

Short communication

Formation of $\text{La}_2\text{Zr}_2\text{O}_7$ or SrZrO_3 on cathode-supported solid oxide fuel cells

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Abstract

Formation of $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 on cathode-supported solid oxide fuel cells has been characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Thin yttria-stabilized zirconia (YSZ) film with a thickness of about 15 μm was fabricated on the porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ($\text{LS}_{0.2}\text{M}$) and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ ($\text{LS}_{0.35}\text{M}$) cathodes by electrophoretic deposition (EPD) followed with sintering at 1400 °C for various times. The $\text{La}_2\text{Zr}_2\text{O}_7$ (LZ) and SrZrO_3 (SZ) formed at the interface between YSZ thin film and $\text{LS}_{0.2}\text{M}$ and $\text{LS}_{0.35}\text{M}$ substrate, respectively, after sintering at 1400 °C for 52 h, were identified by XRD. LZ was also determined by TEM and SAED for the samples sintered at 1400 °C for 2 h. The grain size of LZ suddenly increased from 100 nm to a micrometer scale when the sintered time increased from 2 to 12 h.

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Keywords: SOFCs; $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ |YSZ interface; High temperature instability; $\text{La}_2\text{Zr}_2\text{O}_7$; SrZrO_3

1. Introduction

Currently, the goal of solid oxide fuel cells (SOFCs) development is to decrease the operating temperature, so that the materials selection for cell construction will be easier. For this purpose, yttria-stabilized zirconia (YSZ) is a general material used as a solid electrolyte in SOFCs [1]. Electrophoretic deposition (EPD) has received considerable attention in recent years for YSZ thin film preparation, which is one of the colloidal processes for ceramic production [2] and offers the advantages of almost no restriction in substrate shape, a single deposition apparatus, and mass production.

Strontium-substituted lanthanum manganite based perovskite (LS_xM) is the most promising candidate material as a cathode in SOFCs [1]. The chemical and structural nature of the solid-state interface between the cathode and the electrolyte plays an important role in the cell performance with respect to both long-term stability and efficiency [3]. The formation of new

phases such as $\text{La}_2\text{Zr}_2\text{O}_7$ (LZ) and SrZrO_3 (SZ) at the interface, with less favorable properties as well as interdiffusion of cations between the cell components will have a negative impact on the cell performance.

In the present study, the preparation of the YSZ film on the porous strontium-doped LaMnO_3 substrate by an EPD process was performed. The formation of the secondary phase at the interface between YSZ thin film and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LS_xM) substrate were discussed in detail.

2. Experimental procedure

Porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ($\text{LS}_{0.2}\text{M}$) and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ ($\text{LS}_{0.35}\text{M}$) were used as the electrodes for the deposition of the YSZ thin films by an EPD process. The oxide powders La_2O_3 (purity 99.99%, supplied by Alfa, Ward Hill, USA), $\text{Sr}(\text{NO}_3)_2$ (purity 99%, supplied by Riedel-de Haen, Switzerland, Germany), and MnO_2 (purity 99.99%, supplied by Alfa, Ward Hill, USA) were weighed to the stoichiometric composition of $\text{LS}_{0.2}\text{M}$ and $\text{LS}_{0.35}\text{M}$, respectively. These powders were ball milled, calcined, sieved, pressed, and sintered at 1200 °C for

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8 h. The preparation of the LS_xM substrate and the schematic diagram of EPD for this study have been described in detail elsewhere [4].

The YSZ suspensions was prepared by mixing 2 g l^{-1} YSZ powders with the particle size of 232 nm and the specific surface area of $12 \text{ m}^2 \text{ g}^{-1}$ (Product TZ-8Y, Tosoh, Tokyo, Japan), iodine (I_2), and a solvent that contains a mixture of acetone and ethanol in volume ratio of 3:1. The volume of the plating bath was 300 ml throughout this study. The distance between two electrodes, applied voltage, and deposition time were 10 mm, 40 V, and 10 min, respectively. The green YSZ films were dried at room temperature and then sintered at 1400°C for 2–52 h.

The phases at the interface between the YSZ thin film and the LS_xM substrate were identified via X-ray diffraction with Cu $K\alpha$ radiation and a Ni filter, operated at 30 kV, 20 mA, and $0.25^\circ \text{ min}^{-1}$ (Model Rad IIA, Rigaku Co., Tokyo, Japan). The microstructure of the interface between the YSZ thin film and the LS_xM substrate were examined by a scanning electron microscope (SEM) (Model S-4200, Hitachi Ltd., Tokyo, Japan) and a transmission electron microscope (TEM) (Model HF 2000 Field Emission Transmission Electron Microscopy, Hitachi Ltd.). The composition of the reaction product between the YSZ thin film and the LS_xM substrate was characterized by an energy dispersive spectrometer (EDS) (Noran model Voyager 1000, Noran Instruments, CA, USA). The crystal structure at the interface between the YSZ thin film and the LS_xM substrate was investigated by selected area diffraction (SAED).

3. Results and discussion

Figs. 1 and 2 illustrate the XRD patterns of the interface between the YSZ thin film and the LS_xM substrate when sintered

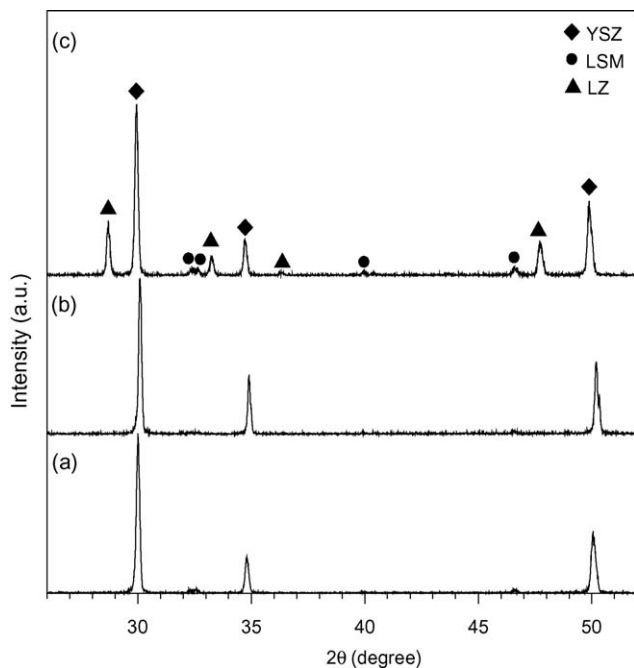


Fig. 1. XRD patterns at the interface between YSZ and $La_{0.8}Sr_{0.2}MnO_3$ ($LS_{0.2}M$), when sintered at 1400°C for various times: (a) 2 h, (b) 12 h, and (c) 52 h.

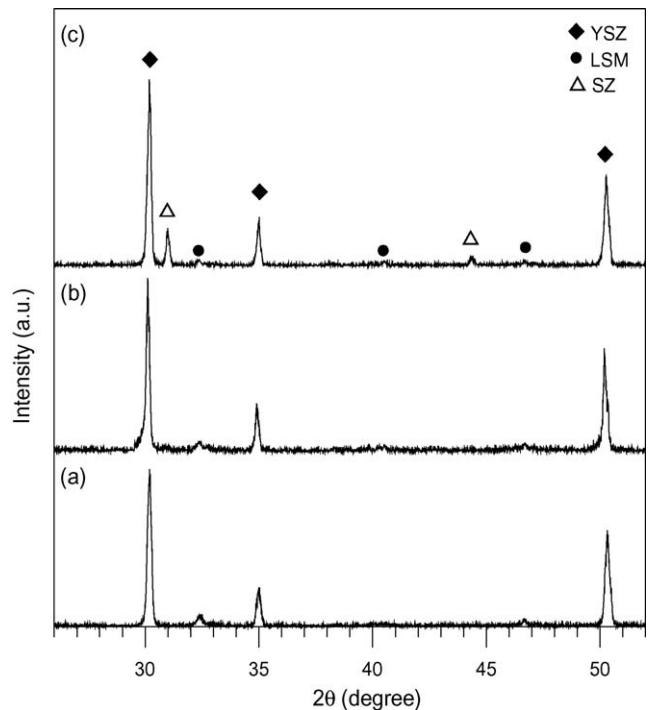


Fig. 2. XRD patterns at the interface between YSZ and $La_{0.65}Sr_{0.35}MnO_3$ ($LS_{0.35}M$), when sintered at 1400°C for various times: (a) 2 h, (b) 12 h, and (c) 52 h.

at 1400°C for various times. Figs. 1(a) and 2(a) show that the patterns of the samples sintered at 1400°C for 2 h, indicating that except ZrO_2 and LSM, no other phases are detected. When sintered at 1400°C for 12 h, the XRD patterns indicate that the present phases are same as in Figs. 1(a) and 2(a). Figs. 1(c) and 2(c) show the samples sintered at 1400°C for 52 h, which reveal that except LSM and ZrO_2 , $La_2Zr_2O_7$ (Fig. 1(c)), and $SrZrO_3$ (Fig. 2(c)) coexist.

Yang et al. [5] have also demonstrated that when the LSM/YSZ green tapes are cofired from 1200 to 1400°C for 1–48 h and then annealed at 1000°C for up to 1000 h, the diffusion of manganese cations first causes the amorphization of YSZ and then the formation of small LZ and SZ crystals if heated at 1400°C for a longer time. In the present study, the XRD patterns show that only LZ and SZ crystals are found at the interface between the YSZ/ $LS_{0.2}M$ and the YSZ/ $LS_{0.35}M$, respectively.

Fig. 3 shows the SEM micrographs and concentration profiles of La, Mn, Sr, Y, and Zr for the YSZ/ LS_xM samples sintered at 1400°C for various times. No reaction products are found for the YSZ/ $LS_{0.2}M$ and YSZ/ $LS_{0.35}M$ samples when sintered at 1400°C for 12 h, as shown in Fig. 3(a and b). According to Figs. 1(b) and 2(b), no LZ and SZ phases are formed in the reaction interface. Fig. 3(c and d) shows the reaction zone with a thickness of about 3.50 and $3.10 \mu\text{m}$ at the interface of the YSZ/ $LS_{0.2}M$ and the YSZ/ $LS_{0.35}M$, respectively, for the samples sintered at 1400°C for 52 h. It illustrates that the reaction thickness increases with increasing soaking time. The reaction zone at the YSZ/ LS_xM interface where Mn has diffused is easily distinguished as a black area with big pores [6]. In addition, it

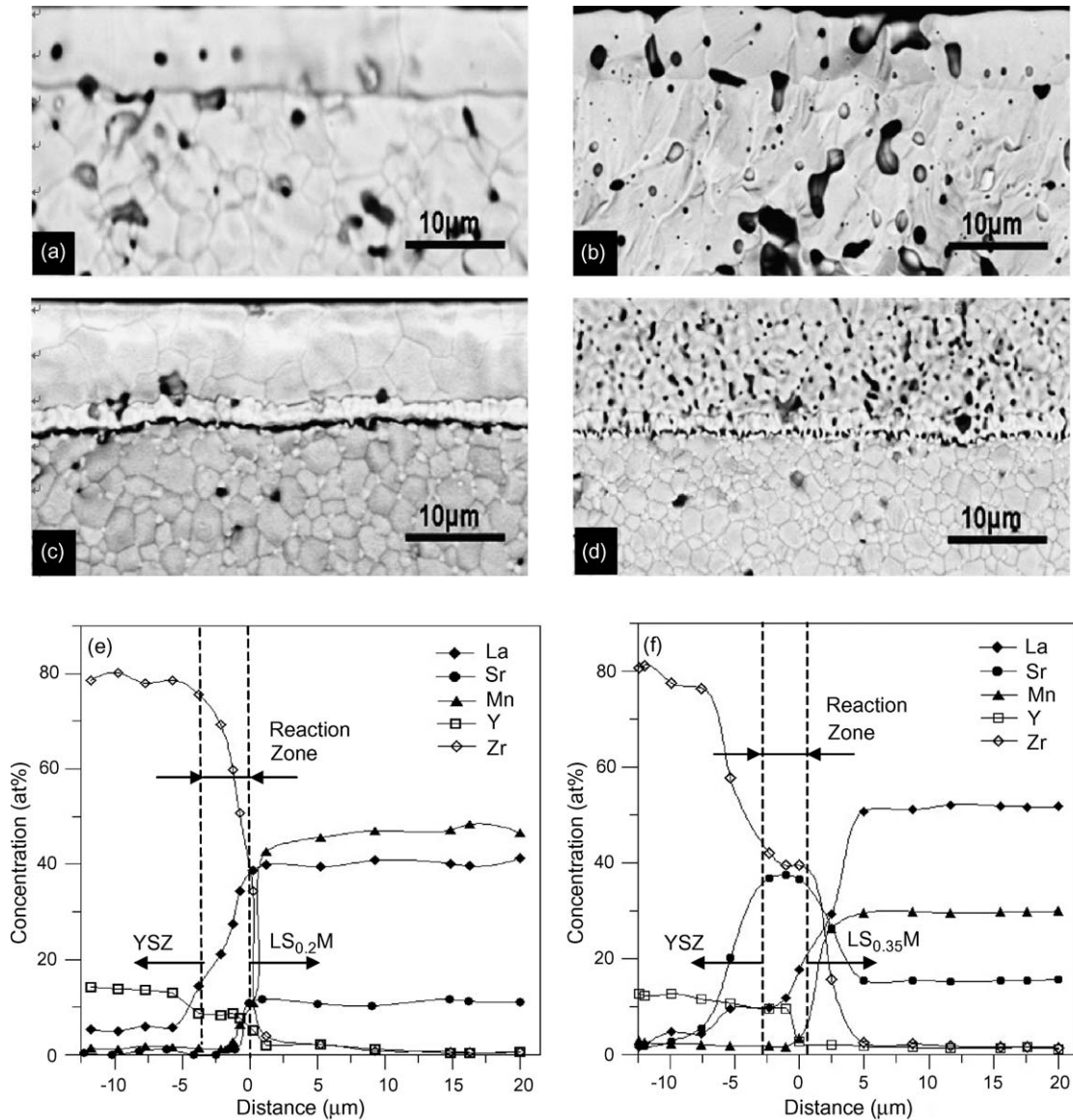


Fig. 3. SEM microstructure of the interface between (a) YSZ thin film and $LS_{0.2}M$ substrate and (b) YSZ thin film and $LS_{0.35}M$ substrate, when sintered at $1400^\circ C$ for 12 h, (c) YSZ thin film and $LS_{0.2}M$ substrate and (d) YSZ thin film and $LS_{0.35}M$ substrate, when sintered at $1400^\circ C$ for 52 h, (e) concentration profile of Mn, La, Sr, Y, and Zr in (c), and (f) concentration profile of Mn, La, Sr, Y, and Zr in (d).

is worth noting that the LZ and SZ layers grow only toward the YSZ thin film. Fig. 3(e and f) shows the concentrations profiles of La, Mn, Sr, Y, and Zr in Fig. 3(c and d), respectively. Fig. 3(c) reveals that Mn, La, and Sr have diffused into the YSZ thin film along the grain boundaries, but less Y and Zr diffuse into the $LS_{0.2}M$ substrate. In the YSZ thin film, the concentration of Y and Zr gradually decreases near the reaction interface.

Fig. 4 shows the TEM micrograph and SAED pattern of the interface between the YSZ thin film and the $LS_{0.2}M$ substrate, in which the sample was sintered at $1400^\circ C$ for 2 h. Fig. 4(a) shows the micrograph of the interface, and the secondary phase with a grain size of about 100 nm. Fig. 4(b) shows the SAED pattern of the secondary phase in the interface, corresponding to $La_2Zr_2O_7$. However, the SAED pattern also provides the criteria for the presence of LZ in the YSZ/ LS_xM sample sintered at $1400^\circ C$ for 2 h.

The TEM micrograph and SAED pattern of the interface between the YSZ thin film and the $LS_{0.2}M$ substrate, when sintered at $1400^\circ C$ for 12 h, are shown in Fig. 5. Fig. 5(a) shows the TEM micrograph of the YSZ, interface, and LSM. Fig. 5(b) shows the SAED patterns of the LZ phase. Moreover, Fig. 5(a) also indicates that the LZ crystal increases from 100 nm to a micrometer scale when the sintering time increases from 2 to 12 h. The EDS microanalysis of the different positions at the interface between the YSZ thin film and the $LS_{0.2}M$ substrate (Fig. 5), when sintered at $1400^\circ C$ for 12 h, are listed in Table 1. It reveals that at the positions 3, 4, and 5, the cations ratio implies the LZ phase.

Labrincha et al. [7] have demonstrated that LZ and SZ phases have been detected by XRD and EDS at the YSZ/electrode interface. Both zirconate materials have similar electrical conduction about two to three orders of magnitude lower than YSZ. On the

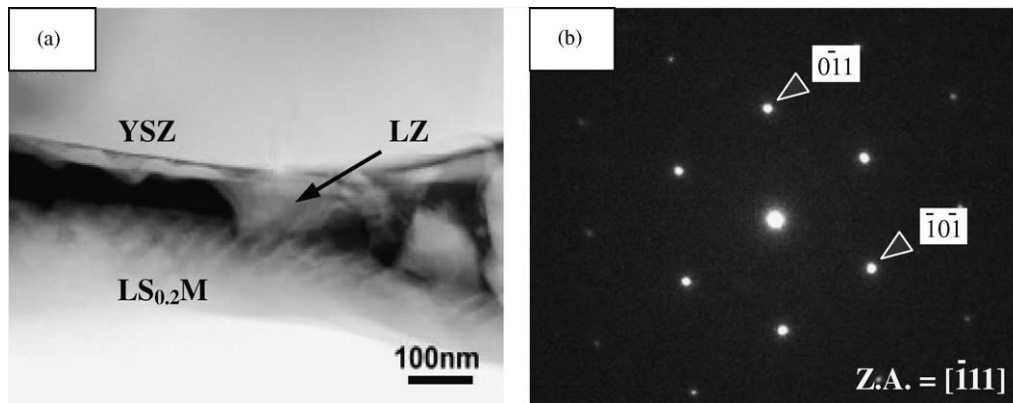


Fig. 4. TEM image and ED pattern of the interface between YSZ film and $LS_{0.2}M$ substrate when sintered at $1400\text{ }^{\circ}\text{C}$ for 2 h: (a) TEM images of YSZ, interface and (b) ED pattern corresponding to the LZ phase.

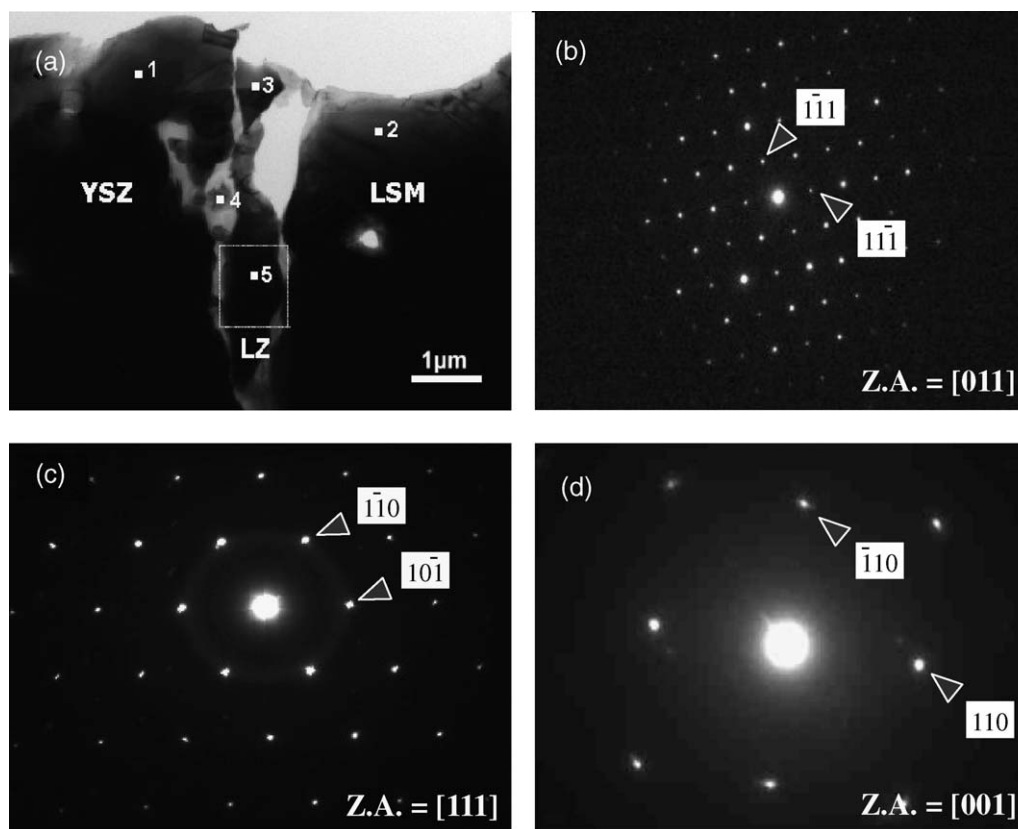


Fig. 5. TEM images of the interface between YSZ film and $LS_{0.2}M$ substrate, when sintered at $1400\text{ }^{\circ}\text{C}$ for 12 h: (a) BF images of YSZ, interface, and $LS_{0.2}M$, (b–d) ED patterns corresponding to (b) YSZ, (c) LSM, and (d) LZ phases.

Table 1
EDS microanalysis of the interface between the YSZ thin film and the $LS_{0.2}M$ substrate sintered at $1400\text{ }^{\circ}\text{C}$ for 12 h

Position in Fig. 5	Concentration (mol.%)						Cation ratio in perovskite and pyrochlore	
	Phase	La	Sr	Mn	Y	Zr	LSM A/B	LZ A/B
1	YSZ	9.38	–	1.64	6.08	85.96		
2	LSM	42.65	12.14	44.11	–	1.10	0.83	
3	LZ	50.86	1.27	0.39	5.24	52.78		1.08
4	LZ	34.47	2.82	1.88	7.92	52.91		0.83
5	LZ	47.62	2.02	3.27	–	47.09		0.99

The analysis was performed on the position shown in Fig. 5(a). The three rightmost columns give the ratio between occupied A and B sites in perovskite, LSM ($A/B = (La + Sr + Y)/(Mn + Zr)$, assuming that Y enters La sites (A') and Mn enters Zr sites (B')).

other hand, Mori et al. [8] also have pointed out that the LZ formed by the reaction between the $\text{La}_{0.9}\text{MnO}_3$ and the YSZ shows lower oxide ionic conductivity than that of YSZ. Although LZ and SZ are found at the interface between YSZ film and LSM and render a negative impact on the SOFC performance, however, introduction of a $(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$ buffer layer between LSM and YSZ alleviates the formation of LZ and SZ phases as recommended by Chen et al. [9].

4. Conclusion

The reaction products observed in the experiment are LZ or SZ. At the interface between the YSZ thin film and the $\text{LS}_{0.2}\text{M}$ substrate, LZ formation is due to low Sr activity. Furthermore, Sr activity at the interface between the YSZ thin film and the $\text{LS}_{0.35}\text{M}$ substrate is higher than La activity and favors the formation of SZ. When sintered at 1400°C , the grain size of LZ suddenly increases from 100 nm to a micrometer scale with soaking time increasing from 2 to 12 h.

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