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Performance of Single Cells with Anode Functional Layer for SOFC

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Abstract To improve the performance of the anode-supported Solid Oxide Fuel Cell (SOFC) which can be operated at an intermediate temperature, the functional layer (FL) is introduced on a anode substrate. And the scandia-stabilized zirconia (ScSZ) and samaria-doped ceria (SDC) which have higher ionic conductivity and better chemical stability than yttria-stabilized zirconia (YSZ) are used as material for the anode FL with the Ni. The fabrication process of anode-supported single cell with the anode FL was established and the power density of those was evaluated. As a result, the sample with anode FL (Ni-YSZ) has higher power density than normal cell. The single cell which was composed of the FL (Ni-YSZ) and electrolyte (YSZ) showed about 550 mW/cm^2 of the maximum power density at 650°C and 1430 mW/cm^2 at 750°C respectively. In case of the single cell using the ScSZ and SDC as anode FL, the performance of samples decreased rapidly and those showed unstable voltage during long-term test. In case of using methane as a fuel, the cell performance with each FL decreased comparing with H_2 fuel. In the region of a high current density, there are large concentration polarizations.

Key words Solid Oxide Fuel Cell (SOFC), Anode, Functional Layer, Methane

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1. Introduction

It is essential to decrease the operating temperature to 750℃ or less for the practical applications of Solid Oxide Fuel Cell (SOFC). The low temperature operated SOFC has many advantages[1,2]. The anode-supported design has been identified by many studies as feasible structure because of the lower internal resistance[3,4]. But there are also the polarization resistance of the anode and the interfacial resistance between anode and electrolyte at intermediate temperature. Therefore, the three phase boundary (TPB) sites which are formed from electrode, electrolyte and pore must be increased in anode and the new anode materials with the high ionic conductivity can be used to enhance the anodic performance. It is essential for the study about the microstructure controlling and material selection to operate SOFC at intermediate temperature[5].

In case of the anode-supported design, the microstructure of anode deeply influences the performance of single cells because that is closely related to the polarization and interfacial resistance. It is assumed that the oxidation and agglomeration of nickel particles caused by the long term operation get the performance worse. For reasons related to those, the part of anode which was close to electrolyte is preferable to have the diminished particle size. This anode functional layer (FL) provides more electrochemical active sites and TPB lengths for the minimal polarization. The yttria stabilized zirconia (YSZ) which shows the high ionic conductivity and chemical stability has been used extensively as electrolyte in SOFC. The scandia stabilized zirconia (ScSZ) and ceria based materials have been considered new materials because their ionic conductivity is much higher than that of YSZ for intermediate temperature. The ceria based materials have particularly been known for mixed ionic and electronic conductor around 700℃[6]. Because hydrocarbons are actually used as fuels in SOFC system, the performance of anode and direct reforming to the hydrocarbon fuels are very critical.

In this work, the anode FL which was made from smaller particles that those of anode substrate was proposed to operate SOFC at intermediate temperature and that was applied between the anode substrate and electrolyte. The performances of the single cells with and without anode FL were compared. The ScSZ and samaria doped ceria were used for anode FL to investigate possibility as alternative materials. In addition, the performances of the single cells are compared in the case of using hydrogen and methane as fuels respectively.

2. Experiments

2.1 Cell Fabrication

As raw materials, commercial powders of nickel oxide (Alfa, 99.9%) and 8 mol% yttria stabilized zirconia (8YSZ, Tosho TZ-8Y) were used to produce the anode substrate and 10 mol% scandia and 1 mol% ceria stabilized zirconia (10Sc1CeSZ, Fine Tech.) and SDC (Nextech.) also were chosen for materials of anode FL. First of all, starting materials were mixed by milling process with weight ratio of NiO:YSZ=6:4. Subsequently the graphite powder (average particle size of 75 mm, volume fraction of 24%) which provided additional pores, organic binders and ethyl alcohol were added in the powder mixture, then the mixture was dried in an oven. The anode substrate was made by pressing of the powder mixture using a rectangular mold and fired at 1400℃ in air for an hour. FL was composed of nickel and YSZ (ScSZ or SDC) without graphite. The FL was screen-printed on the anode substrate. The YSZ was coated on the FL by slurry coating process and co-fired with anode at 1550℃ for two hours in order to densify YSZ with a thickness of 20 mm. Through the production steps, the cell was size of 10 × 10 cm^2 with a thickness of about 1.8 mm. Then they were grinded with a thickness of 1.4 mm to measure by the cell tester. $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8}O_3$ (LSCF) mixed with SDC was deposited on the top of sintered YSZ by screen printing technology. Finally, the active area of cathode is 0.636 cm^2.

2.2 Microstructure and electrochemical characteristics

Fig. 1 shows the schematic diagram of the test instrument for measuring a single cell performance. The performance of anode-supported single cells has been evaluated using test furnace with hydrogen and methane

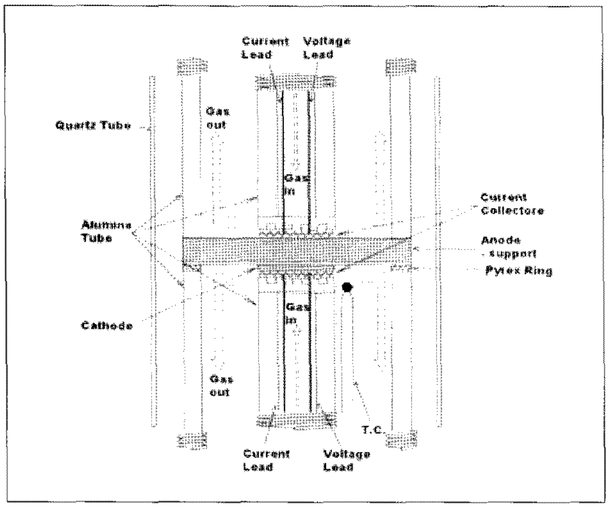

Fig. 1 Schematic diagram of measuring instrument.

as fuels at 650 and 750℃ respectively. A hydrogen as a fuel and an air as a oxidant were supplied at a rate of 100 cc/minute and 250 cc/minute. A methane was supplied at a rate of 5 cc/minute considering the electro-chemical equivalents and the hazard of a carbon deposition. The current-voltage test was conducted using electrical load and digital multi-meter and the impedance analysis was conducted by means of Solartron 1287 potentiostat and 1260 impedance/gain-phase analyser. The frequency range was from 0.01 Hz to 100 kHz and the AC amplitude was fixed at 10 mV. After the cell test, the micro-structure and morphology of the single cell was investigated with cross-section view by scanning electron microscope (SEM, S-4300, Hitachi Co., Ltd., Japan).

3. Results and Discussions

3.1 Cell testing in hydrogen fuel

In order to compare the performances of single cells, those composed of no functional layer (NL) and FL on the anode substrate were evaluated at 650℃ and 750℃ respectively in hydrogen fuel as shown in Fig. 2. NiO and YSZ were used as the raw materials of the FL like

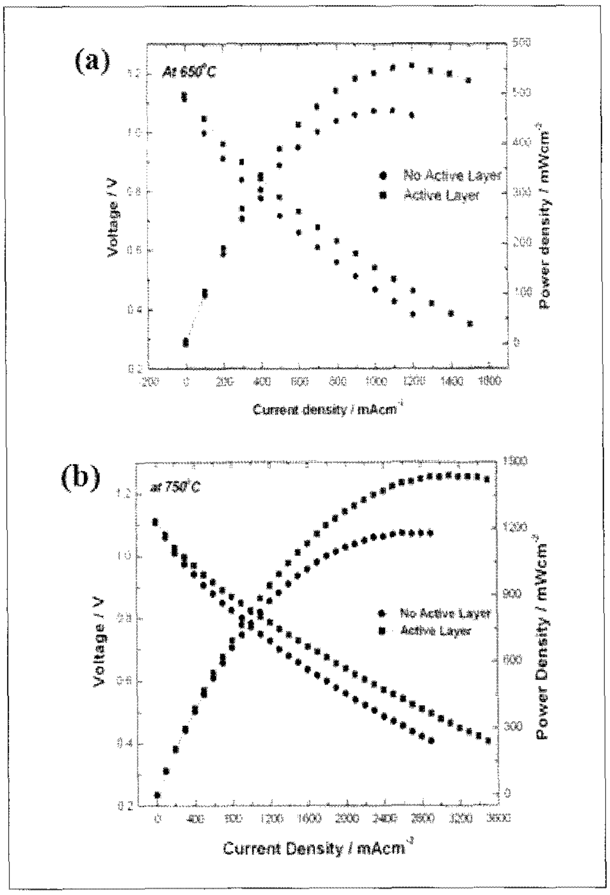

Fig. 2 I-V and I-P characteristics of the single cells: (a) 650℃; (b) 750℃.

those of anode. The open circuit voltage (OCV) of both cells showed about 1.12V, so it was assumed that there is no gas leakage through the electrolyte. The maximum power density (P_{max}) of NL and FL cells were about 430, 550 mW/cm^2 at 650℃ and 1180, 1430 mW/cm^2 at 750℃. The maximum power density was influenced by the operation temperature because the activation energy rapidly decreased at high temperature. The single cell with anode FL showed much higher performance than that with NL, and there are 120, 250 mW/cm^2 as the gaps of value at 650, 750℃. It is expected that the anode FL which have higher TPB length increase the electrical performance.

The impedance spectra was obtained at OCV as a function of the operating temperature as shown in

Table 1. Internal resistance (R_o) and polarization resistance (R_p) of the single cells

Cells	R_o / Ωcm^{-2}		R_p / Wcm^{-2}	
Temperature	650℃	750℃	650℃	750℃
NL cell	0.48	0.23	1.64	0.71
FL cell	0.41	0.19	1.20	0.54

Table 1. The spectra are composed of two depressed semicircles. The equivalent circuit is composed of a series combination of a resistance and two parallel combinations of a resistance and a constant phase element (CPE)[(7-9)].

The internal resistances (R_o) of NL and FL single cell were 0.48 and 0.41 Ωcm^{-2} as the left tangent line of the semicircle located in the high frequency region and the electrode polarization resistances (R_p) were 1.64 and 1.20 Ωcm^{-2} respectively at 650℃. The single cell with anode FL shows lower internal resistances and electrode polarization resistances. It is generally known that the internal resistance includes the resistance of electrolyte and the contact resistance between electrolyte and electrode. This result is resonable in that the anode FL which have larger active area, lowers polarization resistance by decreasing activation polarization and internal resistance by decreasing contact resistance. Therefore, it could be expected that electrical properties are greatly related with the TPB length as electrochemical active area.

In order to identify the microstructure of the fabricated sample, the SEM images were used. The cross section views of NL and FL single cell are shown in Fig. 3 (a) and (b) respectively. The anode FL is well formed on anode substrate and Fig. 3 (b) shows about 20 µm thickness of FL. It is also confirmed that the particle sizes of FL are much smaller than those of anode substrate. From this result, it can be considered that FL could increase the TPB length and the connectivity of nickel particles. From the performance results of Fig. 2, it could be confirmed that the uniform and fine-grained FL could greatly affect the performance of anode supported single cell.

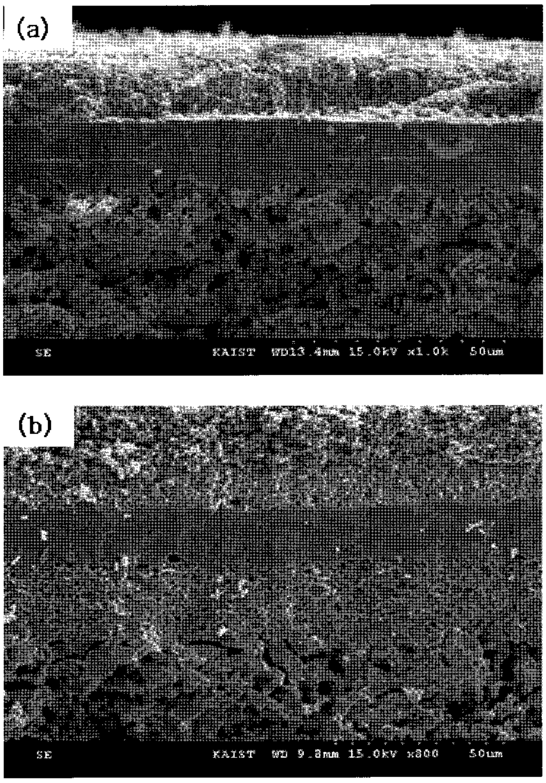

Fig. 3 Scanning electron micrograph of cross section view: (a) NL single cell; (b) FL single cell.

ScSZ and SDC have chemical stability as well as high ionic conductivity so they have been indicated alternative material such as electrolyte at intermediate temperature. They was applied as the materials of anode FL with nickel to investigate the variation of the single cell performance. The single cell performances were compared according to FL components in Fig. 4. The single cell with the anode Ni-YSZ FL which was composed of the same materials as anode substrate had the highest performance as 550 $mWcm^{-2}$ at 650℃ as shown in Fig. 4. In case of using ScSZ and SDC as a component of anode FL, the maximum power densities were 330 and 290 $mWcm^{-2}$ at 650℃ respectively. There is a much difference of 260 $mWcm^{-2}$ as a function of component material of anode FL. These results are likely that

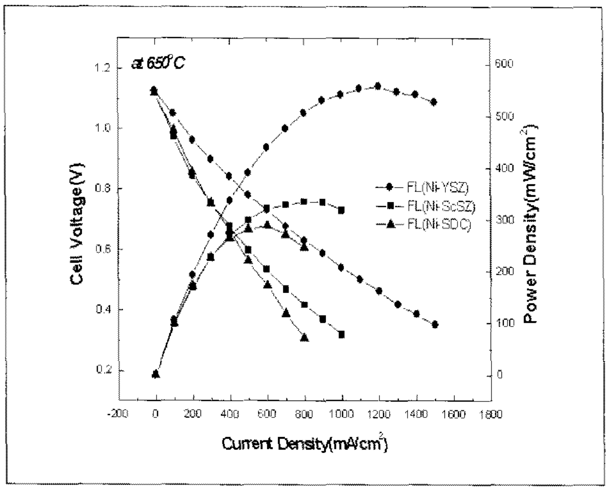

Fig. 4 I-V and I-P characteristics of the single cells as a function of FL materials in hydrogen fuel.

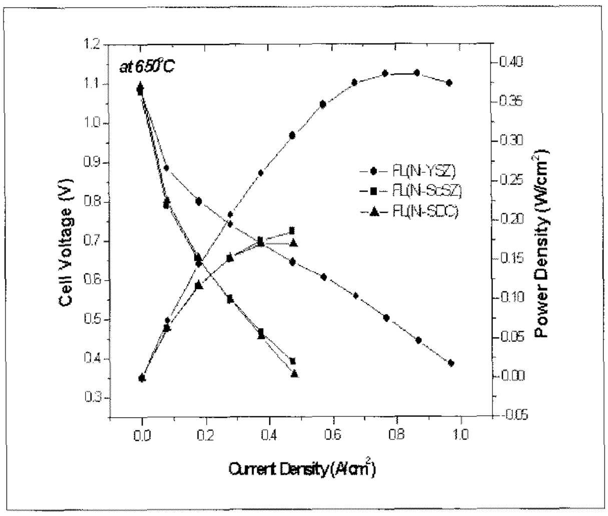

Fig. 5 I-V and I-P characteristics of the single cells as a function of FL materials in methane fuel.

there is a structural problem such as mismatch among electrolyte, anode FL and anode substrate. There can be diffusion of elements at the interface between electrolyte (or anode substrate) and anode FL. It is reported that (Zr, Ce)O2-based solid solution is produced according to many literatures.

3.2 Cell testing in methane fuel

To compare the performances of single cells in methane with hydrogen, the single cell performances were evaluated in methane fuel as shown in Fig. 5. NiO and YSZ/ScSZ/SDC were also used as the raw materials for anode FL. Methane was directly supplied to the anode of single cell without any additional reforming system. Therefore, it is considered that the reforming processes might happen in the anode. The humidity of the supplied methane was about 2.5% and the flow rate of methane was 5 sccm (standard cubic centi-meter per minute). The single cell with the anode FL which was composed of the same component material as anode substrate showed the highest performance as 380 $mWcm^{-2}$ at 650℃ as shown Fig. 5. In case of using ScSZ and SDC as anode FL, the single cell performance showed 200 and 190 $mWcm^{-2}$ at 650℃ respectively. There are large differences of over 100 $mWcm^{-2}$ compared with hydrogen fuel.

Fig. 6 shows the impedance spectra of the single cell with anode FL composed of (a) Ni-YSZ, (b) Ni-ScSZ and (c) Ni-SDC at 650, 700 and 750℃. Table 2 provides the maximum power densities of those. From AC impedance spectra of Fig. 6, it can be seen that the semi-circle in the low frequency region is very large compared with using hydrogen fuel. This semi-circle is related with the polarization resistance affected by mass transfer of gas. Therefore it is considered that the supply of fuel was not sufficient by carbon deposition when the methane was used as a fuel. In case of using Ni-YSZ anode FL, AC impedance spectra does not change at the high temperature. But at the current loading state, the single cell performance increase as the temperature increases (Table 2). It is considered that the oxide ion is continuously supplied to the anode from the electrolyte at the current loading state, therefore carbon deposited to the anode surface is removed to forming CO or CO_2. In AC impedance spectra of the single cell composed of ScSZ and SDC FL (Fig. 6 (b) and (c)), the polarization resistance related with the mass transfer decrease as

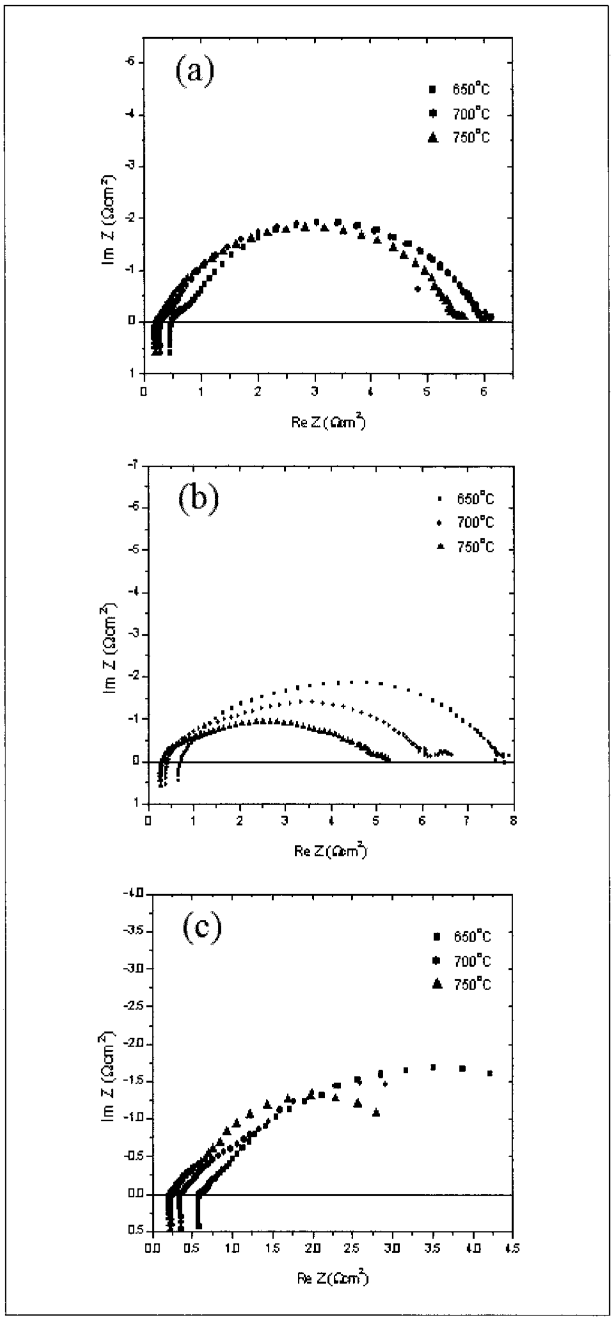

Fig. 6 AC impedance spectra in methane fuel: (a) Ni-YSZ FL; (b) Ni-ScSZ FL; (c) Ni-SDC FL.

the temperature increases. This result can be ascribed to the high oxide ion conductivity of ScSZ and SDC. It is also known that the ceria based materials like SDC especially have an ability to reform hydro-carbon fuels.

Table 2. Maximum power density of single cell as a function of FL from I-V test in methane fuel

FL	P_{max} / Wcm^{-2}		
	650℃	700℃	750℃
Ni-YSZ	0.38	0.67	1.05
Ni-ScSZ	0.20	0.38	0.59
Ni-SDC	0.19	0.35	0.56

4. Conclusions

The anode FL composed of smaller particles was applied on anode substrate to improve the single cell performance at intermediate temperature. The ScSZ and SDC as component materials of FL known for the superior materials to YSZ were used to investigate possibility as the alternatives. The single cell performances were evaluated using AC impedance spectroscopy and current-voltage test. The microstructures of the single cell were analyzed using SEM. The single cell including Ni-YSZ anode FL showed the maximum power density of 550 $mWcm^{-2}$ at 650℃ and 1430 $mWcm^{-2}$ at 750℃ respectively. This result indicated that the uniform FL including high TPB length directly leaded to the reduction of internal resistance and polarization resistance. On the other hand, the single cell with FL composed of ScSZ and SDC showed the lower performance and high polarization resistance due to deteriorate reaction between FL and either electrolyte or anode substrate.

In case of using methane as a fuel, the single cell with FL composed of YSZ showed the maximum power density of 1050 $mWcm^{-2}$ at 750℃. It was considered that there were carbon deposition, therefore in the region of the high current density there are large concentration polarizations.

The performance of single cell increased by anode FL, but the additional study concerned with various manufacturing process and materials selection must be carried out in the future. In addition, the amount and the humidity of the supplied methane need to be optimized in order to reduce carbon deposition.

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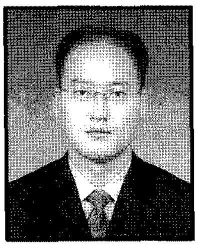

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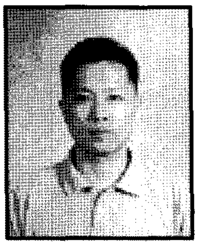

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