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# Ni–Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> anode-supported YSZ electrolyte film and its application in solid oxide fuel cells

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#### Abstract

Ni–Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> anode-supported YSZ electrolyte films were fabricated and a fuel cell based on this film was tested in this paper. The anode/YSZ film interface was investigated by means of SEM–EDX. The SEM results showed that the YSZ film was almost fully dense and crack-free. The analyses of EDX revealed that Ce and Sm cations preferential migrated from the NiO–SDC anode into the YSZ film for less than 3  $\mu$ m while no significant diffusion occurred for Y and Zr. A cell of Ni–SDC/YSZ(14  $\mu$ m)/LSM–YSZ was tested from 700 to 850 °C using humidified hydrogen as fuel and ambient air as oxidant. The cell provided maximum power densities of 304, 625, 980 and 1270 mW/cm<sup>2</sup> at 700, 750, 800 and 850 °C, respectively. Polarization analysis based on the impedance spectra showed that the anode polarization only accounted for 8% of the total electrode polarization while this ratio for cathode was 92%. A negligible anode polarization suggested that the diffusion of Ce and Sm and its negative effect on the performance of the cell were suppressed to an acceptable level in this study. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Fuel cells; Thin films; Electrochemical impedance spectroscopy; Scanning electron microscopy

# 1. Introduction

Solid oxide fuel cells (SOFCs), which can convert chemical energy directly to electrical power with high efficiency and low pollution, attract more and more attentions in recent decades [1–4]. To date, YSZ is the most commonly used electrolyte materials in SOFCs because it possesses unique combination of properties such as excellent mechanical strength, high chemical and thermal stability in both oxidizing and reducing atmospheres and pure oxygen ionic conductivity over a wide range of conditions. However, oxygen ionic conductivity of YSZ is insufficient for SOFCs which operating at intermediate temperature (600–800 °C). The conventional SOFCs based on YSZ electrolyte usually operate at high temperature such as 1000 °C or more to obtain good performance. However, operating SOFCs at such a high temperature may cause a series of problems such as electrode sintering, interfacial diffusion, and thermal mismatch. Therefore, it is difficult to expect a long-term stability. For these reasons, great efforts have been made towards the development of intermediate temperature SOFCs [5,6]. To reduce the operation temperature, the following two approaches can be considered: one way is to replace the traditional YSZ electrolyte with doped-CeO<sub>2</sub> or doped-LaGaO<sub>3</sub> which has higher ionic conductivity than YSZ; the other way is to reduce the thickness of YSZ electrolyte. This paper correlates with the latter case because of the excellent combination properties of YSZ.

Ni-YSZ cermet is a conventional anode materials for YSZ electrolyte-based SOFCs. Compared with the Ni-YSZ cermet anode, Ni-doped-CeO<sub>2</sub> anode has its advantages. The doped-CeO<sub>2</sub> is an ion-and-electron mixed conductor in hydrogen which can increase the length of three-phase boundary (TPB) within anode. Doped-CeO<sub>2</sub>-based anode is more suitable for oxidation of hydrocarbon because of its high activity for hydrocarbon oxidation and its high ionic conductivity [7]. Among the doped-CeO<sub>2</sub> materials, Samaria-doped ceria (SDC) has the highest

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ionic conductivity [8]. NiO–SDC anode was selected in this study for fabrication of anode-supported YSZ film SOFCs.

It is reported that doped-CeO<sub>2</sub> reacts with stabilized-ZrO<sub>2</sub> at elevated temperature forming CeO<sub>2</sub>–ZrO<sub>2</sub>-based solid solutions which have a low electrical conductivity [9]. Shiono et al. [10] introduced a Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub> (GDC) interlayer between Scandia-stabilized zirconia (SSZ) electrolyte and La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> (LSC) cathode to avoid the reaction between them. They found that the reaction between SSZ electrolyte and GDC interlayer was not observed at 1320 °C.

Ni-YSZ anodes were usually used to support the YSZ electrolyte thin films. There are few publications on application of Ni–SDC anode-supported YSZ films in SOFCs. Xu et al. [11] fabricated NiO–SDC anode-supported YSZ electrolyte films by spin-coating and co-firing method. The cell based on this film showed a maximum power density of 535 mW/cm<sup>2</sup> at 750 °C. However, the diffusion at the NiO–SDC anode and YSZ film interface was not investigated in their reports. In this paper, YSZ film was prepared on NiO–SDC green anode substrate by slurry-casting method. The interface between NiO–SDC anode and YSZ electrolyte was examined by SEM–EDX. The performances of the Ni–SDC anode-supported YSZ films SOFCs were tested and discussed.

#### 2. Experimental

#### 2.1. Preparation of starting powders

NiO powder was prepared by ammonia precipitation method. Ammonia (analytical reagent, A.R.) was added to Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (A.R.) solution drop by drop to obtain nickel hydroxide deposition. Then, the as-prepared deposition was aged at 70 °C for 40 min. After washing by alcohol and drying at 105 °C, the resultant deposition was finally fired at 400 °C for 2 h to get nickel oxide powder.

SDC (Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub>) powder was prepared by a citric-nitrate process. Stoichiometric amounts of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (A.R.) and Sm<sub>2</sub>O<sub>3</sub> (A.R.) were dissolved in diluted HNO<sub>3</sub> (A.R.) and citric acid (A.R.) was added as the complexant. The molar ratio of total cation to citric acid was 1/1.15. The solution was evaporated at 75 °C to form a transparent gel. After drying at 100 °C for 12 h, the transparent gel changed to a brown dry gel. The dry gel was subsequently fired at 750 °C for 2 h to get SDC powder.

 $La_{0.7}Sr_{0.3}MnO_3$  (LSM) was used as the cathode material in this study. The method for preparation of LSM powder was similar to that for SDC powder as described above. The starting materials for LSM powder preparation were all analytical reagent in this study. The LSM powder was obtained by firing the as-prepared dry gel at 1000 °C for 4 h.

X-ray diffraction (Bede  $D^1$  X-ray diffraction meter) was used to confirm the crystalline structure of the prepared powders. All the powders of NiO, SDC and LSM exhibited the expected phase structure without impure phases.

#### 2.2. Preparation of NiO–SDC anode substrates

The as-prepared NiO and SDC powders were mixed in a weight ratio of 1:1. In addition, 15 wt.% starch was added as pore former to get sufficient porosity. After mixing and grinding, the anode powder was pressed into pellets of 13 mm in diameter and 0.5 mm in thickness under a pressure of 260 MPa. The green pellets were pre-sintered at 1000  $^{\circ}$ C for 3 h to get the NiO–SDC anode substrates.

# 2.3. Preparation of YSZ electrolyte film and LSM–YSZ composite cathode

YSZ powder with an average particle size of  $0.2\,\mu m$  bought from Tosoh corporation (TZ-8Y, Tosoh Corporation, Tokyo, Japan) was chosen to make



Fig. 1. Schematic diagram of YSZ film deposition equipment.

thin electrolyte films in this study. Terpineol-ethylcellulose vehicle was used to prepare YSZ slurry. YSZ powder was mixed with terpineol-ethylcellulose vehicle in an agate mortar and ground for about 2 h to get a homogeneous and stable YSZ paste. The slurry contained 80 wt.% of YSZ and 20 wt.% of terpineol-ethylcellulose vehicle. Fig. 1 showed a schematic diagram of YSZ film fabrication equipment. The equipment was composed of a flat holder and a revolving rod. The flat holder was used to fix and support the anode substrate for slurry-casting. A certain amount of YSZ slurry was dropped on one side of anode and compacted by the revolving rod. The casting force helped to obtain green YSZ films with high density, which led to dense sintered films. After being dried in air, the anode/YSZ bilayer was fired at 1400 °C for 4 h to increase the density of YSZ film.

The LSM–YSZ composition cathode was prepared using screen-printing technique. LSM and YSZ powders were mixed in a weight ratio of 1.5:1, and then the mixed powders were mixed with terpineol-ethylcellulose vehicle and ground for about 1 h to get a stable cathode printing ink. After that, the LSM–YSZ printing ink was printed onto YSZ electrolyte surface by screen-printing technique and then sintered at 1200 °C for 3 h. The cathode size is 0.5 cm<sup>2</sup>.

#### 2.4. Characteristics of YSZ film and anode/YSZ film interface

Morphology and microstructure of the YSZ film were evaluated by scanning electron microscope (SEM). The density of the film was estimated by the dimensions and the weight of the film. The anode/YSZ film interface was examined by SEM–EDX. The EDX analysis at interface was carried out in a line-scan mode with a probe diameter less than 1  $\mu$ m.

#### 2.5. Single cell testing

Silver paste was current collectors for both anode and cathode. A four-probe set-up was adopted to eliminate the resistive loss in the silver wires. A reference electrode was attached to electrolyte film in the vicinity of the cathode to separate the cathode polarization from that of anode. Hydrogen saturated with water at room temperature was used as fuel while oxygen in the ambient air was used as oxidant. The single cell was tested in the temperature range of 700–850 °C. The cell performance and impedance spectroscopy were measured by SI-1260 impedance/gain-phase analyzer in combination with SI-1287 electrochemical interface (Solartron Instruments, Hampshire, U.K.).

#### 3. Results and discussion

#### 3.1. Microstructures of supported YSZ film and single cell

Fig. 2 showed SEM micrographs of supported YSZ film and a single cell with a 14- $\mu$ m-thick YSZ film. Fig. 2(a) was a surface micrograph of YSZ film before sintering, which showed an underdeveloped microstructure with small grains. There were



Fig. 2. SEM micrographs of (a) surface of YSZ film before sintering, (b) surface of film after sintering, (c) cross-section of anode/film bilayer before sintering, (d) cross-section of anode/film bilayer after sintering, and (e) cross-section of a single cell with a 14- $\mu$ m-thick YSZ film.

some pinholes in the green YSZ film, which came from the volatilization of terpineol-ethylcellulose vehicle during the film drying process. Fig. 2(b) showed the YSZ film surface micrograph after sintering at 1400 °C. All pinholes disappeared and the YSZ thin film was composed of grains of irregular shape. The

grain size varied from 1 to 5  $\mu$ m without any crack and pinhole. Fig. 2(c) and (d) presented the cross-sections of anode/YSZ film bilayer before and after sintering at high temperature, respectively. As shown in Fig. 2(c), there was a clear boundary between the anode and supported YSZ film. After sintered at high tem-

perature, as shown in Fig. 2(d), the boundary disappeared and an interlocking boundary came into being. The green YSZ film was very dense with a relative density of about 45%. After sintering at high temperature, the relative density increased to about 97%. In this study, the stable YSZ slurry, which contained up to 80 wt.% of YSZ particles, was used to prepare YSZ film. This paste led to a green YSZ film with a small amount of organic additive compared with the conventional slurry coating [12]. Furthermore, the casting force also helped to compress the green YSZ film, leading a dense sintered film after sintering. It was believed that the high-quality sintered YSZ film was ascribed to the dense green YSZ film as shown in Fig. 2(c). Fig. 2(e) showed a single cell of Ni-SDC/YSZ(14 µm)/LSM-YSZ. The electrochemical testing in this paper was based on this cell. The YSZ film was fully dense while both the Ni-SDC anode and LSM-YSZ composite cathode were porous.

#### 3.2. SEM–EDX analysis at anode/YSZ film interface

Fig. 3(a) showed the cross-section of the NiO-SDC anode/YSZ film interface after sintering. The YSZ film was homogeneous and almost pinhole-free in the cross-section. The results of EDX analyses for Y, Zr, Sm and Ce at anode/YSZ interface were presented in Fig. 3(b). It was observed that there was no significant diffusion occurred for Y and Zr. The Ce and Sm cations migrated from NiO-SDC anode into the supported YSZ film for less than 3 µm. These diffusions of Ce and Sm cations resulted in CeO2-ZrO2-based solid solutions in the YSZ film side. Mitsuyasu et al. [13] have investigated the solid state reaction at the interface of Y2O3-doped-CeO2 (YDC) and YSZ by XRD. Their XRD results showed that the solid state reaction between YDC and YSZ accompanied a significant shift of the zirconia lines to lower angle while no obvious lines shift observed for ceria. They believed that the reaction between ceria and zirconia proceeded by preferential migration of the ceria component into the zirconia side. Tsoga et al. [9] also found a similar phenomenon between GDC and YSZ interface. Our experiment results suggested the reaction at the interface between the NiO-SDC anode and the YSZ film mainly resulted from the migration of the Ce and Sm cations into the YSZ side.

### 3.3. Results of electrochemical testing

The temperature dependence of cell performance in the temperature range of 700–850 °C were shown in Fig. 4. The observed open circuit voltages (OCVs) of higher than 1.0 V implied that the gas leakage across YSZ film was insignificant. The maximum power densities were 304, 625, 980 and 1270 mW/cm<sup>2</sup> at 700, 750, 800 and 850 °C, respectively. The present fuel cell performance is better than that of previous reported Ni–SDC anode-supported YSZ electrolyte films SOFCs [11].

The impedances of the whole cell and the half cell (cathode side only) tested at 800 °C were shown in Fig. 5. For the whole cell impedance, the intercepts on the real axis at high frequency corresponded to the cell ohmic resistance while the arcs at intermediate and low frequency were the whole electrodes





Fig. 3. (a) SEM micrograph of a cross-section of NiO–SDC anode/YSZ film interface after sintering; the white line indicates the position of the EDX analyses; (b) EDX analyses of Y, Zr, Sm and Ce in the line-scan mode at the NiO–SDC anode/YSZ film interface.



Fig. 4. Cell voltage (solid symbols) and power density (open symbols) as functions of current density for a thin film cell with humidified hydrogen as fuel and ambient air as oxidant from 700 to  $850 \,^{\circ}$ C.



Fig. 5. Impedances of the whole cell and half cell (cathode side only) measured at 800 °C under open circuit condition.

Table 1

Fitting results of the whole cell and cathode impedances tested at 800  $^\circ$ C under open circuit condition

	The whole cell impedance $(\Omega \text{ cm}^2)$	The cathode impedance $(\Omega \text{ cm}^2)$
$\overline{R_1}$	0.041	0.023
$R_2$	0.027	0.024
$R_3$	0.153	0.129
$R_4$	0.108	0.114
$R_2 + R_3 + R_4$	0.288	0.267

polarization resistance including both anode and cathode polarization. For the half cell impedance, the intercepts on the real axis at high frequency also corresponded to the ohmic resistance while the arcs at intermediate and low frequency were only the cathode polarization resistance. The inset in Fig. 5 showed an equivalent circuit which was used to resolve the impedance data. The fitting results were listed in Table 1. The whole electrode (including both cathode and anode) polarization resistance is  $0.288 \,\Omega \,\mathrm{cm}^2$  while the polarization resistance for cathode process is  $0.267 \,\Omega \,\mathrm{cm}^2$ . It could be readily seen that the cathode polarization accounted for up to 92% of the total electrode polarization while the anode polarization was almost negligible. As shown in Fig. 3, the diffusions of Ce and Sm cations from NiO-SDC anode into YSZ film resulted in a CeO<sub>2</sub>-ZrO<sub>2</sub>based solid solution on the YSZ side, which had low electrical conductivity. This solid solution restricted the anode reaction and thus resulted in a high anode polarization. From the analyses of impedance, the anode polarization only accounted for about 8% of the total electrode polarization at 800 °C. This result suggested that the diffusion of Ce and Sm and its effect on performance of the cell were kept at an acceptable level in this study. Tsoga et al. [9] reported that although pure GDC reacted readily with YSZ at elevated temperature, suppression of the reaction between YSZ and GDC could be achieved in the presence of Ni because of the good chemical compatibility of Ni for both YSZ and ceria. They recommended that a ceria–40 vol.% Ni cermet should be considered when ceria was to be employed at the YSZ electrolyte and Ni–YSZ anode interface to reduce anode polarization losses. The insignificant reaction between NiO–SDC and YSZ film in this study seemed to agree with this case.

## 4. Conclusions

Ni-SDC anode-supported YSZ films were prepared by slurry casting to study the solid reaction at the interface of the anode and the supported YSZ film and to evaluate the performances of the fuel cells. A compacted YSZ green film with relative density of 45% was obtained after one-time coating. The relative density of the YSZ film increased to 97% after sintered at 1400 °C for 4 h. The SEM-EDX analyses showed that there was not obvious diffusion occurred for Y and Zr. On the other hand, Ce and Sm cations migrated from NiO-SDC anode into the supported YSZ film for less than 3 µm. A single cell, Ni-SDC/YSZ/LSM-YSZ, was tested using humidified hydrogen as fuel and ambient air as oxidant from 700 to 850 °C. The open circuit voltage of above 1.0 V was observed. The cell provided the maximum power densities of 304, 625, 980 and 1270 mW/cm<sup>2</sup> at 700, 750, 800 and 850 °C, respectively. The cell performance was basically limited by cathode polarization, instead of anode polarization and electrolyte ohmic resistance. The effect of the interfacial reaction between NiO-SDC anode and YSZ film on the performance of the cell was not significant in this study.

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