중온형 고체산화물 연료전지의 공기극 물질로서 $Sm_{0.5}Sr_{0.5}CoO_3$의 전기화학적 특성

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Electrochemical Properties of $Sm_{0.5}Sr_{0.5}CoO_3$ as IT-SOFC Cathode Material

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Introduction

Solid oxide fuel cells(SOFCs) are attractive candidates for power generation that convert chemical energy directly into electricity with high efficiency while causing little pollution. Cost reduction in the fabrication of SOFC has been considered an important factor for successful commercialization. One approach of cost reduction is to lower the operating temperature from the range of 900 - 1000℃ to 600 - 800℃and to utilize inexpensive alloys for interconnector, heat exchanger and structural component. In addition, single-step co-firing of cathode material in multi-layered cells could reduce the costs of manufacturing compared to a high temperature firing step [1].

At the intermediate temperature, the kinetics of the cathodic reaction is essential to determine the cell performance. Hence, the properties of electrode materials and performance are essential. The cathode should have high electrical conductivity and morphological stability, and be compatible with the other materials in the cell [2]. Recently, it was reported that $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) has been considered as a potential cathode material of an intermediate temperature solid oxide fuel cell(IT-SOFC).

In this work, $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) as a cathode material for internal reforming of CO_2 by CH_4 in IT-SOFC system was prepared by Pechini method, and the structural and electrochemical properties of $Ni_{0.55}YSZ_{0.45}CeO_2$ | YSZ | $Sm_{0.5}Sr_{0.5}CoO_3$ were investigted by XRD, SEM, GC and Impedance analyzer.

Experimental

1. $Ni_{0.55}$-$YSZ_{0.45}$-CeO_2 | YSZ | $Sm_{0.5}Sr_{0.5}CoO_3$ Electrode Preparation

$Sm(NO_3)_2{\cdot}6H_2O$(99.9%, Sigma-Aldrich Co.), $SrNO_3{\cdot}6H_2O$(99.9965%, Alfa Aesar Co.) and $Co(NO_3)_2{\cdot}6H_2O$(99%, Sigma-Aldrich Co.) were used to prepare cathode materials. These chemicals were dissolved in a distilled water, stirred for 3 h and then dried 100℃ for 2 h. The resultant was calcined at 900 ℃ for 3 h and grinded to nanosize range. Anode catalyst ($NiO_{0.55}YSZ_{0.45}CeO_2$) was prepared by a physical mixing of NiO (99.99%, Sigma-Aldrich Co.) and YSZ(TZ-8Y, TOSOH Co.) with a mole ratio of NiO/YSZ = 55/45. The CeO_2 (99.9%, Sigma-Aldrich Co.) powder was added to the mixture. Structure of prepared catalyst was characterized by XRD (Target = Cu, voltage = 40.0 kV, current = 30.0 mA and scan speed = 5.0 deg/min). The SOFC system consists of feed supply, electric furnace, single cell, GC, Potentiostat-Galvanostat and Impedance/Gain-phase analyzer. Platinum wires were connected to platinum meshes placed on both electrode surfaces to serve as current collectors [3].

2. Internal Reforming of CO_2 by CH_4

Flow rates of reactant gases were controlled by mass flow controllers. A mixture of 50% CO_2 and 50% CH_4 was passed through the anode chamber with a flow rate of 10 cc/min, while air (40 cc/min) was introduced to the cathode side. The outlet gas from the anode side was analyzed by an on-line GC (Hewlett Packard Co., HP6890 series II) equipped with a carbosphere column (0.0032 m O.D. and 3.048 m length) and thermal conductivity detector (TCD).

3. Electrochemical Porperties

The electrocatalytic reactor was operated at 500~800℃. Electrochemical properties were measured by Solartron 1287 Electrochemical Interface (Potentiostat-Galvanostat) with Solatron 1260 Impedance/Gain-phase analyzer (Frequency Response Analyser) [4-5].

<u>Results and discussion</u>

1. Charicterization of cathode material

$Sm_{0.5}Sr_{0.5}CoO_3$ and $Ni_{0.55}$-$YSZ_{0.45}$-CeO_2 powders were synthesized to apply as cathode and anode electrodes, respectively, in IT-SOFC system. It is well known that perovskite-type oxide has desirable structure as cathode catalyst for SOFC [6]. From the XRD measurement, it was observed that the amorphous phase of catalyst prepared was changed to the perovskite structure after calcining at 800℃ as shown in Fig. 1. Fig. 2 represents the X-ray diffraction (XRD) pattern of $NiO_{0.55}YSZ_{0.45}CeO_2$ catalyst. It was found that the peaks corresponding to the monoclinic phase were smaller than those of pure YSZ(not shown).

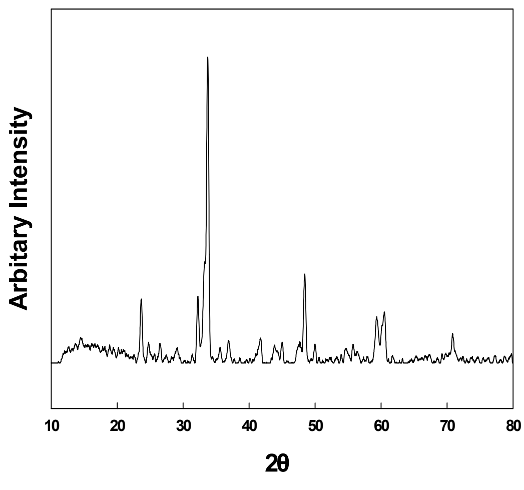

Fig. 1. XRD pattern of $Sm_{0.5}Sr_{0.5}CoO_3$.

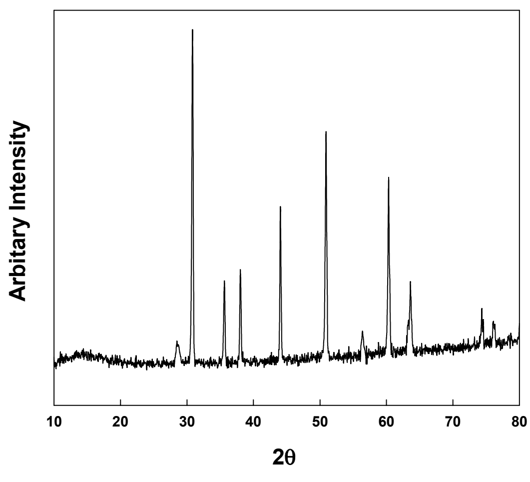

Fig. 2. XRD patterns of $Ni_{0.55}$-$YSZ_{0.45}$-CeO_2.

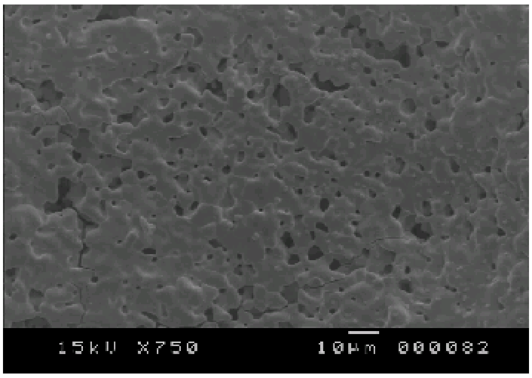

Fig. 3. SEM image of $Sm_{0.5}Sr_{0.5}CoO_3$ cathode electrode.

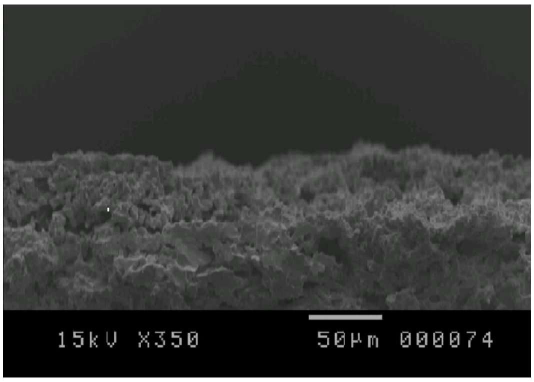

Fig. 4. SEM image of $Sm_{0.5}Sr_{0.5}CoO_3$ cathode on YSZ electrolyte.

It was reported that the dense $Sm_{0.5}Sr_{0.5}CoO_3$ cathodic performance was decided by the adsorption-desorption rates of oxygen at the surface of the electrode [7]. Thus, the structural properties such as particle size and surface area of the $Sm_{0.5}Sr_{0.5}CoO_3$ play a important role in determining the SOFC performance. Figure 3 and 4 show SEM images of the surface and intersection of $Sm_{0.5}Sr_{0.5}CoO_3$ cathode on YSZ electrolyte, respectively. It was observed that porous cathode region was well adhered to a dense electrolyte region. The thickness of cathode is about 40 ~ 50 ㎛ and both the particle size of cathode and the pore size are also within the magnitude of micron. The BET surface area and total pore volume of electrode are 0.09 ㎡/g and 0.0053 cc/g, respectively.

2. Methane reforming by carbon dioxide

Carbon dioxide reforming by methane was performed to produce synthesis gas and electricity in SOFC system [8]. The effect of reaction temperature on the conversion of CO_2 and CH_4 during the internal reforming of CO_2 by CH_4 is illustrated in Fig. 5. It was observed that the conversions of CO_2 and CH_4 were very low at temperature less than 600℃. However, the conversions of CO_2 and CH_4 increased at temperature more than 600℃. Especially, significant increasing of conversions was observed at higher temperature than 700℃. It was considered that $Sm_{0.5}Sr_{0.5}CoO_3$ is a promising cathode material in the intermediate temperature solid oxide fuel cell system.

3. Electrochemical properties of $Ni_{0.55}YSZ_{0.45}CeO_2$ | YSZ | $Sm_{0.5}Sr_{0.5}CoO_3$

OCV(Open Circuit Voltage) in SOFC system was measured by a galvanostatic method. Fig. 6 shows that the open-circuit voltage over $Ni_{0.55}YSZ_{0.45}CeO_2$ | YSZ | $Sm_{0.5}Sr_{0.5}CoO_3$ was 0.8 ~ 0.9 V at 600 ~ 800℃ during the internal reforming of CO_2 by CH_4 in SOFC system. It was observed that the electrical properties measured almost stable with 600 ~ 800℃ as shown in Fig. 6. Thus, the OCV values at 600 ~ 800℃ were acceptable for application in SOFC system. But OCV decreased rapidly from 0.8 V at 600℃ to about 0 V at 500℃ due to decreasing oxygen ion permeability through the YSZ electrolyte at low temperature in SOFC system [9].

It was found that the electrochemical properties of $Sm_{0.5}Sr_{0.5}CoO_3$ were suitable to be used as cathode material in the IT-SOFC system.

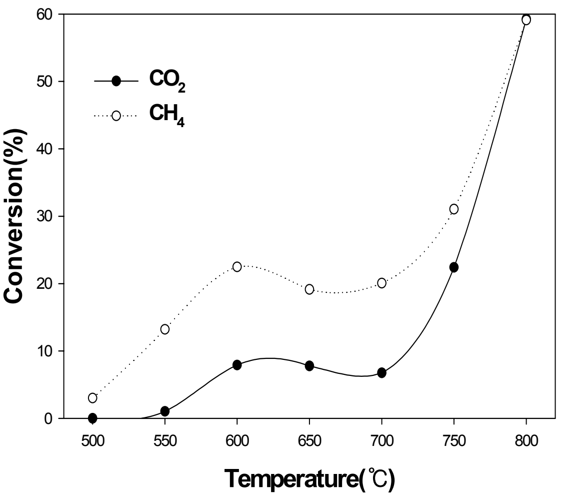

Fig. 5. The effect of temperature on the conversions of CO_2 and CH_4 during the internal reforimng of CO_2 by CH_4 in SOFC system.

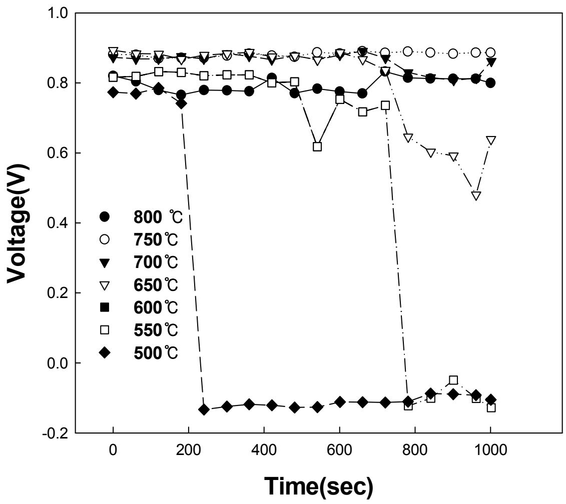

Fig. 6. The open-circuit voltage (OCV) over $Ni_{0.55}YSZ_{0.45}CeO_2$ | YSZ | $Sm_{0.5}Sr_{0.5}CoO_3$ during the internal reforimng of CO_2 by CH_4 in SOFC system.

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