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Methane-Air 혼합 Gas에서 구동하는 하니컴 형태의 SC-SOFC

박 병탁[1),2)], 윤 성필[1,*)], 김 현재[1)], 남 석우[1)],
한 종희[1)], 임 태훈[1)], 홍 성안[1)], 이 덕열[2)]

Honeycomb-type Single Chamber SOFC Running on Methane-Air Mixture

Byung-Tak Park[1),2)], Sung Pil Yoon[1,*)], Hyun Jae Kim[1)], Suk Woo Nam[1)],
Jonghee Han[1)], Tae-Hoon Lim[1)], Seong-Ahn Hong[1)] and Dokyol Lee[2)]

[1)] *Fuel Cell Research Center, Korea Institute of Science & Technology, Seoul 136-791, South Korea*

[2)] *Division of Materials Science and Engineering, Korea University, 5-1 Anam-Dong, Sungbuk-Ku, Seoul 136-701, South Korea*

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Abstract : One of the most critical issues in solid oxide fuel cell (SOFC)running on hydrocarbon fuels is the risk of carbon formation from the fuel gas. The simple method to reduce the risk of carbon formation from the reactions 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 auxiliary power unit (APU) and potable 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. However, coking can be suppressed only by the operation with a high current density, which may be a drawback especially for the APU and PPG systems.

The single chamber fuel cell(SC-SOFC) is a novel simplification of the conventional SOFC into which a premixed fuel/air mixture is introduced. It relies on the selectivity of the anode and cathode catalysts to generate a chemical potential gradient across the cell. Moreover it allows compact and seal-free stack design. In this study, we fabricated honeycomb type mixed-gas fuel cell (MGFC) which has advantages of stacking to the axial direction and increasing volume power density. Honeycomb-structured SOFC with four channels was prepared by dry pressing method. Two alternative channels were coated with electrolyte and cathode slurry in order to make cathodic reaction sites. We will discuss that the anode supported honeycomb type cell running on mixed gas condition.

1. Introduction

It is well known that conventional solid oxide fuel cells(SOFCs) which, compared to other types of current electric generation, offer a number of distinctive and surpassing features due to their mainly ceramic structures and high operating temperatures(800-1000℃)[(1)]. However, material problems associated with the high operating temperature(1000℃), which include electrode sintering, gas tight sealing, interfacial diffusion between the electrode and electrolyte, mechanical stress due to different thermal expansion coefficients of the cell components, and a limited choice of expensive interconnects, give rise to recent attention towards the prospect of SOFCs being operated at reduced temperatures (500-800℃). Unfortunately, the low operating temperature decreases the cell performance due to an increase in the electrolyte polarization and high over-potentials of electrodes. Incidentally, much efforts has been devoted to reducting the ohmic losses of the electrolyte at these low operating temperatures[2]. Recently, Hibino et al.[3] reported that mixed-gas SOFCs can be operated with a high performance of 0.4Wcm^{-2} even at a low operating temperature of 500℃. The working mechanism of the mixed gas fuel cell is based on the difference in the catalytic activity of the oxidationof the fuel between two electrode materials: one material catalyzes the fuel oxidation to form the synthesis gas while the other is inactive to this reaction. This situation leads to an oxygen concentration difference with a low partial pressure of oxygen at the former electrode and a high P_{O2} at the latter electrode, thereby resulting in an electromotive force(EMF) between the two electrodes even in a uniform atmosphere. One of the advantages of the mixed-gas SOFC is that because there is no need to separate the fuel gases, gas sealing is not necessary and the effects of an imperfect thin electrolyte layer resulting from cracks or pinholes can be minimized. Our target is to make an anode-supported honeycomb type SOFC with a thin YSZ electrolyte and to investigate a performance and a property of unit cell from this novel structure. Fig. 1 shows the schematic illustration of the honeycomb type SOFC which has four unit cell segments.

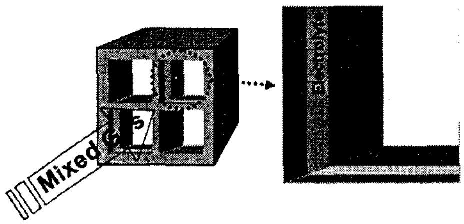

Fig. 1 A schematic illustration of the honeycomb-type single chamber SOFC.

2. Experimental

2.1 Preparation of honeycomb structured anode substrate

In the "Honeycomb type-SOFC", 65vol% NiO(YSZ),(NiO(70%) -YSZ(30%), PRAXAIR) and 30vol% pore former(1-2㎛ Graphite, ALDRICH) were employed to fabricate anode substrate which has a proper porosity. This prepared powder was mixed well through a wet milling process and grinded after drying . Fig 2 shows the honeycomb type anode substrate which was prepared by dry pressing and pre-fired at 1250℃ (bright green) and 1400℃(dark green) for 2 hours.

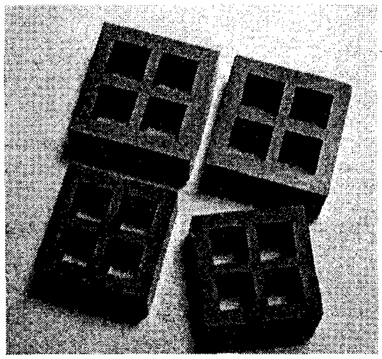

Fig 2. Honeycomb type anode substrate.

2.2 Preparation of coating slurry

In this study, we employed 8YSZ powder (TZ8Y, Tosoh) and LSM powder (La0.85Sr0.15Mn oxide, PRAXAIR) as an electrolyte and cathode material, respectively. All coating slurry were prepared by ball milling of powder and additives including, poly vinyl butyral(PVB) as a binder, dibutyl phthalate as a plasticizer, Troton-X as a homogenizer, fish oil as a dispersant, and toluene and 2-propanol as solvents.

2.3 Fabrication of honeycomb type SOFC

We filled two channels with silicon glue to prepare anode electrode, and the electrolyte slurry was coated on the surface of unfilled channels, dewaxed at 400℃ for 2 hours. After coating two times, the electrolyte coated andoe was sintered at 1400℃ for 2 hours. The cathode layer also fabricated and sintered at 1100℃ for 2 hours through the same procedure.

3. Results

3.1 Microstructure of honeycomb type SOFC

Fig. 3 shows the mercury porosimetry result of anode substrate sintered at 1400℃, and reduced at 700℃ in reduction atmosphere. In the result, anode sample including 35vol% pore former shows 35.79% porosity and 0.37㎛ median pore diameter after reduction.

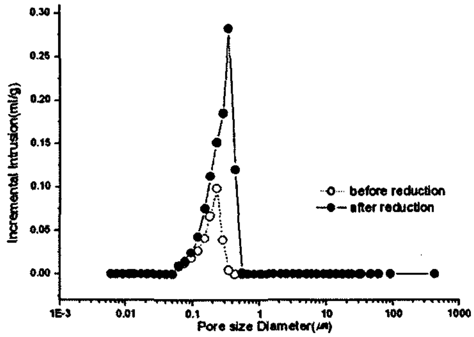

Fig. 3 Pore size diameter of honeycomb anode substrate.

In fig. 4, the SEM image shows that dense and about 33μm thin YSZ film was obtained on the porous anode substrate through a slurry coating method. The cathode layer which has enough porosity and thickness was fabricated on the YSZ electrolyte.

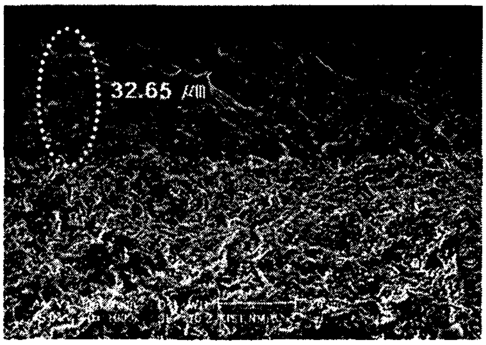

Fig. 4 SEM image of an anode-electrolyte bilayer fabricated as described in the test.

3.2 OCV and Impedance data of Honeycomb type SC-SOFC

The single cell fabricated was placed in a mixed-gas station and tested. The partial oxidation of methane can proceed to form hydrogen and carbon monoxide as follows[(4)]:

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO \quad (1)$$

Therefore, at the anode of the single cell, the hydrogen and carbon monoixde produced from reaction (1) react with oxygen ions taken from the electrolyte, releasing electrons an carbon dioxide and water as the products. Meanwhile oxygen at the cathode reacts with electrons taken from the electrode to form oxygen ions as follows:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3)$$

$$O^2 + 4e- \rightarrow 2O^{2-} \quad (4)$$

According to reaction (1), a stoichiometric value of CH_4:O_2 ration for the partial oxidation of methane should be 2. Fig. 5 shows the OCV variation according to various temperatures. As can be seen, as the temperature increased, the OCV value was decreased, however its stability is increased.

Fig. 6 shows the impedance spectra of cell under the single chamber fuel cell condition. As furnace temperature increased, the cell IR was decreased slightly.

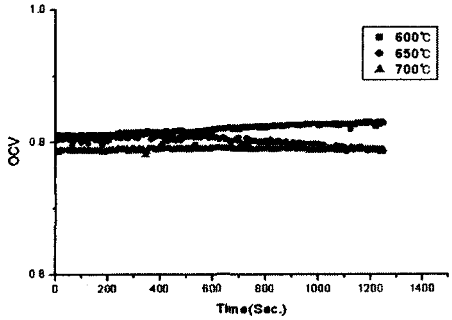

Fig. 5 OCV of the cell under single chamber configuration as a funtion of time.

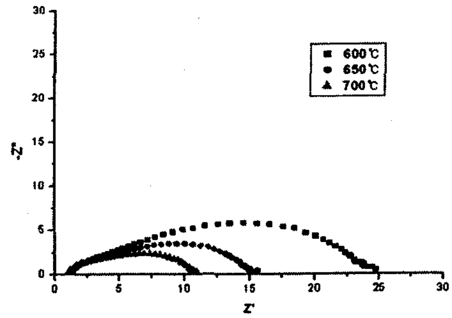

Fig. 6 Impedance spectra of cell under the single chamber fuel cell condition.

4. Conclusions

The Honeycomb type SC-SOFC which has 35.79% anode porosity and 33㎛ thin YSZ elelctrolyte film was fabricated. Form the result, the OCV and impedance spectra of this cell at various temperature has been presented. The cell was stable over the time of measurement as the OCV 0.8V at 700℃.

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