

Pergamon

0025-5408(95)00062-3

CHEMICAL COMPATIBILITY OF PEROVSKITE-TYPE OXIDE La_{0.7}Ca_{0.3}Cr_{1-v}Co_vO₃ WITH Y₂O₃ STABILIZED ZrO₂

Hiroyuki KAMATA*, Akio HOSAKA,

Research Institute, Ishikawajima-harimaHeavy Industries Co.,Ltd. 3-1-15 Toyosu, Koto-ku, Tokyo 135 Japan

Junichiro MIZUSAKI,

Research Institute for Scientific Measurements, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-77 Japan

and

Hiroaki TAGAWA

Institute of Enviromental Science and Technology, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240 Japan

*author to whom any correspondence should be addressed.

(Received March 20, 1995; Communicated by Koizumi)

ABSTRACT

In order to evaluate the compatibility between the SOFC(Solid Oxide Fuel Cells) interconnector material of the perovskite-type La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO₃ (y=0.05, 0.1 and 0.2) and 8mol%Y₂O₃-ZrO₂ (YSZ), two types of experiments were carried out in air. One was by the reaction of powder mixtures. The reaction products were identified by X-ray analysis after heating at 1000-1300 °C. The other was the experiments using diffusion couples. The distribution of elements at the interface was observed by EPMA for the couples heated at 1300 °C and 1400 °C. The reaction progressed mainly by the dissolusion of calcium ions from the perovskite phase into

H. KAMATA et al.

YSZ. In the perovskite phase, due to the loss of A-site Ca ion, the activity of B-site ions increased, resulting in the deposition of the spinel-type CoCr₂O₄. The excess amount of calcium ions incorporated in YSZ reacted ZrO₂ to form CaZrO₃. Increase of cobalt content enlarge the reactivity of the perovskite phase with YSZ. The parabolic rate constant of the reaction, k_p, was determined by the thickness of CaZrO₃ at the interface of the diffusion couples. Calculated k_p were 2.9×10^{-12} cm²sec⁻¹ and 2.1×10^{-11} cm²sec⁻¹ at 1300°C and 1400°C, respectively. For the practical application as the SOFC interconnector material, the content of cobalt as a sintering accelerator in (La, Ca)CrO₃ must be controlled at low level to keep the chemical interaction to a minimum.

MATERIAL INDEX: perovskite-type oxide, yttria stabilized zirconia, lanthanum calcium chromium cobalt oxide

1.Introduction

Perovskite-type oxide (La, A)CrO₃ (A=alkaline earth metals) is one of the most promising interconnector material for Solid Oxide Fuel Cells(SOFC) [1,2]. The oxide shows the chemical stability against the reducing atmosphere and the high electrical conductivity over a wide range of oxygen partial pressures at high temperatures [3,4]. The application to planar-type SOFC is, however, difficult for its poor sinterability in air [5]. To obtain dense, gas tight structure without sintering aids, it is necessary that the densification is carried out in a reducing atmosphere [6]. Recentry, Sakai et al.[7] found that a slight chromium deficiency enhanced the sinterability of La_{1-x}Ca_{x+y}CrO₃. Another attempt to densify (La, A)CrO₃ was conducted by Nasrallah et al.[8] to substitute B-site chromium ions of the perovskite-type structure for other transition metals such as cobalt. They investigated that the partial displacement of lanthanum by calcium and chromium by cobalt enhances the sinterability of LaCrO₃, and the dense structure with 95% of theoretical density was achieved at 1500°C in air.

To apply the calcium and cobalt-substituted LaCrO₃ to SOFCs, one of the difficulty is its chemical instability with other cell components, such as electrolyte and electrode materials during the cell operation because the mutual diffusion of some elements is an important factor that limits the life time of SOFCs. In addition, co-firing process of all SOFC components needs the heat treatment at high temperature above $\sim 1350^{\circ}$ C, and it implies high risk of the cell degradation using La_{1-x}Ca_xCr_{1-y}Co_yO₃ as the interconnector material. In this study, to make clear the chemical

compatibility of calcium and cobalt-substituted LaCrO₃ with yttria stabilized zirconia(YSZ) and to determine the rate constant of the reaction.

2.Experiments

2.1. Sample preparation The powder samples of $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ with y=0.05, 0.1 and 0.2 were prepared using solid state reaction: The powders of La_2O_3 , CaCO₃, MnCO₃ and Co₃O₄ were mixed together in desired metal ratios. The mixed powders were milled in ethanol and dried up, and were calcined at 1200 °C for 12 hours in air. These process was repeated twice. Obtained powder samples were confirmed to be the single perovskite-type phase by powder X-ray analysis.

<u>2.2. Reaction experiments</u> To identify the reaction products, the experiments were carried out using both the mixtures of the powders and the diffusion couples.

Powder experiment; La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO₃ powder and 8mol% Y₂O₃ stabilized ZrO₂ (YSZ, Daiichi Kigenso Co.) powder were mixed together by 1:1 molar ratio. The mixed powders were pressed into pellets, and heated in air at 1000 $^{\circ}$ C~1300 $^{\circ}$ C until 72 hours. The heated pellets were crashed into powder, and the reaction products were identified by X-ray powder analysis.

Experiments using diffusion couples; The green bodies in pellets of $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ and YSZ were sintered at 1400°C in air. The relative densities of the pellets of $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ and YSZ were 91-93% and 95%, respectively. After the surface of the pellets was polished, YSZ pellet was put together face to face with $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ pellet. The couples were heated at 1300°C and 1400°C in air for various reaction periods. After the diffusion couples were either gradually cooled or quenched to room temperature, they separated into two pieces in almost original shapes. To confirm the reaction products and the distribution of elements, the surface of each pellets were observed by X-ray analysis and either the surface or the cross-section of each pellets were observed by EPMA.

To determine the rate constant of the reaction, one of the reaction products, CaZrO₃, was quantified as a function of the reaction period at 1300 °C and 1400 °C for the experiments using the diffusion couples. The thickness of CaZrO₃ layer on YSZ pellet was determined by SEI or SEM observations. Because the diffusion couples separated into original two pellets as mentioned above, the reacted surface of YSZ pellet was used for natural maker.

3.Results and discussion

<u>3.1. Reaction products</u> The reaction products identified by X-ray analysis are listed in TABLE.1. The reaction between $La_{0.7}Ca_{0.3}Cr_{1-v}Co_vO_3$ and YSZ is classified into the three domain by the H. KAMATA et al.

reaction products. For y=0.05, the reaction product is not observed after heating at 1000°C until 72 hours, however the spinel-type oxide $CoCr_2O_4$ is confirmed as the reaction product above 1100°C. $CoCr_2O_4$ is confirmed under all experimental conditions for the reaction of YSZ with y=0.1 and 0.2. Further, for the reaction between y=0.2 and YSZ at 1100°C ~ 1300°C, $CaZrO_3$ is observed in addition to $CoCr_2O_4$.

For the experiment using the diffusion couples of y=0.2 and YSZ, CoCr₂O₄ is not confirmed on the surface of y=0.2 pellet but on that of YSZ pellet after heating at 1300°C and 1400°C. Typical X-ray patterns are shown in FIG.1. Compared with two X-ray patterns for the reaction of y=0.2with YSZ, the powder mixing sample(a) and the surface of YSZ pellet(d), the intensity of CoCr₂O₄ for the pellet sample is much lower than that for the powder mixing sample. Since the contact area between YSZ and the perovskite-type oxides for powder sample is much larger than that of the diffusion couple, the relative density of the reaction product became much larger for the powder mixing samples.

<u>3.2.Distribution of elements</u> To clarify the difference in the reaction between YSZ and $La_{0.7}Ca_{0.3}CrO_3$ with different Co content, we observed the distribution of each elements for the diffusion couples of y=0.1/YSZ and y=0.2/YSZ, respectively.

For the reaction between y=0.1 and YSZ, the results of the qualitative analysis on the reacted surface of each pellets are shown in FIG.2. While CaZrO₃ was not confirmed as a reaction product for the powder mixing sample, the high intensity of calcium is observed on YSZ surface, suggesting that much Ca ions dissolved into YSZ. The intensity of other components of the perovskite-type oxide such as lanthanum and chromium are small compared with that of calcium, and the distribution of zirconium into the perovskite-type oxide is not confirmed.

For the reaction between y=0.2 and YSZ at 1400 °C, SEI and X-ray maps of the cross-section at the reacted interfaces are shown in FIG.3. The tendency of the distribution of each elements are similar to that for the reaction of y=0.1 and YSZ. The remarkable dissolusion of Ca ions and slight amount of La ions into YSZ were confirmed. Also, the reaction layer of CaZrO₃ phase in YSZ pellet is clearly observed in SEI. At the surface of CaZrO₃ phase, thin layer of Cr and Co ions is confirmed. It suggests that CoCr₂O₄ deposits in close vicinity to CaZrO₃ phase, and the result is consistent with that by the X-ray analysis.

In consequence, the progress of the reaction between $La_{1-x}Ca_xCr_{1-y}Co_yO_3$ and YSZ is considered as follows. First, Ca ions in the perovskite-type oxides diffuse into YSZ at high temperatures.

 $CaO(in perovskite phase) \rightarrow CaO(in YSZ)$

(1)

The preferential dissolution of Ca ions is considered to be due to lower stability of CaCrO₃ in LaCrO₃, as suggested by Yokokawa et al.[9]. With decreasing in the concentration of Ca ions in the perovskite phase according to eq.(1), the activity of B-site ions becomes larger compared with that of A-site ions. Excess amount of B-site ions cause the deposition of the spinel type oxide, $CoCr_2O_4$, and excess amount of Ca ions in YSZ react with ZrO₂ to form CaZrO₃.

 $CaO(in YSZ) + ZrO_2(in YSZ) \rightarrow CaZrO_3(in YSZ)$

We can conclude that the increase of Co content enhances the activity of Ca ion in the perovskite phase, resulting in the formation of the reaction phase such as $CoCr_2O_4$ and $CaZrO_3$.

<u>3.3. Determination of rate constant</u> For the reaction using the diffusion couple of y=0.2 and YSZ, CaZrO₃ phase appears clearly in YSZ, and the growth of the reaction layer obey parabolic low at 1300°C and 1400°C as shown in FIG.4. Therefore, the parabolic rate constant for the reaction, k_p , is calculated by

$$\mathbf{x}^2 = 2\mathbf{k}_p \mathbf{t}$$

where x and t are the thickness of CaZrO₃ layer and the reaction period, respectively. In FIG.5, k_p is described in the C.G.S system of units, cm²sec⁻¹. The calculated k_p is comparable to that determined by the reaction of La_{0.6}Ca_{0.4}CoO₃ electrode with YSZ [10]. In addition, k_p in the formation of BaTiO₃ by the reaction of BaCO₃ with TiO₂[11] is also comparable to that in the perovskite-type oxides/YSZ system. It implies that the diffusion coefficient of A-site cations in the perovskite-type structures, such as Ca ions in CaZrO₃ and Ba ions in BaTiO₃, are essentially similar irrespective of the kinds of the A-site cations.

4.Conclusion

The reaction of $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ with YSZ is mainly progressed by the diffusion of Ca ions in perovskite phase to YSZ. Increase of Co content in (La, Ca)CrO₃ causes much dissolusion of Ca ions into YSZ, resulting in the formation of the reaction products, such as CoCr₂O₄ and CaZrO₃. The rate constant in the formation of CaZrO₃, k_p, is relatively large, suggesting that Co content in (La, Ca)CrO₃, as a sintering accelerator, must be controlled at a low level to keep the chemical interaction to a minimum for the practical application as the SOFC interconnector material.

References

- B.K.Flandermayer, J.T.Dusek, P.E.Blackburn, D.W.Dees, C.C.McPheeters and P.B.Poeppel, Abstruct of 1986 Fuel Cell Seminar, Tucson, Ariz., p.68. Courtesy Associates Inc., Washington D.C. (1986).
- W.Shafer and R.Schmidberger, High Teck Ceramics, Ed.by P.Vincenzini, p.1737 Elsevier Science Publishers B.V., Amsterdam(1987).
- 3. W.J.Weber, C.W.Griffin and J.B.Bates, J.Amer.Ceram.Soc., 70, 265(1987).
- 4. I.Yasuda and T.Hikita, Proceedings of the 2nd Internat.Sympo.on SOFCs, Ed.by F.Gross, P.Zegers, S.C.Singhal and O.Yamamoto, p.645, Commission of E.C., Luxemboug(1991).
- 5. H.Yokokwa, N.Sakai, T.Kawada and M.Dokiya, J.Electrochem.Soc., 138, 1018 (1992).
- 6. L.Groupp and H.U.Anderson, J.Amer.Ceram.Soc. <u>59</u>, 449(1976).
- 7. N.Sakai, T.Kawada, H.Yokokawa, M.Dokiya and T.Iwata, J.Mat.Sci., 25, 4531 (1990).

(2)

(3)

- M.M.Nasralla, J.D.Canter, H.U.Anderson and R.C.Koc, Proceedings of the 2nd Internat. Sympo. on SOFCs, Ed.by F.Gross, P.Zegers, S.C.Singhal and O.Yamamoto, p.637, Commission of E.C., Luxemboug(1991).
- 9. H.Yokokwa,N.Sakai,T.Kawada and M.Dokiya,Proceedings of the 2nd Internat. Sympo.on SOFCs, Ed.by F.Gross,P.Zegers,S.C.Singhal and O.Yamamoto, p.663,Commission of E.C., Luxemboug(1991).
- 10.H.Tagawa,J.Mizusaki,M.Kato,K.Hirano,A.Sawata and K.Tsuneyoshi,Proceedings of the 2nd Internat.Sympo.on SOFCs, Ed.by F.Gross,P.Zegers,S.C.Singhal and O.Yamamoto, p.681, Commission of E.C., Luxemboug(1991).
- 11.H.Tagawa, J.Mizusaki, Y.Mozumi and R.Ueda, to be published.



Typical X-ray diffraction patterns of powder mixing experiments of y=0.2(a), y=0.1(b)and y=0.05(c) with YSZ after heating at 1300°C for 72 hours, and YSZ surface(d) and y=0.2 surface(e) of the diffusion couples after heating at 1300°C for 96 hours.

TABLE.1.						
Reaction products	between	La _{0.7} Ca _{0.3} Cr _{1.y} CoyO ₃	and YSZ	after heating at		
1000°C~1400°C	for the	powder mixing reactio	n until 72	hours in air.		

Co content	Reaction temperatures					
у	1000℃	1100°C	1200°C	1300°C		
0.05		CoCr2O4	CoCr ₂ O ₄	CoCr ₂ O ₄		
0.1	CoCr ₂ O ₄	CoCr ₂ O ₄	CoCr ₂ O ₄	CoCr ₂ O ₄		
0.2	CoCr ₂ O ₄	CoCr ₂ O ₄ +CaZrO ₃	CoCr ₂ O ₄ +CaZrO ₃	CoCr ₂ O ₄ +CaZrO ₃		



EPMA results for La_{0.7}Ca_{0.3}Cr_{0.9}Co_{0.1}O₃ surface(a) and YSZ surface(b) of the diffusion couple after heating 1300°C for 48 hours.



 $---- 10 \,\mu\,{\rm m}$



SEI and X-ray maps for the cross-section of La_{0.7}Ca_{0.3}Cr_{0.8}Co_{0.2}O₃/YSZ interface after heating at 1300°C for 48 hours.



FIG.4. Relationship between reaction period and thickness of CaZrO₃ layer in reaction of La_{0.7}Ca_{0.3}Cr_{0.8}Co_{0.2}O₃ with YSZ at 1390°C and 1400°C.





Relationship between parabolic rate constant, k_p, and temperature of CaZrO₃ formation by reaction of La_{0.7}Ca_{0.3}Cr_{0.8}Co_{0.2}O₃ with YSZ. Dashed line showes k_p of CaZrO₃ formation by reaction of La_{0.6}Ca_{0.4}CoO₃ electrode with YSZ[10]. Marks, A and R, show k_p of BaTlO₃ formation by reaction of BaCO₃ with anatase and rutile in TiO₂, respectively[11].