

## Chemical stability between NiO/8YSZ cermet and alkaline-earth metal substituted lanthanum chromite

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### Abstract

The reaction between the separator in solid oxide fuel cells, alkaline-earth substituted lanthanum chromite ( $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ,  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ ), and the fuel electrode, NiO/8YSZ cermet, was investigated at high temperature. No chemical reaction was observed at the fuel electrode/separator interface of all samples annealed in a temperature range up to 1350 °C. In the combination of fuel electrode and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  annealed at 1400 °C, no diffusion of specific elements was observed at the interface even for an annealing period of 12 h. In the case of the fuel electrode and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ , which was annealed at 1400 °C, a dissolution of Ca into 8YSZ of the NiO/8YSZ cermet was observed at the NiO/8YSZ side of the interface. For the couple of the fuel electrode and  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$  treated at 1400 °C, the Ni concentration increased and the Mg concentration decreased at the  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$  side of the interface. It was expected that a  $\text{LaCr}_{1-x}\text{Ni}_x\text{O}_3$  solid solution was formed by the replacement reaction of Mg by Ni.

**Keywords:** Alkaline-earth metals; Nickel oxide; Ytria stabilized zirconium oxide; Lanthanum chromite

### 1. Introduction

Solid oxide fuel cells (SOFC) are quite an attractive electric power generation system because of their high energy conversion efficiency, simple system design, long-term stability, variety of acceptable fuel and the utilization of high quality by-product heat. However, there are still many problems to be solved in order to realize a high performance SOFC, especially chemical stability arising from the high operation and fabrication temperatures over 1000 °C. Chemical reactions among the SOFC components are of technological importance for avoiding possible degradation during the fabrication process and long-term stack operation. Many investigations have been reported for reactions among the cell component materials [1–3]. We have already made a series of experiments on chemical stability of electrolyte/fuel electrode, electrolyte/air electrode, air electrode/separator and electrolyte/sealing material/separator interfaces [4,5]. The interaction between yttria stabilized zirconia (electrolyte) and lanthanum chromites (separator) has been studied at the SOFC operating and fabrication temperatures [6]. However, the interaction between the fuel electrode and the separator has not been examined in detail. The cermet of nickel oxide and yttria doped zirconia has been widely used

for the fuel electrode [7]. The systems of alkaline-earth doped lanthanum chromite  $\text{La}_{1-x}\text{A}_x\text{Cr}_{1-y}\text{B}_y\text{O}_3$  ( $\text{A} = \text{Ca}, \text{Sr}$ ;  $\text{B} = \text{Mg}$ ) have been widely studied for use as the separator material [6]. In the case of a planar SOFC, the separator has direct contact with the fuel electrode. The good electrical connection and chemical stability of these materials at high temperature should be ensured in order to obtain a high performance SOFC. In this study, solid-state reactions at the interface between the fuel electrode (NiO/8YSZ cermet) and the alkaline-earth metal substituted lanthanum chromite separator ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ ,  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  and  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$ ) have been investigated.

### 2. Experimental

Lanthanum chromite powders were prepared by the usual ceramic procedure. Well-dried raw materials,  $\text{La}_2\text{O}_3$ , MgO,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{Cr}_2\text{O}_3$ , were purchased from Nacal Tesque Ltd., Japan. The powders were weighed in selected proportions and mixed by a planetary-type ball mill for 15 min with acetone. After being dried, the mixtures were heated in air at 1500 °C for 24 h. The milling and heating procedures were repeated two times. The product was ground for the

powder reaction tests. A tablet for the counter diffusion experiment was prepared by heating a pressed disk at 1900 °C in Ar/CO atmosphere for 24 h [8].

8 mol% yttria stabilized zirconia (8YSZ) was purchased from TOSO, Japan, and nickel oxide (NiO) from Nacal Tesque Ltd., Japan. For the powder reaction test, 8YSZ and NiO were heated at 1500 °C for 3 h, and then ground to a powder. A tablet of NiO/8YSZ cermet for the counter diffusion test, which was composed of equimolecular amounts of nickel and zirconia, was prepared by heating a pressed disk of the mixture of 8YSZ and NiO powder in air at 1450 °C for 3 h.

The mixtures of NiO/8YSZ, NiO/lanthanum chromites, and 8YSZ/lanthanum chromites were pressed into pellets. The pellets were fired in the 1300–1400 °C temperature range for 12 h in air. The reaction products were examined using the X-ray diffraction (XRD) technique. XRD patterns were obtained on a Rigaku-RC (12 kW) diffractometer using monochromated Cu K $\alpha$  radiation and a scintillation detector.

Scanning electron microscope (SEM) and energy dispersion X-ray (EDX) measurements were carried out to examine the reactivity between the NiO/8YSZ cermet electrode and the lanthanum chromite separator. The polished surface of an NiO/8YSZ cermet disk was combined face to face with a polished surface of a lanthanum chromite disk. The samples thus constructed were annealed to accelerate the diffusion in the 1200–1400 °C temperature range for 12 h in a 1%H<sub>2</sub>/N<sub>2</sub> atmosphere. The samples were buried in epoxy resin and polished finely to observe the reaction interface [4].

### 3. Result and discussion

The reaction between NiO and 8YSZ was studied in the 1300–1400 °C temperature range. The mixtures of NiO and 8YSZ were pressed and reacted for 12 h in air. No reaction product between NiO and 8YSZ was detected and no peak shift of the NiO diffraction peak was observed. A small deviation of the peak of 8YSZ was observed and the lattice parameter of 8YSZ was smaller than that of the starting 8YSZ. A dissolution of Ni into 8YSZ was examined in the same conditions. Fig. 1 shows XRD pattern of the reaction products of the mixture between 8YSZ and NiO. No diffraction peaks of NiO were detected in a limited compositional range up to 2 mol%. Refined lattice constants of 8YSZ decreased with increasing Ni content in the same compositional range up to 2 mol%. These results suggested that 8YSZ and NiO formed a series of solid solutions by replacement of Zr by Ni in the limited range less than 2 mol%. Electrical conductivities of the mixture between NiO and 8YSZ were measured in a temperature range between 300 and 1000 °C. No significant reduction in the electrical conductivity of 8YSZ was observed in these mixtures. It was suggested that the formation of solid solutions of Ni substituted by 8YSZ caused no harm to the capability of the fuel electrode.

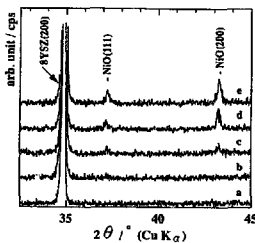


Fig. 1. XRD pattern of the reaction mixture between 8YSZ and NiO. Fractional mol% of NiO in the mixture are (a) 0 mol%, (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, and (e) 4 mol% 8YSZ.

The reactivity of lanthanum chromite with NiO or 8YSZ was studied in the temperature range between 1300 and 1400 °C. The mixtures of lanthanum chromite/NiO or 8YSZ were pressed and reacted for 12 h in air. No reaction product was detected and no peak shift of the NiO and lanthanum chromite was observed in the mixture of lanthanum chromites with NiO. On the other hand, reaction products were observed in the couples of lanthanum chromite and 8YSZ. Figs. 2–4 show the reaction products of these mixtures. La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> formation was observed in the reaction product between LaCr<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub> and 8YSZ in all temperature ranges shown in Fig. 2. The formation of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and SrZrO<sub>3</sub> was observed up to

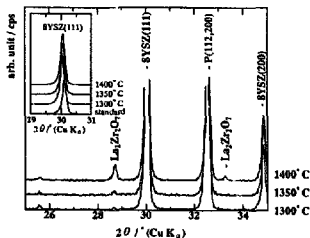


Fig. 2. XRD pattern of the reaction mixture between LaCr<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub> and 8YSZ after heating at various temperatures. Profiles of the (111) diffraction of 8YSZ are superimposed.

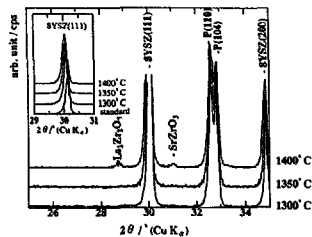


Fig. 3. XRD pattern of the reaction mixture between La<sub>0.8</sub>Sr<sub>0.2</sub>CrO<sub>3</sub> and 8YSZ after heating at various temperatures. Profiles of the (111) diffraction of 8YSZ are superimposed.

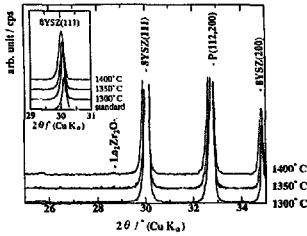


Fig. 4. XRD pattern of the reaction mixture between  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  and 8YSZ after heating at various temperatures. Profiles of the (111) diffraction of 8YSZ are superimposed.

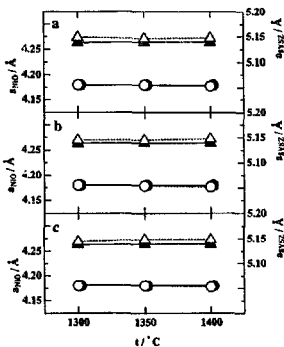


Fig. 5. Lattice parameters of 8YSZ and NiO heated with lanthanum chromite: (a)  $\text{LaCr}_{0.9}\text{Mg}_{0.2}\text{O}_3$ ; (b)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ , and (c)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ . Circles and triangles represent the lattice parameters,  $a$ , of NiO and 8YSZ, respectively. Filled and open marks represent the value of the raw materials and the mixture annealed with each lanthanum chromite, respectively.

1400 °C in the case of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ , see Fig. 3. In the case of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ , no formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  was observed in the temperature ranges as shown in Fig. 4. Diffraction peaks of 8YSZ (111) shifted to a lower  $2\theta$  angle by heat treatment with lanthanum chromite as shown in these figures. Fig. 5 shows lattice parameters of 8YSZ and NiO heated with lanthanum chromite. In the series of reaction products, the lattice parameter of 8YSZ heat-treated with lanthanum chromite was larger than that of raw 8YSZ. It was suggested that a solid solution forms by replacement of Zr with La which has a larger ionic radius. Fig. 6 shows the lattice parameters of lanthanum chromite heat-treated with 8YSZ and NiO. A remarkable change in the lattice parameter was observed in the cases of  $\text{LaCr}_{0.9}\text{Mg}_{0.2}\text{O}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  annealed with 8YSZ and NiO. In the case of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  and 8YSZ, an anomalous elongation of the  $c$ -axis was observed. The lattice parameter,  $c$ , of the  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  solid solution decreased with increasing Ca content. It was suggested that the anomalous elongation of the  $c$ -axis was caused by the decreasing Ca content in the  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  solid solution owing to

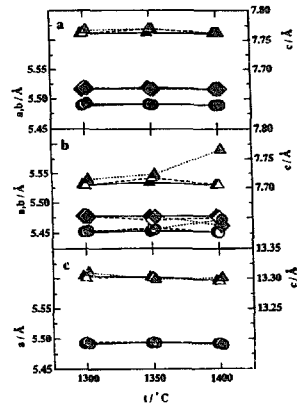


Fig. 6. Lattice parameters of lanthanum chromite: (a)  $\text{LaCr}_{0.9}\text{Mg}_{0.2}\text{O}_3$ ; (b)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ , and (c)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ , heated with NiO and 8YSZ in air. Circles, rhombuses and triangles represent the lattice parameters,  $a$ ,  $b$  and  $c$  of the lanthanum chromites, respectively. Filled, open and shading marks represent the value of the raw material, the mixture with NiO and 8YSZ annealed with each of the lanthanum chromites, respectively.

dissolution of Ca into 8YSZ. These results concerning the reaction between lanthanum chromite and 8YSZ corresponded to the study of the reaction between lanthanum chromite and 8YSZ electrolyte, see Ref. [6].

Microstructure observations and reactivity tests at the interface between the fuel electrode and the separator were carried out in the temperature range between 1300 and 1400 °C in a 1% $\text{N}_2/\text{N}_2$  atmosphere using SEM and EDX techniques. No change of the microstructure nor chemical reaction was observed at the fuel electrode/separator interface of the samples annealed in a temperature range up to 1350 °C. In the combination of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  and NiO/8YSZ annealed at 1400 °C, no formation of an impurity phase was observed at the interface. No significant diffusion of special elements was observed at the interface even for an annealing period of 12 h as shown in Fig. 7. A slight amount of La and Sr was confirmed at the NiO/8YSZ cermet side of the interface less than 1  $\mu\text{m}$  in depth and a small amount of Ni dissolution into  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  was observed by EDX analysis. However, no trace of  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$  formation was confirmed at the interface.

In the case of the reaction couple between  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$  and the NiO/8YSZ cermet heated at 1400 °C, no formation of an impurity phase was observed at the interface. An anomalous concentration of Ca was observed at the NiO/8YSZ side of the interface as shown in Fig. 8. Calcium was distributed about 7  $\mu\text{m}$  in depth at the NiO/8YSZ cermet side of the interface. A high Ca concentration was observed at the interface between lanthanum chromite and 8YSZ of the cermet. Mizusaki and co-workers [9] suggested dissolution of Ca into 8YSZ and formation of  $\text{CaZrO}_3$  at the surface of

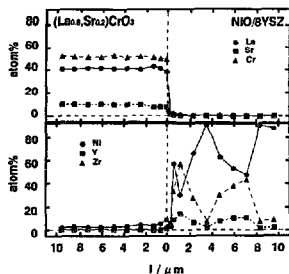


Fig. 7. Concentration profiles at the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ /(NiO/8YSZ) cross-sectional boundary. The dashed line represents the interface between lanthanum chromite and NiO/8YSZ cermet.

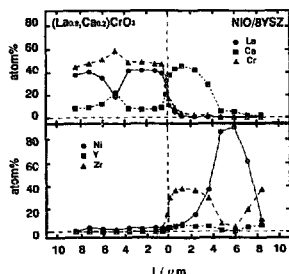


Fig. 8. Concentration profiles at the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ /(NiO/8YSZ) cross-sectional boundary. The dashed line represents the interface between lanthanum chromite and NiO/8YSZ cermet.

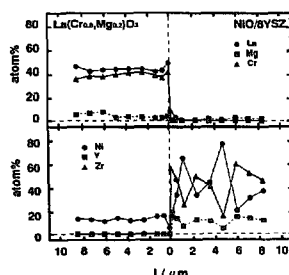


Fig. 9. Concentration profiles at the  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$ /(NiO/8YSZ) cross-sectional boundary. The dashed line represents the interface between lanthanum chromite and NiO/8YSZ cermet.

$\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Co}_x\text{O}_3$ /8YSZ couple reacted at 1400 °C. In this study, the formation of  $\text{CaZrO}_3$  was not observed by XRD. Considering the result of the 8YSZ/(La, Ca)CrO<sub>3</sub> mixed powder reaction, it was reasonable to understand that Ca ions dissolved into 8YSZ and the fluorite-type solid solutions formed by replacement of Zr by Ca at the interface.

In the combination of  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$  and the NiO/8YSZ cermet annealed at 1400 °C, no change in texture and no formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  at the phase boundary was observed. The Ni concentration increased and the Mg concentration decreased at the  $\text{LaCr}_{0.9}\text{Mg}_{0.1}\text{O}_3$  side interface at 1400 °C as shown in Fig. 9. The anomalous decrease in Mg concentration was observed 5 μm in depth at the lanthanum chromite side and the increase in Ni concentration was observed about 10 μm in depth at the NiO/8YSZ side. It was expected that the  $\text{LaCr}_{1-x}\text{Ni}_x\text{O}_3$  solid solution was formed by the replacement reaction of Mg by Ni.

#### 4. Conclusions

The reaction between alkaline-earth substituted lanthanum chromites and NiO/8YSZ cermet was investigated at high temperatures. In the combination of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  and NiO/8YSZ, no diffusion of special elements and no formation of impurity phases was observed in the temperature ranges examined in this study. In the case of the couple of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$  and NiO/8YSZ cermet heated at 1400 °C, dissolution of Ca into 8YSZ was observed at the boundary of the NiO/8YSZ cermet. In the couple of  $\text{LaCr}_{0.8}\text{Mg}_{0.1}\text{O}_3$  and NiO/8YSZ cermet heated at 1400 °C, a formation of  $\text{LaCr}_{1-x}\text{Ni}_x\text{O}_3$  and Mg dissolution into 8YSZ was observed. These reactions mainly occurred at the interface between lanthanum chromite and the NiO/8YSZ cermet and the reaction zone was a few μm in depth. We consider that these reactions do not cause serious problems for a fuel electrode/separator interaction in terms of the capability of the fuel electrode.

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