Preparation of double-doped BaCeO$_3$ and its application in the synthesis of ammonia at atmospheric pressure

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Abstract

Perovskite-type oxides BaCe$_{0.90}$Sm$_{0.10}$O$_{3-\delta}$ (BCS) and BaCe$_{0.80}$Gd$_{0.10}$Sm$_{0.10}$O$_{3-\delta}$ (BCGS) were synthesized by the sol–gel method and characterized by thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Using the sintered samples as solid electrolytes and silver–palladium alloy as electrodes, ammonia was synthesized from nitrogen and hydrogen at atmospheric pressure in a solid-state proton-conducting cell reactor. The maximum rate of production of ammonia was 5.82 $\times$ 10$^{-9}$ mol s$^{-1}$ cm$^{-2}$.

1. Introduction

High-temperature proton conductors have the potential for use in solid-oxide fuel cells (SOFCs), hydrogen separation membranes, and hydrogen sensors. They are typically aliovalent dopant-substituted solid-solution materials based on perovskite oxides. The use of perovskite-structured oxides as membrane materials or electrodes in SOFCs has been pursued for many years [1–3]. In our previous studies, we synthesized high-temperature proton conductors and applied them to the synthesis of ammonia at atmospheric pressure. Doped ABO$_3$ oxides are of particular interest because they exhibit high proton and oxygen ion conductivities, high electronic conductivity, and excellent chemical stability over a wide range of temperatures. Doped BaCeO$_3$ exhibits the highest ionic conductivity out of these materials. Many studies have focused on the structure, defect chemistry, conductivity, and the processing and consolidation of doped BaCeO$_3$ compounds [4–7]. In this study, compounds of BaCe$_{0.90}$Sm$_{0.10}$O$_{3-\delta}$ (BCS) and BaCe$_{0.80}$Gd$_{0.10}$Sm$_{0.10}$O$_{3-\delta}$ (BCGS), double doped in the B position, were prepared by the sol–gel method. The electronic conductivity of BCGS is much higher than that of BCS.

The conventional method for ammonia synthesis is the Haber process, in which gaseous nitrogen and hydrogen react on a catalyst at high temperatures (450–500 °C) and high pressures (150–300 bar). There are stringent requirements for the equipment used for the Haber process, and its efficiency is limited by thermodynamic requirements. Ammonia synthesis at atmospheric pressure using solid-state proton conductors as the electrolyte has been electrochemically investigated. Marnellos and Stoukides used SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ as the electrolyte, and the yield was 10$^{-11}$ mol s$^{-1}$ cm$^{-2}$ [8,9]. In our previous studies, an NH$_3$ production rate of 10$^{-9}$ mol s$^{-1}$ cm$^{-2}$ was obtained using SrCe$_{0.95}$Y$_{0.05}$O$_{3-\delta}$ as a solid electrolyte [10]. In this study, the perovskite-type oxides BCS and BCGS were employed as electrolytes in the synthesis of ammonia at atmospheric pressure. An ammonia production rate of 10$^{-9}$ mol s$^{-1}$ cm$^{-2}$ was obtained.
2. Methods and experiments

2.1. Preparation of BCS

The synthesis of BCS ceramics was carried out as follows. Sm$_2$O$_3$ (AR) was dissolved in HNO$_3$. Calculated amounts of Ba(NO$_3$)$_2$ and (NH$_4$)$_2$Ce(NO$_3$)$_6$ were added to the solution. Subsequently, solid citric acid was added to the solution, resulting in a mole ratio of [citric acid]:[Ba$^{2+}$]:[Ce$^{4+}$]:[Sm$^{3+}$] = 2:1:1. The solution was then slowly evaporated using a water bath at 60°C until a viscous liquid was obtained. When the temperature was maintained at 100°C for 5 h, a gel-like porous mass was formed. This gel was placed in a constant-temperature drying oven at 110°C for 5 h. A solid mass was obtained. Then, the solid mass was ground slightly in an agate mortar and calcined in an electric burner at 700°C for 5 h. An ultrafine powder of BaCe$_{0.90}$Sm$_{0.10}$O$_3$ was formed. The calcined powder was then pressed into pellets at about 30 MPa pressure and sintered in air at 1400°C for 10 h to prepare ceramic samples [11,12]. BCGS ceramics were prepared in the same way.

2.2. Characterization

The thermal decomposition of the samples was characterized by thermal analysis (TG-DTA), from which the optimum calcination temperature was obtained. The topography was observed by scanning electron microscopy (SEM). A single perovskite-type phase was confirmed by X-ray diffraction (XRD) ($\text{CuK}_\alpha$ radiation, $\lambda = 1.54056$ Å).

2.3. Application of ceramics as an electrolyte in the synthesis of ammonia at atmospheric pressure

After polishing both surfaces of sintered plates (20 × 20 × 0.8 mm$^3$) of BCS and BCGS, the surfaces were coated with commercially available Ag–Pd paste and the plates were baked at 800°C for 15 min to form a porous electrode on each surface of the plates. The area of each electrode was 1.13 cm$^2$. A Pt lead wire served as the output terminal for Ag–Pd electrodes. Then, the electrode was placed in a custom-built stainless-steel reactor (see Fig. 1). The cathode was exposed to a dry pure nitrogen stream (by passing through P$_2$O$_5$ at a volumetric flow rate of 3.0 × 10$^{-3}$ m$^3$ s$^{-1}$). A flow of 99.999% hydrogen at a flow rate of 1.0 × 10$^{-4}$ m$^3$ s$^{-1}$ at atmospheric pressure was maintained over the anode (saturated with water vapor at room temperature). The two electrodes were connected to a potentiostat on which the desired potential was applied (a potential of 0.6 V was used in this study). Then, ammonia was synthesized in the cell with the structure H$_2$, Ag–Pd | La$_{1.9}$Ca$_{0.1}$Zr$_2$O$_{6.95}$| N$_2$, N$_2$, H$_3$. The synthesized ammonia in the outlet gas was adsorbed by 10 mL of dilute sulfuric acid with an initial pH of 3.48. The concentration of NH$_4^+$ in the adsorption solution was measured by spectrophotometry after Nessler’s reagent was added to the adsorption solution. The concentration of NH$_4^+$ in the adsorption solution obtained at different temperatures was measured to determine the optimum operating temperature. At this temperature, the dependence of the rate of NH$_3$ formation on the potential was obtained.

3. Results and discussion

3.1. Thermal decomposition

Fig. 2 shows the TG and DTA results of the thermal decomposition of BCS, which consisted of several stages. A small exothermal peak first appeared at around 220–280°C, corresponding to a weight loss of about 55%. This mainly resulted from the desorption of the adsorbed water, structural water, nitric acid, and citric acid in the primary powders. Subsequently, the highest exothermal peak appeared at around 320–540°C in the DTA curve, corresponding to a further weight loss of 25.6%. This was mainly due to the decomposition of organic compounds, nitrates, and partial carbonates. Carbon dioxide and complex oxides were formed at this stage along with a large amount of heat. A further increase in temperature did not result in further weight loss, and the weight remained constant. The total weight loss was 83.25% during the entire process. From these results, 650°C appears to be the optimum temperature for the calcination of BCS powder. Similarly, 680°C appears to be the optimum temperature for the calcination of BCGS powder.

3.2. XRD analysis

The XRD patterns of the sintered samples are shown in Fig. 3. The specimen shows a single perovskite-type phase corresponding to the JCPDS files nos.: 22–74. Although a few impurities are present, their very low content should not bring about a phase transition. The relative densities of the samples were more than 90% of the theoretical values after annealing at 1400°C for 10 h [13].

![Diagram](image1.png)

Fig. 1. Diagram of the device used in the experiment.
3.3. SEM analyses

The microstructures of the ceramics were examined by SEM, and were characterized by well-defined grains with a wide distribution of sizes and high porosity, as shown in Fig. 4 (BCS) and Fig. 5 (BCGS). Doping resulted in the formation of larger grains surrounded by small interconnected grains. The similarity of these microstructural features to those reported in Ref. [14] suggests that the enhancement in ionic conductivity in doped perovskite-type oxides could be attributed to improvements of both grain interior and grain boundary conductivities, by resolving the total conductivity into the grain interior and grain boundary contributions.

BCGS had higher conductivity than BCS under an atmosphere of hydrogen gas saturated with water vapor; the former produced more ammonia than the latter. This could be due to the fact that the proton transport number of BCGS is very close to unity under the experimental conditions of the present study in which proton conduction is predominant:

\[
\text{H}_2\text{O} + 2\text{h}^+ = 2\text{H} + \frac{1}{2}\text{O}_2
\]

\[
\text{H}_2\text{O}(g) + V_{O} = 2\text{H} + O_{O}^x
\]

In addition to proton conductivity, BCS probably showed oxygen ion conductivity, which contributes less to the formation of ammonia:

\[
V_{O} + \frac{1}{2}\text{O}_2 = O_{O}^x + 2\text{h}^+.
\]

Fig. 2. TG and DTA curves for the thermal decomposition of BCS.

Fig. 3. XRD patterns of samples.

Fig. 4. SEM image of BCS sintered at 1400 °C.
Also, a small amount of electronic conduction results from the charge transfer between two ions of different valences:

\[ \text{Ce}^{3+} + \text{h} \leftrightarrow \text{Ce}^{4+}. \]

Thus, BCGS had better electrocatalytic properties. This is evident from the results of electrochemical studies on BCS and BCGS.

3.4. Electrochemical studies

Fig. 6 shows an Arrhenius plot of the conductivity of BCS and BCGS in different atmospheres. It can be seen that the electronic conductivity of BCGS is much higher than that of BCS. Both samples showed higher electrical conductivity in wet H\textsubscript{2}/dry N\textsubscript{2} than in dry air. This also demonstrated the proton conductivity of the samples. Thus, we could separately determine the proton conductivity and the electrical conductivity by considering the Arrhenius plot. Our results also indicated that the presence of water vapor promotes proton conductivity.

3.5. Synthesis of ammonia at atmospheric pressure using the new electrolytes

The concentration of NH\textsubscript{4}\textsuperscript{+} in the adsorption solution was measured at different operating temperatures by spectrophotometry. The rate of ammonia formation was calculated and results are listed in Table 1.

The rate of ammonia formation for both samples reached a maximum at 620 °C. Moreover, BCGS had a maximum formation rate of 5.82 × 10\textsuperscript{-9} mol s\textsuperscript{-1} cm\textsuperscript{-2}. Therefore, 620 °C was used as the optimum temperature in our study. This can be explained by the fact that the rate of ammonia formation depends not only on the proton conductivity and the flow rates of H\textsubscript{2} and N\textsubscript{2} but also on the rate of NH\textsubscript{3} decomposition. Increasing the temperature causes the conductivity to increase. At the same time, the rate of NH\textsubscript{3} decomposition also increases. This explains the peak that appears if the rate of NH\textsubscript{3} formation is plotted against temperature.

A blank test was conducted by bubbling the exit gas from the cathode through dilute sulfuric acid for 10 min with the cell operating under open-circuit conditions. The lack of pH or color change after adding Nessler’s reagent to the absorption solution confirms the absence of ammonia. The effect of the potential on the rate of ammonia formation was also evaluated. Fig. 7 shows the result. At above 0.6 V, the rate of ammonia formation for both samples increased only slightly. It was concluded that 0.6 V was the optimum potential for synthesizing ammonia in this study. It was also demonstrated to be the optimum potential for the temperature range of the experiments.

In the process of synthesizing ammonia at atmospheric pressure using electrochemical methods, the rate of ammonia formation is affected by several factors, including the volumetric flow rates of H\textsubscript{2} and N\textsubscript{2}, the potential, the rate of NH\textsubscript{3} decomposition, and the area of the electrode. In this study, the area of the electrode was 1.13 cm\textsuperscript{2}, which is too small to convert all the H\textsubscript{2} into NH\textsubscript{3}, but the flow of N\textsubscript{2} rapidly removed the ammonia that formed, which effectively decreased the NH\textsubscript{3} decomposition at high temperatures. In addition, recycling the unused H\textsubscript{2} also improved the efficiency of hydrogen utilization.

![Fig. 5. SEM image of BCGS.](image)

![Fig. 6. Arrhenius plot of conductivity for samples in different atmospheres.](image)

| Temperature (°C) | 550 | 600 | 620 | 640 | 660 | 680 |
|------------------|-----|-----|-----|-----|-----|-----|
| BCS              | 3.47| 4.91| 5.23| 4.85| 3.92| 3.66|
| Rate of ammonia  | 4.26| 5.61| 5.82| 5.44| 4.66| 4.16|
4. Conclusion

Doped perovskite-type oxides of BaCe$_{0.90}$Sm$_{0.10}$O$_{3-\delta}$ (BCS) and BaCe$_{0.80}$Gd$_{0.10}$Sm$_{0.10}$O$_{3-\delta}$ (BCGS) were synthesized by the sol–gel method. Single-phase and well-defined perovskite-type structures were obtained. The relative densities of sintered plates of BCS and BCGS were more than 90% of their theoretical values after heat treatment at 1400°C for 10 h. The codoped BCGS ceramic shows much greater electrocatalytic activity than BCS. Using sintered samples as a solid electrolyte, ammonia was synthesized from nitrogen and hydrogen at atmospheric pressure in a solid-state proton-conducting cell reactor using electrochemical methods. Both samples showed high proton conductivity. However, the double-doped BCGS system is more useful for the electrocatalysis of ammonia formation. The maximum rate of ammonia formation was $5.82 \times 10^{-3}$ mol s$^{-1}$ cm$^{-2}$.

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