Decomposition reaction of BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} in carbon dioxide atmosphere with nickel sintering aid

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The perovskite-type proton conductor with the composition of BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb) has been reported to exhibit the highest proton conductivity among proton conductors. However, cerate-based perovskite materials such as BZCYYb are also known to react with carbon dioxide which causes phase decomposition through the formation of barium carbonate. This is a significant issue because chemical stability is an important property to enable these materials to be utilized for fuel cell applications. In this study, the chemical stability of BZCYYb was investigated in CO_2 or CO_2 + H_2 atmosphere, with or without nickel addition as sintering aid. Some nickel addition is assumed to occur from nickel diffusion in anode-support-type fuel cells. The enhancement of reactivity with carbon dioxide species by adding nickel into BZCYYb was attributed to barium enrichment at grain boundary regions and the formation of an impurity phase of Ba(Y_{(1-x)}Yb_{x})_2NiO_4. Moreover, different decomposition reactions depending on the atmosphere have been inferred. In a pure CO_2 atmosphere, barium carbonate formation occurred without appearance of the CeO_2-based phase, in other words, without decomposition of the perovskite phase. On the other hand, in hydrogen-containing CO_2 atmosphere, both the barium carbonate and CeO_2-based phase were observed.

Key-words : Proton conductor, BZCYYb, Nickel, Carbon dioxide, Raman spectroscopy

1. Introduction

Proton conducting materials are receiving attention due to their potential to improve the electrical generation efficiency in fuel cell applications.¹ Acceptor-doped-perovskite-type oxide such as barium zirconate, barium cerate and similar composites are well-known as proton conductive oxide materials, following the report by Iwahara et al.² Generally speaking, the cerate materials exhibit higher proton conductivity than zirconate materials but have a disadvantage of poor chemical stability, in particular against CO_2.³⁻⁵ Recent approaches to obtain both high proton conductivity and high chemical stability include forming a solid solution of the zirconate and cerate materials.²⁻⁶ In particular, yttrium and ytterbium co-doped BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb) has been reported to exhibit the highest proton conducting material among the acceptor-doped-type proton conductors.⁷⁻¹¹ In some reports, the chemical stability of BZCYYb was improved by adding multi-dopants into the cerate-based system, resulting to stability of BZCYYb even in CO_2 atmosphere.¹² However, other studies reported on its reactivity with carbon dioxide.¹³⁻¹⁴ Thus, the chemical stability of this BZCYYb proton conductor is still not clear. Furthermore, the effect of nickel sintering aid on chemical stability is also important because nickel is dissolved into the electrolyte in the case of anode-support-type cell. Fundamental information about chemical stability is therefore important to determine the applicability of these materials.

In this study, the chemical stability of Ni-added BZCYYb (BZCYYb–Ni) against CO_2-containing atmosphere was evaluated at around 400–800°C in order to investigate the effect of nickel sintering aid. A 2 wt% of nickel was added into BZCYYb as sintering aid. This value was determined from the solid solubility limit of Ni into BZCYYb electrolyte in anode-support-type fuel cell.¹⁵ The chemical stability was then evaluated in either pure CO_2 or hydrogen-containing CO_2 under the assumption that fuel was supplied by methane gas reforming in usual SOFC operation. The effect of nickel sintering aid on chemical stability was discussed by focusing not only on the formation of the barium carbonate spics but also phase changes of the perovskite oxide. Further understanding about the decomposition reaction occurring in these materials would be useful in the development of new chemically stable proton conductors.

2. Experimental

2.1 Sample preparation

Commercial BZCYYb powders (Kyoritsu Material Corp.) were used to make BZCYYb and BZCYYb–Ni pellets. The BZCYYb powder was pressed into a disk-shaped pellet with a size of 25 mm diameter using a Newton pressing apparatus, and consecutively pressed again using a cold isostatic press (CIP) apparatus with a pressure of 392 MPa. The obtained pellets were sintered at 1600°C for 2 h by embedding in raw BZCYYb powders.¹⁶ For the nickel-added (BZCYYb–Ni) sample, a 2 wt% of nickel was added to the BZCYYb powder as NiO and mixed by milling with zirconia balls (diameter: 8 and 3 mm) and pot with ethanol as solvent. The pressed BZCYYb–Ni pellets were sintered at 1300°C for 2 h. The sintered pellets of both BZCYYb and BZCYYb–Ni compositions were polished and cut into some smaller pieces, and used for the subsequent CO_2 exposure test.

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2.2 CO₂ exposure test
The CO₂ exposure test was conducted in an aluminum tube chamber by flowing 100% CO₂ gas or 80%H₂ + 20% CO₂ mixed gas at a 50 sccm flowing rate. The chemical compatibility test for the two different gases were investigated at 400–800°C by exposing the samples for 20 h at each set temperature.

2.3 Sample analysis
The surface of the pellets after exposure test to CO₂ or H₂–CO₂ atmosphere was analyzed by X-ray diffraction (XRD) and Raman spectroscopic technique. The XRD patterns were measured by using RINT-Ultima III (Rigaku) with Cu X-ray source. The Raman spectra were used by using NR-3300 (JASCO) with a green laser (532 nm). The grain sizes of as-prepared pellets were determined by observation of the fractured surface using field-emission scanning electron microscopy. The chemical composition of impurity phase was analyzed by technique with scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM/EDX, JEOL, JE-2100) operated at 200 kV. The sample for STEM/EDX measurements was prepared by thinning an as-sintered BZCYYb–Ni pellet using an Ar⁺ ion milling apparatus (JEOL, EM-091001S).

3. Results

3.1 Phase change of BZCYYb after exposure to CO₂ and H₂–CO₂ atmosphere
The XRD patterns and Raman spectra of as-prepared BZCYYb pellets are shown in Figs. 1 and 2(a), respectively. Both XRD and Raman analyses showed that the crystal phase in BZCYYb pellets before exposure to CO₂ gas is a single phase perovskite structure. Figures 2(b)–2(d) show the Raman spectra of BZCYYb pellets after exposure to H₂–CO₂ mixed atmosphere at 400–600°C for 20 h. The peaks of BaCO₃ appeared with increasing exposure temperatures from 400 to 600°C. The carbon deposition was observed only at 500°C, which indicated that the perovskite phase still remained after exposure to H₂–CO₂ atmosphere. In Fig. 3, the Raman spectra of BZCYYb pellets after exposure to pure CO₂ gas at 400–800°C for 20 h is shown. Similar to the case of exposure to H₂–CO₂ gas, the formation of BaCO₃ progressed with increasing temperatures. The phase stability was examined up to 800°C in pure CO₂ condition. The strong peaks of BaCO₃ and CeO₂-based phase were observed after such a high-temperature annealing. According to thermochemical equilibrium calculations, the cerate-based perovskite proton conductors are not stable in CO₂-containing atmosphere under around 1000°C. Therefore, the more significant phase decompositions occurred with increasing temperature due to the enhancement of reaction kinetics. Indeed, a significant phase decomposition of BZCYYb perovskite phase into BaCO₃ and CeO₂ phase in 50% CO₂ and 50% H₂ atmosphere at 750°C, which is higher than this study, was reported.

3.2 Phase change of BZCYYb–Ni after exposure to CO₂ and H₂–CO₂ atmosphere
The XRD pattern and Raman spectra of as-prepared BZCYYb–Ni pellets are shown in Figs. 1 and 4(a), respectively. The crystal phase in BZCYYb–Ni pellets before exposure to CO₂-containing atmosphere was confirmed to be only the single phase of perovskite structure, similar to BZCYYb. The XRD peaks of BZCYYb–Ni were slightly shifted to higher 2θ positions and became sharper compared to BZCYYb. These results indicate that the unit cell lattice constant had decreased due to the doping of nickel oxide into the perovskite BZCYYb phase, and grain growth was enhanced by the effect of nickel as sintering aid.

Fig. 1. XRD patterns of BZCYYb (top) and BZCYYb–Ni (bottom) before exposure to CO₂ gas. A magnified view is also shown in (b).

Fig. 2. Raman spectra of BZCYYb pellet (a) before and (b), (c), (d) after exposure to H₂–CO₂ mixed gas at 400–600°C.

Fig. 3. Raman spectra of BZCYYb pellet after exposure to CO₂ gas at 400–800°C.
The SEM images of the BZCYYb pellets with and without Ni are shown in Fig. 5. Larger grains were observed for BZCYYb–Ni compared to BZCYYb. The grain size distribution is summarized and shown in Fig. 6. These results clearly show that the nickel was doped into BZCYYb perovskite as a sintering aid. In Fig. 4, the Raman spectra of BZCYYb–Ni pellets after the exposure to pure CO$_2$ atmosphere at 400–600°C for 20 h are shown. The peaks attributed to BaCO$_3$ were observed after the exposure to CO$_2$ atmosphere, similar to those of BZCYYb.

In Fig. 7, the Raman spectra of BZCYYb–Ni pellets after the exposure to H$_2$–CO$_2$ mixed atmosphere at 400–600°C for 20 h are shown. Significant BaCO$_3$ and CeO$_2$-based phases are observed as compared to the case of the exposure to pure CO$_2$; moreover, carbon deposition was also observed in this case. It seemed that phase decomposition was almost completed at 600°C. The phases after exposure test in pure CO$_2$ or H$_2$–CO$_2$ atmosphere were analyzed using XRD technique. In Figs. 8(a) and 8(b), the XRD patterns of BZCYYb–Ni after the exposure to H$_2$–CO$_2$ mixed gas at 400–600°C.
pure CO$_2$ and H$_2$–CO$_2$ are shown, respectively. As observed in Raman spectra, with increasing exposure temperature, for the case of H$_2$–CO$_2$ the BaCO$_3$ phase increased and in particular, the perovskite phase was completely decomposed into BaCO$_3$ and CeO$_2$-based phase. Magnification of the XRD peaks in the range of $2\theta = 28$–30° are shown in Fig. 9. The solid lines show the peak position of the original BZCYYb–Ni perovskite phase. Additional peaks appeared at either higher or lower $2\theta$ position for the case of pure CO$_2$ or H$_2$–CO$_2$ atmosphere, respectively. The CeO$_2$-based phase was not observed so clearly for the case of pure CO$_2$. The peak shift to higher $2\theta$ position indicates decreasing of lattice constant of perovskite phase due to deficiency of Ba component. On the other hand, the additional CeO$_2$-based phase was clearly observed at a lower $2\theta$ position in XRD for the case of H$_2$–CO$_2$.

4. Discussion

4.1 Effect of Ni addition on phase stability in CO$_2$-containing atmosphere

The enhancement of the reactivity to CO$_2$ gases with nickel addition was clearly observed via comparison of the stability of BZCYYb and BZCYYb–Ni against CO$_2$-containing gas. The change in lattice constant of the perovskite phase by nickel addition implies some nickel dissolution. Recently, the study of Han et al. suggested that the nickel dissolved into interstitial sites in the perovskite structure for the case of barium zirconate. Consequently, barium vacancies are formed due to this dissolution. Such Ba deficiency as induced by nickel dissolution into perovskite phase is also applicable for the case of barium-cerate-based materials. Han et al. also suggested that the barium composition became relatively abundant at the grain boundary region due to the barium deficiency of the inner grain. According to such behavior, the decrease in chemical stability by nickel addition can be attributed to the barium activity being higher at the surface region as compared to the case without nickel addition.

Another effect of nickel addition is related to the BaY$_2$NiO$_5$ phase formation as reported for yttrium-doped barium zirconate system, as this phase has been reported to react with CO$_2$. In this study, some indication of a BaY$_2$NiO$_5$-like phase was observed using STEM-EDX analysis in the as-prepared BZCYYb–Ni sample as shown in Fig. 10. This impurity phase can be written as Ba(Y$_{1-x}$Yb$_x$)$_2$NiO$_5$. It appears that for the case of BZCYYb–Ni, the reactivity was enhanced due to the formation of Ba(Y$_{1-x}$Yb$_x$)$_2$NiO$_5$ phase by nickel addition.

4.2 Phase decomposition reactions

As discussed above, different phase changes were observed depending on whether hydrogen-containing CO$_2$ or pure CO$_2$ atmosphere was used for BZCYYb–Ni. After exposure to pure CO$_2$, the Ba-deficient perovskite phase was observed with BaCO$_3$ formation without any CeO$_2$-related phase precipitation. However, in the case of BZCYYb without nickel, some CeO$_2$-related phase was also observed after exposure to pure CO$_2$ at high temperatures. These results suggest enhanced reaction with carbon dioxide in pure CO$_2$, i.e. at relatively higher pO$_2$ atmosphere than that of hydrogen-containing CO$_2$. Ba component was extracted without decomposition of the perovskite phase, thus resulting to some Ba deficiency in the initial stages of reaction with carbon dioxide. Then, the perovskite phase decomposed when the...
amount of Ba deficiency in the perovskite phase reached a threshold value above which the perovskite phase becomes unstable. As a result, the CeO$_2$-based phase appeared due to phase decomposition.

For the case of hydrogen-containing CO$_2$ atmosphere, the enhancement of reactivity with CO$_2$ was observed as discussed above. The precipitation of CeO$_2$-based phase was implied even at initial stage of reaction with CO$_2$ based on the results of XRD analysis after exposure H$_2$–CO$_2$ gas at 400°C as shown in Fig. 9(b). These results show that the decomposition reaction with CO$_2$ in reducing atmosphere is different from that in pure CO$_2$ atmosphere. In the reducing atmosphere, the perovskite phase is directly decomposed to barium carbonate and CeO$_2$-based phase without resulting to a Ba-deficient perovskite phase. Such feature can be explained by the property that the cerate perovskite materials tend to decompose at reducing conditions.\(^{23}\) A different decomposition reaction will occur in either pure CO$_2$ or H$_2$–CO$_2$ due to the dependency of the phase stability on oxygen partial pressure. Here, a significant carbon deposition was observed at H$_2$–CO$_2$ condition for the Ni–BZCYYb sample. This implies that the nickel metal formed via reducing treatment and it acted as a catalyst for carbon deposition reaction. However, the carbon deposition was observed also in the case of BZCYYb without nickel only at 500°C. The reason for this behavior is not yet clear in this study and will need further investigation.

5. Conclusion

In this study, the phase stability of yttrium and ytterbium co-doped BaZ$_{0.9}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$ perovskite type proton conductor in pure CO$_2$ or H$_2$–CO$_2$ condition at 400–800°C was investigated. In particular, nickel-added BaZ$_{0.9}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$ as in anode support type cell was analyzed in detail by means of Raman spectroscopy, XRD and STEM/EDX. Results suggest the increasing of Ba activity by nickel dissolution into perovskite phase due to the enrichment barium component near the grain boundary region. Furthermore, the formation of impurity Ba(Y$_{1-δ}$Yb)$_3$NiO$_5$ phase enhanced the reactivity with carbon dioxide. A different decomposition was observed depending on whether a hydrogen-containing CO$_2$ or pure CO$_2$ was used. For the pure CO$_2$ atmosphere, the BaCO$_3$ was formed by extracting the Ba component from perovskite phase without decomposition. On the other hand, for the hydrogen-containing CO$_2$, both the BaCO$_3$ and CeO$_2$-based phase were observed even after exposure at low temperatures. This is because the phase stability also depends on oxygen partial pressure. A significant decomposition reaction was not observed at low temperatures, however, the barium carbonate formation could still have occurred even at such low temperature region according to thermochemical calculations. Therefore, long-term durability remains a critical issue for BZCYYb-based perovskite proton conductor. Moreover, BZCYYb-based materials must be used in atmospheres without CO$_2$, a limitation which needs to be overcome for practical applications.

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