ANODE-SUPPORTED THIN FILM SOFC FABRICATION FOR MIXED GAS FUEL CELL
혼합가스 연료전지용 박막 고체 산화물 연료전지 제조

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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 effort has been devoted to reducing the ohmic losses of the electrolyte at these low operating temperatures [2]. For example, Samaria-Doped Ceria (SDC) has been widely studied because of its high ionic conductivity, about 30-times higher when compared to that of YSZ at 800℃ [3]. Even though CeO_2 is unstable at low oxygen partial pressures [4], this demerit can be overcome by operating at a lower temperature and a higher oxygen partial pressure when compared to the conventional operating conditions for an SOFC running on hydrogen fuel at 1000℃.

Recently, Hibino et al. [5] reported that mixed-gas SOFCs can be operated with a high performance of 0.4 $W\,cm^{-2}$ 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 for the oxidation of 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 [3]. This situation leads to an oxygen concentration difference with a low partial pressure of oxygen at the former electrode and a high P_{O_2} 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 SOFC with a thin SDC electrolyte that can be directly operated at the reduced temperatures (500-800℃) under partial oxidation of methane (POM) conditions. The key issues of overcoming the excessive ohmic loss of the electrolyte and the over-potentials of the electrodes at such lower operating temperatures are the fabrication of thin-film electrolytes and the extension of the triple-phase boundary (TPB) at the electrodes. Several methods for deposition of thin films onto porous substrates (electrochemical vapor deposition (EVD), RF/DC-magnetron sputtering, spray pyrolysis, sol-gel deposition, colloidal deposition) have been applied in the literature [4-8].

Experimental

The porous anode of Ni-5 wt.% Al alloy was used as a substrate for deposition of the electrolyte thin film by sol-gel hot-spin coating method. In the present study, the substrates with about 60% of porosity, 0.6 mm thickness and 30 mm diameter were used.

The thin electrolyte fabrication procedure is shown in fig.1. To make a thin layer of electrolyte, the SDC sol (5 ml) was sprayed by a spray gun on the substrate heated and spun on a hot/stirrer plate. And then the sample was sintered in N_2 atmosphere at 1000°C for 2 hours.

The green layer of cathode with 1cm x 1cm area was deposited on the SDC electrolyte by slurry coating of cathode materials. For cathode, LSM powders (Praxair) was mixed with binder and then ground in agate mortar.

The single cell thus fabricated was placed in a mixed-gas station as illustrated in Fig.2. Mixtures of methane and air, with different ratios of methane to oxygen, were supplied to the station at a flow rate of 270 $mL\cdot min^{-1}$ at 700℃ so that both electrode compartments were exposed to the same composition of methane and air.

In addition, hydrogen was also tested as a fuel for comparison. Using the same configuration as the mixed-gas furnace, the discharge properties of the single cell with the arrangement; (H_2, N_2, H_2O), Ni5Al(SDC)/SDC/LSM(SDC), (air), was investigated.

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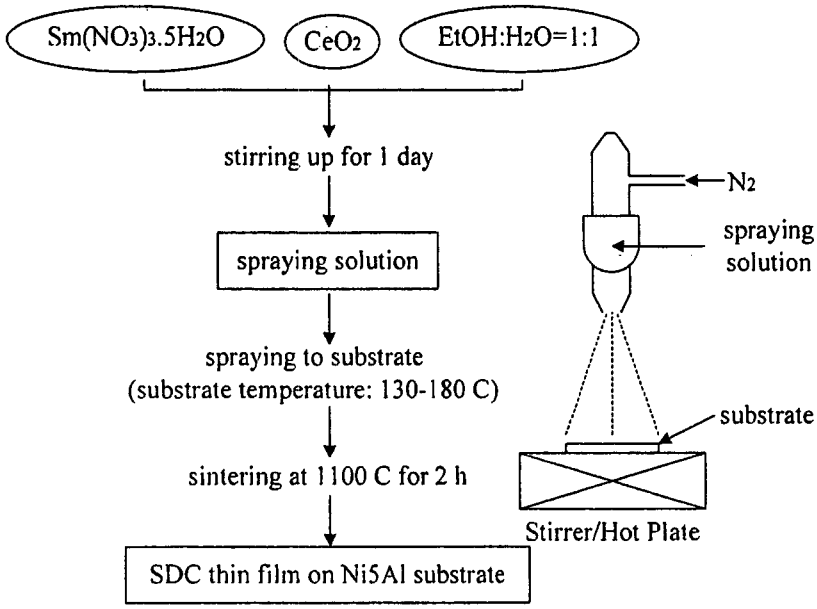

Figure 1. The sol-gel hot-spin coating procedure.

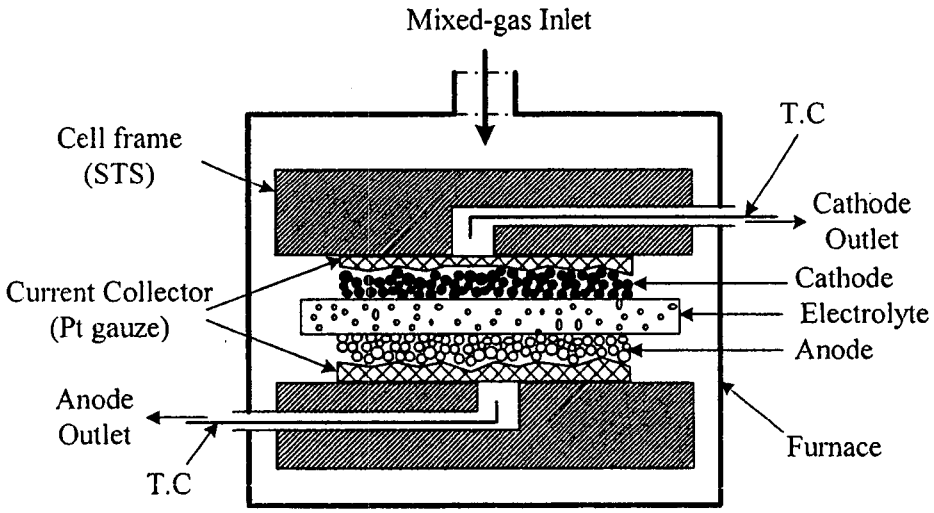

Figure 2. A schematic illustration of the mixed-gas test cell.

Results and Discussion

When nitrogen was introduced into the test cell while heating the unit up to the desired operating temperature, the terminal voltage was almost zero. However, when a mixture of methane and air, with any ratio of methane to oxygen, was supplied at 700℃, the Ni5Al(SDC)/SDC/LSM(SDC) cell gave a stable EMF in the range of 0.81 to 0.84V. In those cases, the mixed-gas SOFC cell was operated using a low current density, as shown in Fig.3. The performance of the Ni5Al(SDC)/SDC/LSM(SDC) cell was evaluated under various current densities with different compositions of methane and air. Fig.3 shows the current-voltage (I-V) characteristics of the test cell when measured at 700℃ and a gas mixture flow rate of 270 $mL \cdot min^{-1}$. The maximum power density of the cell at 700℃ was 305 $mW \cdot cm^{-2}$ under a current load of 700 $mA \cdot cm^{-2}$ when the cell was exposed to the mixed gas with a CH_4:O_2 ratio of 0.65.

Fig. 4 shows a comparison of the discharge properties for two cells operating with a methane and air mixture or hydrogen and air. Each was run at different temperatures. Similar power densities were observed as the mixture of methane and air, supplied in one inlet and at a operating temperature of 700°C, was changed to H_2 and air, supplied

separately by two different inlets and at 600℃. Even though the cell was not sealed gas-tight, the OCV and the performance of cell were between 1.0V and 1.1V and reached 0.34 W/cm^{-2}, respectively, at 600℃ with humidified hydrogen as the fuel and air as the oxidant.

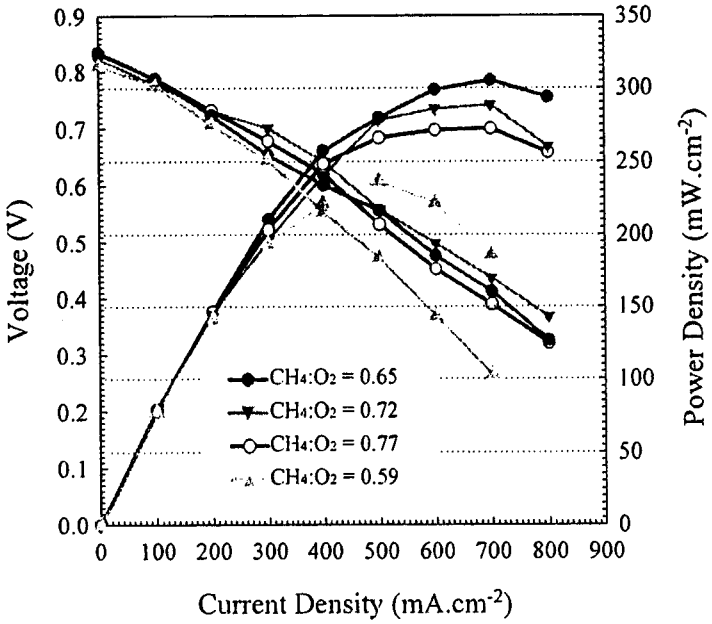

Figure 3. I-V characteristics of a single cell in a mixed gas station at 700℃.

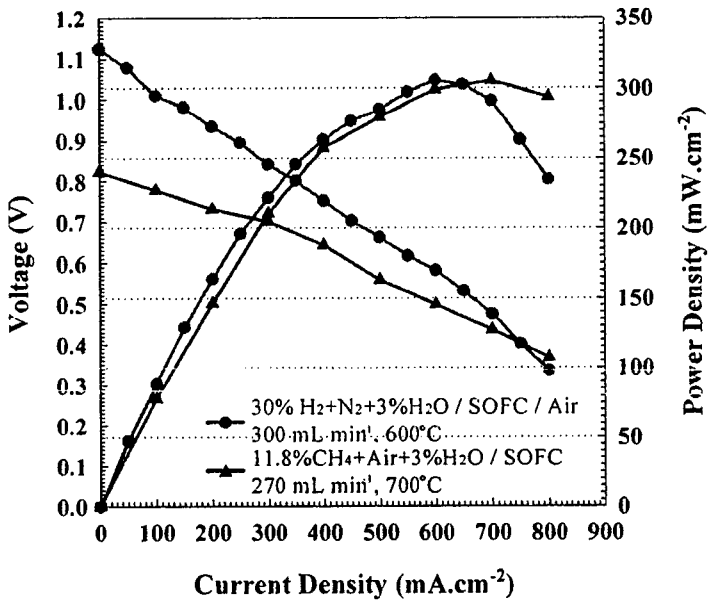

Figure 4. Performance comparison for a single cell with different fuel types.

The partial oxidation of methane can proceed to form hydrogen and carbon monoxide as follows:

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

According to reaction (1), a stoichiometric value of $CH_4:O_2$ ratio for the partial oxidation of methane should be 2. However, the I-V curves in Fig. 5 show less than 18.25 mol % of oxygen in the gas inlet while, the higher the

concentration of oxygen, the higher the peak power density we can obtain. It reached a highest value of 305 $mW.cm^{-2}$ with a methane to oxygen ratio of 0.65. It is likely that higher concentrations of oxygen in the mixture may decrease the polarization of the cathode. The peak power density was enhanced when the concentration of oxygen in the gas mixture increased, but was limited to 18.25 mol %. The reason for the decrease in the cell performance may result from an increase in the anode polarization brought on by the excessive amount of oxygen, which easily consumes the hydrogen and carbon monoxide produced from reaction (1).

From Fig.4 the OCV of the cell performed with a hydrogen and air atmosphere almost reached the theoretical value but the OCV in the mixed-gas atmosphere was much lower than the theoretical value where a complete partial oxidation of methane occurs. This means that the catalytic activity of the anode for the partial oxidation of methane should increase and an excess amount of oxygen should be avoided to obtain a sufficiently high concentration of hydrogen and carbon monoxide at the anode.

Consequently, it is supposed that the cell performance with hydrogen as the fuel and at 600℃ primarily depends on the internal resistance differences brought on by the low operating temperatures but, for the mixed-gas SOFC, the decrease of cell performance results from an increase in the anode polarization, and is due to the low catalytic activity of the anode.

Conclusions

Thin films of Samaria-Doped Ceria (SDC) were formed on porous substrates and within the pores of electrodes using a sol-gel coating method. The SDC-electrolyte film, with a thickness of less than 20 μm, was prepared by sol-gel hot-spin coating and was bound tightly to the anode substrate. However, some of the single cells were short-circuited at room temperature, presumably due to cracks and pinholes within the SDC-electrolyte film. Therefore, techniques to reduce the effects of cracks and/or pinholes and enhance the reproducibility are under investigation in our laboratory. We also plan to develop a system having a high catalytic activity for the partial oxidation of methane and a more optimal stack design for the mixed-gas SOFC in to the hopes of increasing the methane concentration.

The maximum power density of the single cells was 305 $mW.cm^{-2}$ at 700℃ with a mixed-gas fuel of 11% methane in air. The long-term stability of the cell as well as the effects of various operating conditions, such as temperature, flow rate, gas composition, fuel type, etc., on the cell performance will be continuously studied.

References

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