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Fabrication of an ionic/electronic nanocomposite for a high flux oxygen ion transport membrane

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 $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC)/Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) nanocomposites were fabricated by a conventional power processing technique from a commercially available GDC and a BSCF powder prepared in-house. The BSCF was synthesized via the glycine-nitrate process (GNP). XRD analysis indicated that the GDC was found to be compatible with the BSCF at a sintering temperature of 1150 °C. Dense GDC/BSCF nanocomposites having a relative density above 95% could be obtained when a green compact of BSCF and GDC powder mixture was sintered at 1150 °C for 5 h. GDC particles were found to be homogeneously dispersed in the BSCF matrix and some smaller GDC particles less than a few hundred nm in size were incorporated inside the large BSCF grains. The grain size of the BSCF was decreased by an addition of the GDC, suggesting the GDC can hinder the grain growth of the BSCF.

Key words: Oxygen ion transport membrane, Perovskite, BSCF, Mixed ionic and electronic conductor.

Introduction

Oxygen ion transport membrane (OTM) technology facilitates the exclusive mediation of oxygen from the atmosphere to a desired reaction site. Dense ceramic materials exhibiting mixed ionic and electronic conductivity can be used as a membrane material. These materials selectively separate oxygen from air at high temperature under an oxygen partial pressure difference. Bredesen and Sogge have addressed that a membrane with at least an oxygen flux of 10 ml/cm² ·min is needed to commercialize an oxygen separation membrane [1].

If the bulk transport through the membrane is the ratedetermining step, the theoretical oxygen flux of the membrane is generally determined by the Wagner equation [2, 3]. According to the equation, the oxygen flux depends on an ambipolar conductivity ($\sigma_{el}\sigma_{ion}/\sigma_{el} + \sigma_{ion}$), not just ionic or electronic conductivity. Since the publication of Teraoka et al. [4], the most promising membrane materials are known to be the family of perovskites of the general formula ABO₃, where A is alkaline and rare earth metals and B is a mixture of Co and Fe. Among the perovskite compounds, Ba-Sr-Co-Fe (BSCF) has attracted a great deal of attention due to its high mixed ionic and electronic conductivity and favorable phase stability [5-8].

On the other hand, BSCF suffers from a high thermal expansion coefficient (TEC) above 30×10^{-6} /K [9] and low chemical stability. The TEC of BSCF can be reduced by

increasing the Fe doping concentration in $(Ba,Sr)(Co,Fe)O_3$. However, the increase in Fe doping resulted in a reduction of electrical conductivity and also of the oxygen permeation flux. In this study, we fabricated a GDC/ BSCF nanocomposite membrane in order to reduce the TEC of the BSCF membrane without degrading its ionic and electronic conductivity. The sintering behavior and microstructure of the GDC/BSCF nanocomposites were investigated in terms of the weight fraction of the GDC and sintering temperature.

Experimental procedure

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) powder was synthesized via the glycine-nitrate process (GNP). Ba(NO₃)₂ (Acros, 99%), Sr(NO₃)₂ (Acros, 99%), Co(NO₃)₂ \cdot 6H₂O (Acros, 99%), and Fe(NO₃)₃ \cdot 9H₂O (Kanto Chemical Co. Inc., 99%) were used as starting raw materials. Glycine (Kanto Chemical Co. Inc., 99%) was used as an oxidizer and fuel. The processing details are described in our previous paper [9].

The BSCF and 25, 35, 45 and 55 wt% gadolinium-doped ceria, GDC (Ce_{0.9}Gd_{0.1}O_{2- δ}, Anan Kasei Co. Ltd., Tokyo, Japan) powders were mixed by ball milling in a polyethylene container using ethyl alcohol and ZrO₂ balls for 24 h. Mixed slurries were dried with a rotary evaporator. The dried powder mixtures were dry-milled and then sieved through a 320 µm mesh screen. Green pellets were uniaxially pressed at a pressure of 40 MPa, subsequently followed by cold isostatic pressing (CIP) at 200 MPa. After CIPing, the pressed pellets were fired at various temperatures (800, 900, 1000, 1100 and 1150 °C) for 5 h in air. The heating rate was 300K/h. Sintered specimens were ground using 400 and 800-grit resin-bond diamond

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Fig. 1. X-ray diffraction patterns of GDC/BSCF composites sintered at 1150 $^{\rm o}C$ for 5 h.

wheels.

For phase characterization, X-ray diffraction patterns were obtained with a powder diffractometer (DMAX-2500, Rigaku Co. Ltd., Japan) with Ni-filtered CuKa radiation. The bulk density was determined via the Archimedes method in water. The surface microstructure was observed by field emission scanning electron microscopy (S-4300, HITACH, Japan). The surface of the samples were polished using SiC papers and diamond paste ($\sim 1 \ \mu m$) and thermally etched at 1000 °C for 15 minutes.

Results and Discussion

The X-ray diffraction analysis revealed that the BSCF had a perovskite structure, regardless of sintering temperature and the weight fraction of GDC. Fig. 1 shows X-ray diffraction profiles of the BSCF and GDC/ BSCF nanocomposites sintered at 1150 °C for 5 h. All the peaks in profiles were assigned to perovskite BSCF and the fluorite GDC structure. During the sintering process, it seems that the reaction between the BSCF and GDC doesn't occur, and no unwanted phases were found in the composites. The intensities of GDC peaks increased with an increase in the GDC content, indicating that the BSCF matrix is a phase compatible with the GDC.

Fig. 2 shows relative density changes of the BSCF and GDC/BSCF nanocomposites as a function of the sintering temperature. The samples were sintered at each temperature for 5 h. In the case of the BSCF, increasing the sintering temperature from 800 to 1100 °C gradually increases the relative density. When the sample is sintered at 1100 °C, about 90% of theoretical density can be achieved, however, a further increase in sintering temperature does not result in a relative density increase. Similar sintering temperature has been reported by Wang et al. [6]. On the other hand, the sinterability of the nanocomposite is monotonically improved with an increase in the sintering temperature from 1000 to 1150 °C. A maximum relative



Fig. 2. Relative density change as a function of sintering temperature of GDC/BSCF composites sintered at 1150 °C for 5 h.



Fig. 3. Relative density change as a function of GDC content of GDC/BSCF composites sintered at $1150 \,^{\circ}$ C for 5 h.

density of 95% can be obtained for the nanocomposites sintered at 1150 °C for 5 h. It has been known that a relative density higher than 90% is required to be applied to an oxygen permeation membrane [7].

The effect of the GDC on sinterability of the BSCF was shown in Fig. 3. As can be seen in Fig. 3, it seems that the GDC inhibits the densification of the BSCF. However, densification was slightly improved with further additions of GDC. This tendency was observed in the nanocomposites sintered at 1000 and 1100 °C. When the sintering was carried out at 1150 °C, the relative density of the nanocomposites was higher than that of the BSCF. Generally, GDC is more difficult to sinter than the BSCF, which suggests the densification would be retarded with an addition of the GDC into the BSCF. This speculation was true in the composites sintered at 1000 and 1100 °C. The reason why the relative density of the composites sintered at 1150 °C is higher than that of the BSCF is not clear, and should be investigated in the future.

Fig. 4 shows low magnification SEM images of the



Fig. 4. SEM images of polished surfaces of GDC/BSCF composites sintered at 1150 °C for 5 h.



Fig. 5. High magnification SEM images of polished surfaces of 25 wt%GDC/BSCF and 45 wt%GDC/BSCF composites sintered at 1150 °C for 5 h.

BSCF and GDC/BSCF nanocomposites sintered at 1150 °C for 5 h. Comparing Fig. 4(a) with (b) to (e), it was found that a denser microstructure is observed in the nanocomposites which is consistent with the relative density results mentioned before. It would appear that

relatively large BSCF grains are surrounded by fine GDC particles. In the case of the 25 wt%GDC/BSCF nanocomposite, the relatively darker and continuous phase is BSCF. GDC (bright and spherical particles), which was homogeneously dispersed in the BSCF matrix, was



Fig. 6. SEM images of fracture surfaces of GDC/BSCF composites sintered at 1150 °C for 5 h.

fragmented or partially continuous. As the GDC content is increased, the bright phase (GDC) increased and the GDC becomes the continuous phase.

High magnification SEM images are shown in Fig. 5. From Fig. 5(a), it is seen that fine GDC particles a few hundred nm in size are dispersed not only at grain boundaries but also inside the GDC grains. Relatively larger GDC particles are located at the grain boundaries, while smaller ones are incorporated within the large BSCF grains. This observed phenomenon suggests that the grain growth of the BSCF would be hindered by the GDC particles. As the GDC content increases, agglomerated GDC particles are located mainly at triple or quadruple points of the BSCF grains.

Fig. 6 shows fracture surfaces of the BSCF and GDC/BSCF nanocomposites sintered at 1150 °C for 5 h. It is observed that grain growth in the BSCF is extremely rapid at 1150 °C and the BSCF consists of grains a few hundred μ m in size. The grain size of the GDC/BSCF

nanocomposites is gradually decreased with an increase in the GDC content. This result indicates that the GDC can effectively suppress the grain growth of the BSCF and a fine microstructure can be obtained in the nanocomposites. The fracture mode is completely transgranular (intragranular) in the BSCF and fractured surfaces are very flat. On the other hand, the fracture was found to be partially intergranular in the GDC/BSCF nanocomposites.

Conclusions

In order to fabricate a high flux oxygen ion transport membrane, BSCF nanocomposites containing 25, 35, 45 and 55 wt% GDC were examined in this study. XRD analysis revealed that the nanocomposites consisted of a BSCF perovskite and fluorite GDC phases. There were no unwanted reaction phases between the two phases. A bulk density higher than 95% of theoretical density was obtained when the BSCF and GDC were sintered at 1150 °C for 5 h. At such a temperature, it was considered that the GDC addition does not hinder the sinterability of the BSCF. On the other hand, adding a GDC into the BSCF matrix resulted in a grain size reduction because the GDC particles at grain boundaries could effectively hinder the grain growth of the BSCF. In the case of the 25 wt% GDC/BSCF nanocomposite, it was observed that some smaller GDC particles were incorporated inside the BSCF grains. The effect of the GDC additions on electrical properties such as conductivity and oxygen flux should be investigated.

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References

- R. Bredesen, J. Sogge, Seminar on the ecological applications of innovative membrane technology in the chemical industry (1996).
- 2. C. Wagner, Z. Phys. Chem. B21 (1933) 25-41.
- 3. K. Wiik, S. Aasland, H.L. Hansen, I.L. Tangen and R. Odegard, Solid State Ionics 152-153 (2002) 675.
- 4. Y. Teraoka, H.M. Zhang, S. Furukawa and N. Yamazoe, Chem. Lett. (1985) 1743-1746.
- P. Zeng, Z. Chen, W. Zhou, H. Gu, Z. Shao and S. Liu, J. Membrane Sci. 291 (2007) 148-156.
- H. Wang, C. Tablet, A. Feldhoff and J. Caro, J. Membrane Sci. 262 (2005) 20-26.
- A. Mosadeghkhah, M.A. Alaee and T. Mohammadi, Mater. and Design 28 (2007) 1699-1706.
- J.F. Vente, W.G. Haije and Z.S. Rak, J. Membrane Sci. 276 (2006) 178-184.
- Y.H. Lim, J.S. Yoon, J. Lee, C.E. Kim and H.J. Hwang, J. Power Sources 171 (2007) 79-85.