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Preparation of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ by the citrate method and its application in the synthesis of ammonia at atmospheric pressure

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Abstract $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ is a kind of high-temperature proton conductor. A precursor of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ solid electrolyte was synthesized by the citrate method and characterized by thermal analysis (thermogravimetric analysis–differential thermal analysis), X-ray diffraction and scanning electron microscopy. Using the sintered samples as a solid electrolyte and silver–palladium alloy as electrodes, we synthesized ammonia from nitrogen and hydrogen at atmospheric pressure in the solid-state proton-conducting-cell reactor. The rate of evolution of ammonia was up to $3.09 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$.

Keywords High-temperature proton conductor · $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ · Ammonia synthesis · Citrate method · Perovskite type

Introduction

High temperature proton conduction in perovskite-type oxides has received much attention since their discovery in 1981 [1]. At present, several oxides of the perovskite structure are good protonic conductors in water or hydrogen-containing atmospheres. The development of proton-conducting oxides is of considerable interest, as they can be used as solid electrolytes in fuel cells, sensors for hydrogen and water, and for other electrochemical and catalytic applications [2, 3, 4, 5]. Perovskite oxides based on BaCeO_3 in which some trivalent cations are partially substituted for cerium exhibit appreciable proton conduction [6]. This is especially so for Gd-doped barium cerate, which has the highest electrical

conductivity [7]. In this study, Gd-doped barium cerate $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ ceramics were prepared.

High-temperature proton conduction has been reported for a large number of solid materials, and much research has been performed on the conduction mechanism, structure characterization, electrical measurements and applications. The high-temperature proton-conducting ceramics were traditionally synthesized by solid-state methods, in which the sintering temperature is above 1,600 °C for several hours. Obviously, it required much more time and a much higher temperature. Moreover, the hardness of the sinters obtained by solid-state methods was poor as the sintering density. In previous work, we synthesized ammonia with $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ which had been prepared by the citrate method; the rate of ammonia formation was much higher than that of the samples prepared by solid-state methods [8]. In this study, the citrate method was employed to prepare ultrafine powders of perovskite-type oxides.

The traditional method for ammonia synthesis is the Haber process, in which gaseous nitrogen and hydrogen react on a catalyst at high temperature (450–500 °C) and high pressures (150–300 bar). There was a stringent requirement for the equipment and it was limited by thermodynamics. Ammonia synthesis at atmospheric pressure using solid-state proton conductors as the electrolyte has been investigated. Marnellos and Stoukides used $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ as the electrolyte; ammonia was synthesized and the yield was $10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$ [9, 10]. In this study, perovskite-type oxide, $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$, was employed as the electrolyte in the synthesis of ammonia at atmospheric pressure. An ammonia production rate of $3.09 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$ was obtained.

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Experimental

Preparation of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ ceramic

Gd_2O_3 (analytical reagent) was dissolved in HNO_3 . Calculated amounts of $\text{Ba}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$

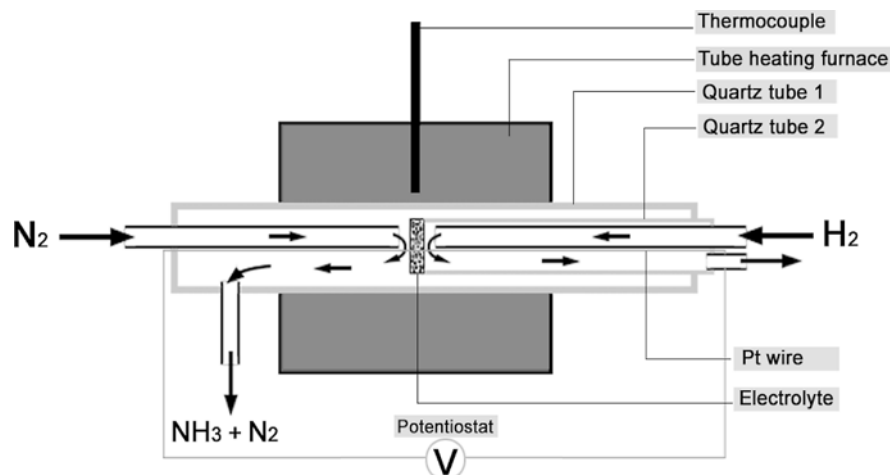
were added to the solution. Subsequently, solid citric acid was added to the solution, resulting in a molar ratio of citric acid to barium to cerium plus gadolinium of 2:1:1. The solution was then slowly evaporated on a water bath at 60 °C until a viscous liquid was obtained. When the temperature was maintained at 100 °C for 5 h, a gel-like porous mass formed. This gel was placed in a constant-temperature drying oven at 110 °C for 5 h. A solid mass was obtained. Afterwards, the solid mass was ground slightly in an agate mortar and calcined in an electric burner at 600 °C for 5 h. Ultrafine powders of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ were formed. The calcined powders were then pressed into pellets with about 30 MPa pressure and sintered in air in at 1,300 °C for 10 h to prepare ceramic samples [11, 12].

The thermal decomposition was characterized by thermal analysis (thermogravimetric analysis, TG–differential thermal analysis, DTA; NETZSCH-STA-449C), from which the optimum calcination temperature was obtained. The topography was characterized with scanning electron microscopy (SEM; JSM-6300). A single perovskite-type phase was confirmed by X-ray diffraction (XRD; MAC.M18XCE).

Application of the ceramic as an electrolyte in the synthesis of ammonia at atmospheric pressure

Commercial Ag–Pd pastes were baked as porous electrodes on each side of the sintered plate (20 mm×20 mm×8 mm) at 800 °C for 15 min. The area of the electrode was 1.13 cm². The Pt lead wire served as output terminals for the Ag–Pd electrodes. Then the electrode was placed in a homemade stainless steel reactor (Fig. 1). The cathode was exposed to a dry pure nitrogen stream (by passing through P₂O₅, volumetric flow rate of 3.0×10⁻⁴ m³ s⁻¹). Hydrogen (99.999%, saturated with water vapor at room temperature) was flowed over the anode at a rate of 1.0×10⁻⁴ m³ s⁻¹ at atmospheric pressure. The two electrodes were connected to a potentiostat (DLS-292), which provided the desired potential (0–3.0 V).

Fig. 1 Schematic diagram of the experiment



Then ammonia was synthesized in the cell $\text{H}_2, \text{Ag-Pd}|\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}|\text{N}_2, \text{NH}_3$. Ammonia synthesized in the outlet gas was adsorbed by 10 ml dilute sulfuric acid with an initial pH of 3.48. The concentration of NH_4^+ in the absorption solution was analyzed by spectrophotometry.

Results and discussion

Characterization

Figure 2 shows TG and DTA results of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$. It can be seen that the processes of thermal decomposition consisted of several steps. A slight exothermal peak evolved around 210–320 °C in the curves, corresponding to a weight loss of 50.56%. This mainly resulted from desorption of the adsorbed water, structural water, nitric acid, and citric acid, etc., in the

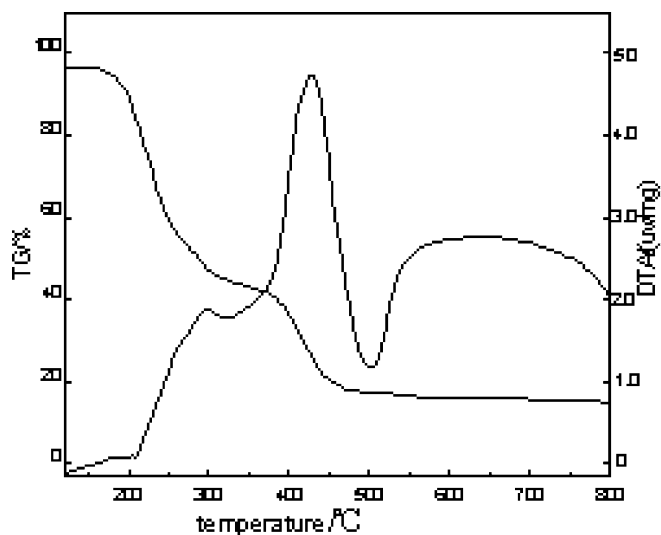


Fig. 2 Thermogravimetric (TG) analysis and differential thermal analysis (DTA) curves for $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ in an air atmosphere

primary powders. Subsequently, the highest exothermal peak was around 320–500°C in the DTA trace, corresponding to the greatest weight loss of 27.57%. This mainly arose from the decomposition of organic compounds, nitrate and partial carbonates. Carbon dioxide and complex oxides were formed in this step with a large amount of heat liberation. With further temperature increase, the weight approached a constant value. The total weight loss was 84.46% for all the processes. From the overall change of the curve, 600 °C appears to be the optimum temperature to calcine the powders.

The $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ ceramic was also examined using SEM for the microstructure, which was characterized by well-defined grains with a wide distribution of sizes, as seen in Fig. 3. The grains were quite distinct. In addition, there is a considerable amount of porosity in the grains. Gd-doping resulted in larger grains surrounded by small interconnected grains.

The powder XRD patterns of the sintered $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ are shown in Fig. 4. The specimens show a single phase of the perovskite-type corresponding to the standard spectrum which the JCPDS card recorded [13]. Although there are a few impurities (25–30°, 40–45°, etc.), as their content is very low, they should not affect transport properties.

The practical density is 6.041 g cm^{-3} measured using Archimedes' methods of samples, which indicated that the practical density is 94.658% sintered referenced to the theoretical density (6.383 g cm^{-3}).

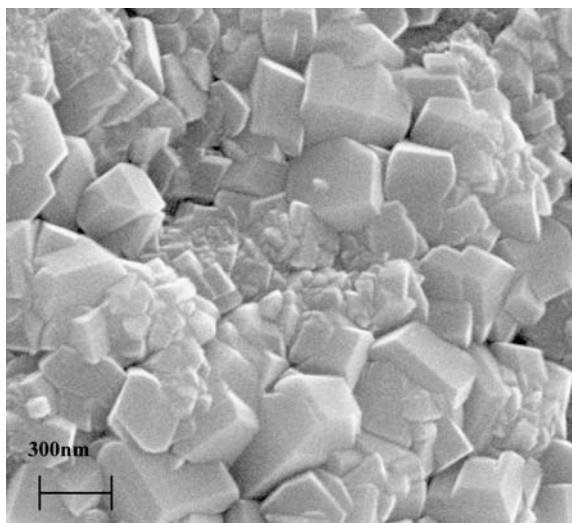


Fig. 3 Scanning electron microscopy image of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$

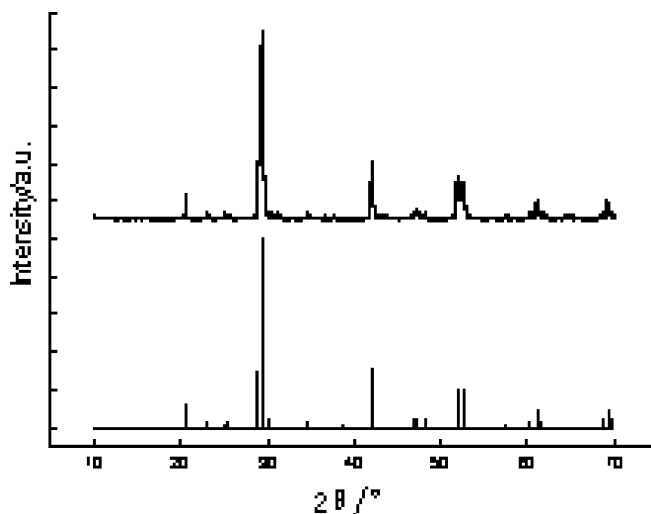


Fig. 4 X-ray diffraction pattern of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ sintered at 1,300 °C

Synthesis of ammonia at atmospheric pressure with $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ as the electrolyte

When Nessler's reagent is added to the adsorption solution, a stable yellow color appears immediately. This indicated that there was NH_4^+ in the adsorption solution and that it reacted with Nessler's reagent. The concentration of NH_4^+ in the adsorption solution was maintained for 15 min, which can make it achieve a steady state, and was measured at different operating temperatures by spectrophotometry [14]. The rate of ammonia formation was calculated, as listed in Table 1.

The rate of ammonia formation reached a maximum at 480 °C. As a result, 480 °C was used as the optimum temperature in our study. This can be explained by the theory that the rate of ammonia formation depends not only on the capability of proton conduction and the flow rate of H_2 and N_2 , but also on the rate of NH_3 decomposition. If the temperature increases, conductivity increases. At the same time, the rate of NH_3 decomposition also increases. This explains the peak appearing in the curve of the rate of NH_3 formation and temperature [10].

A blank test was conducted by bubbling the exit gas from the cathode for 10 min through the 10 ml dilute sulfuric acid with the cell operating under open-circuit conditions. There was no pH change in the blank test and no color change after adding Nessler's reagent. This indicated that no NH_3 was produced. And we also tested the effect of potential on the rate of ammonia formation. Figure 5 shows that after 0.6 V, the rate of ammonia

Table 1 The rate of ammonia formation at different operating temperatures under 0.6-V potential

Temperature (°C)	460	480	500	520	540	560
Rate of NH_3 formation ($\pm 0.02 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$)	1.26	3.09	1.83	1.27	0.92	0.86

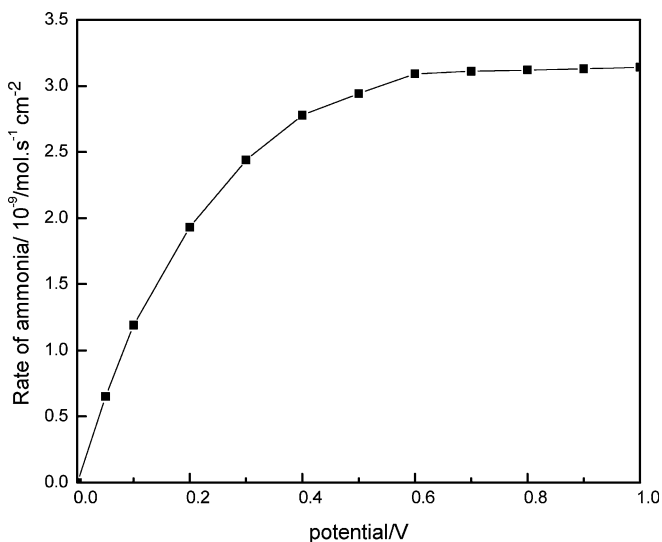


Fig. 5 Effect of potential on the rate of ammonia formation

formation increases slightly. It can be seen that 0.6 V was the optimum potential for the synthesis of ammonia in this study. And it is also proved to be the optimum potential for all the temperature ranges as determined by experiment.

When synthesizing ammonia at atmospheric pressure using electrochemical methods, the rate of ammonia formation is affected by several factors, including volumetric flow rate of H_2 and N_2 , potential, the rate of ammonia decomposition and the area of the electrode. In this study, the area of the electrode was 1.13 cm^2 , which is too small to convert all H_2 into NH_3 . To increase the conversion rate of H_2 and ensure that the conversion is carried out quantitatively, it is necessary to increase the area of the electrode.

Conclusion

Perovskite-type complex oxides of $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ were synthesized by the citrate method. A single phase with a well-defined perovskite-type structure was obtained. The relative density of the sintered plates was more than 90% when they were prepared at $1,300 \text{ }^\circ\text{C}$ for 10 h.

Using sintered samples as a solid electrolyte, we synthesized ammonia from nitrogen and hydrogen at atmospheric pressure in the solid-state proton-conducting-cell reactor using electrochemical methods. The rate of evolution of ammonia was up to $3.09 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$.

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