interface from SDC instead of following reaction (2) on the Ni surface. The SDC can be re-oxidized by dissociation of water or oxygen molecules adsorbed on oxygen vacancy sites of SDC to H<sub>2</sub> and atomic oxygen [12]. More work is required over a broad range of temperatures and various volume ratios of methane to oxygen to clarify the effect of the SDC coating on catalytic activities for partial oxidation of methane.

Performance of a single cell with the SDC-coated anode is shown in Fig. 8. The maximum power density of the cell with the modified anode was 0.45 W/cm<sup>2</sup> at 700 °C in humidified hydrogen as the fuel and air as the oxidant in comparison with the performance of 0.3 W/cm<sup>2</sup> at 700 °C in the mixture of methane (25%) and air (75%) as the fuel and air as the oxidant. The cell was operated for 1000 h without significant degradation of cell performance, resulting from suppression of nickel sintering and carbon deposition.

#### 4. Conclusions

We demonstrated that a SDC coating on an anode increased the anode performance in terms of increase of ERS and suppression of nickel sintering and carbon deposition. The main results are as follows:

1. From ac impedance analysis, it was observed that the anode polarization became four-times lower by sol–gel coating than using an unmodified anode.
2. The maximum power density of the cell with the modified anode was  $0.3 \text{ W/cm}^2$  and carbon deposition was not observed in the region of anode/electrolyte interfaces, when the cell was operated at  $700^\circ\text{C}$  in the mixture of methane (25%) and air (75%) as the fuel and air as the oxidant.
3. The modified cell was successfully operated for more than 1000 h without significant degradation of cell performance due to an increase of the structural and catalytic stability with the SDC coating on the anode.

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