

FREEZE-DRYING SYNTHESIS OF $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_3$ WITH IN SITU GENERATED COFE ALLOY FOR AMMONIA SYNTHESIS

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Abstract

Ammonia is not only an important chemical feedstock but also a promising hydrogen carrier, and its synthesis process strongly depends on the development of efficient catalysts. To address the critical issue of insufficient active sites in perovskite cathode materials for ammonia synthesis in proton-conducting solid oxide electrolyzer cell (PCEC), this study achieves the in situ exsolution of numerous small-sized CoFe alloy nanoparticles on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_3$ by regulating the preparation method and the B-site Co doping content. At 600 °C and 1.8 V, the catalyst achieves a maximum ammonia production rate of $79.2 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, and there is no damage to the cell after continuous working for 5 h.

1 Introduction

Ammonia is a key raw material in various industries, including fertilizer production, pharmaceuticals, and chemical manufacturing. The synthesis of ammonia depends primarily on the Haber–Bosch (HB) technology. However, this process requires sustained harsh reaction conditions of high temperature (above 400 °C) and high pressure (200–300 atm), which not only consumes substantial amounts of fossil fuels (accounting for approximately 2% of global total energy consumption) but also results in significant CO_2 emissions (up to 300 million tons annually) [1].

In recent years, numerous studies have focused on green electrocatalytic ammonia synthesis [2-5], but most current research on electrocatalytic nitrogen reduction reaction (ENRR) is still based on liquid-phase reaction systems. Constrained by the low solubility of N_2 in aqueous electrolytes and the difficulty of activating N_2 , these systems suffer from low ammonia yield rates and faradaic efficiencies, while also increasing the subsequent cost of ammonia separation [6-9].

In contrast, high-temperature solid oxide electrolysis cells operate via a gas-solid reaction mode, where N_2 directly contacts the solid catalyst. The high-temperature conditions not only enhance mass transfer during the reaction process but also effectively reduce the required overpotential. Notably, compared to traditional oxygen-ion conducting solid oxide electrolysis cells, which typically exhibit high conductivity at elevated temperatures (700–800°C), proton-conducting electrolysis cells can achieve favorable conductivity at relatively lower temperatures (approximately 450–600°C). This lower temperature is both thermodynamically beneficial for the ammonia synthesis equilibrium and critical to suppress the decomposition of the produced ammonia [10-12].

In 1998, Skodra and Stoukides [13] first proposed the use of proton-conducting electrolysis cells for ammonia synthesis, utilizing steam as the hydrogen source, which offered a more efficient route for ammonia production. Subsequently, the research groups of Ma [14-20] and Wang [21-23] optimized the electrolyte composition, significantly improving its ionic conductivity and successfully applying it to electrochemical ammonia synthesis. In recent years, the research focus in this field has gradually shifted toward the development of high-performance perovskite cathode materials for the nitrogen reduction reaction.

In 2017, Ibrahim [24] et al. synthesized a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_3$ composite material via the sol-gel method for electrochemical ammonia synthesis in a humid nitrogen atmosphere; however, the resulting material exhibited significant particle agglomeration. In 2022, Wang [25] et al. synthesized $\text{Sr}_{0.9}\text{Ti}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$, also using the sol-gel method. Although some improvements have been achieved in the particle dispersion and pore uniformity of the catalyst, the issue of large particles remains unresolved. The microstructure of the catalyst plays a decisive role in its ammonia production performance. However, limited by traditional preparation methods, it is difficult to achieve the preparation of smaller-sized catalysts, which fundamentally restricts the further enhancement of its ammonia production performance.

Here, we synthesizes a series of perovskite cathode materials for proton-conducting electrolysis cells, focusing on both optimization of the preparation method and rational design of material composition. These materials were mainly doped in the content of Co on the B-site, which induced the precipitation of Co and Fe metal particles on the surface and the formation of CoFe alloy. Large quantities of fine-sized CoFe alloy nanoparticles are identified as the primary active

sites for N₂ adsorption and activation, and we aim to fabricate BSCF perovskite materials with optimal ammonia synthesis rate through systematic regulation of the material preparation process and B-site cobalt doping content. The results revealed that the Ba_{0.5}Sr_{0.5}Co_{0.3}Fe_{0.7}O₃ catalyst prepared by freeze-drying exhibits the highest ammonia synthesis rate at 600 °C and 1.8 V, with the rate of 79.2×10⁻¹² mol·cm⁻²·s⁻¹.

2. Methods

2.1 Material synthesis

The cathode materials ceramic oxide powders Ba_{0.5}Ce_{0.5}Co_xFe_{1-x} (x=0.1, 0.2, 0.3, 0.4, 0.5) (BSCF) were prepared using three different methods respectively. First, the cathode materials were synthesized by the solid phase method [11]. The raw materials (Ba₂O₃, SrCO₃, Co₂O₃, and Fe₂O₃) were accurately weighed stoichiometrically and combined with ethanol dissolution in two ball milling tanks for about 3 h. After drying, the powder was sintered at 950 °C for 10 h in air to obtain BSCF. Secondly, the cathode materials were prepared by the sol-gel method [26]. To avoid the occurrence of nitrate ions during the ammonia synthesis process and prevent nitrogen pollution, the synthesis of the material was carried out using acetate. The (CH₃COO)₂Ba, (CH₃COO)₂Sr·0.5H₂O, Fe(OH)(CH₃COO)₂·nH₂O, and (CH₃COO)₂Co were dissolved in deionized water at a certain stoichiometric ratio. According to the ratio of C₁₀H₁₆N₂O₈: C₆H₈O₇·H₂O: total number of metal oxides ions = 1: 1.25: 1, C₁₀H₁₆N₂O₈ and C₆H₈O₇·H₂O were added to the mixed solution, and ammonia water was added to adjust the pH. After heating and stirring to completely dissolve and form a clear and transparent solution, the pH was adjusted to 7-8. The prepared solution was further heated and stirred at 80 °C to remove moisture and form a gel-like substance. The temperature was raised to 150 °C and kept for 10 h to form a dry gel. The dry gel was ground into powder and placed in a muffle furnace for 600 °C sintering for 4 h to remove hydrocarbons. After ball milling the calcined powder for 10 hours, it was sintered at 950 °C for 10 h to obtain BSCF. Finally, the cathode material was prepared by the freeze-drying method [27-28]. The solution was synthesized by the sol-gel method. The prepared solution was then heated and stirred at 80 °C to remove water and form a gel-like substance. The gel was frozen with liquid nitrogen for 20 min and then placed in a freeze vacuum drying machine for drying for 36 h to form a dry gel. The dry gel was ground into powder and placed in a muffle furnace for sintering at 600 °C for 4 h to remove carbon and hydrogen compounds. After calcination, the powder was ball-milled for 10 h and then sintered at 950 °C for 10 h to obtain BSCF.

The BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O₃ (BZCYYb) ceramic proton conducting electrolyte powder was synthesized via glycine-nitrate combustion and held in the muffle furnace at 1050 °C about 3 h.

2.2 Cell preparation

The anode, electrolyte and cathode in the battery with anode support were prepared respectively by dry pressing method, spin coating method and screen printing method.

Mix the powders in a ratio of NiO: BZCYYb: starch (foaming agent) = 6: 4: 2. After grinding with alcohol for 48 h to ensure complete mixing, dry it to obtain the anode material. Prepare the electrolyte coating slurry according to the proportion of 5 g BZCYYb, 0.36 g C₆H₁₅NO₃, 0.3 g HO(CH₂CH₂O)_nH, 0.3 g C₁₆H₂₂O₄, and 15g ethanol. Ball-mill it for 60 hours. Mix the powders in a ratio of BSCF: BZCYYb = 1: 1. Add alcohol for grinding for 48 h to ensure complete mixing. After drying, add the powder in a 1: 1 ratio to the binder (C₁₀H₁₈O: ethyl cellulose = 94:6) and ball-mill for 10 h to obtain the cathode slurry. Weigh 6 g of the anode material and add it to a 18 mm diameter mold. Keep it under a pressure of 300 MPa for 30 s to obtain the anode support layer. Bake the anode support layer at 1000°C for 2 h to remove the organic matter and form a porous structure. Use a spinner to spin-coat 150 mg of the electrolyte slurry on the surface of the anode support three times at a speed of 8000 rpm. Pre-sinter it at 800 °C for 2 h to remove the organic matter, then sinter it at 1450 °C for 5 h to form a dense electrolyte layer. Obtain a half-cell with a total area of 1.32 cm². Brush the cathode catalyst on the electrolyte surface using a 300-mesh template. Sinter the battery at 950 °C for 2 h to remove the organic matter from the cathode slurry. Obtain a battery with an effective area of 0.2826 cm² by coating both the anode and cathode electrodes with silver paste. Stick the silver wires onto the electrodes and seal the battery in one end of an alumina ceramic tube using ceramic glue to complete the battery assembly.

2.3 Characterization

The crystal information was collected by the X-ray powder diffraction (XRD-6100, Shimadzu). Scanning electron microscope (SEM) was used for analyzing the microscopic morphology of the catalyst (MAIA3LMH, TESCAN).

2.4 Ammonia synthesis

At a temperature range of 400-600 °C, different voltages were applied to the battery, and 20 mL·min⁻¹ of H₂ was introduced to the anode. Meanwhile, 20 mL·min⁻¹ of N₂ was introduced to the cathode. 2 mL of HCl (9 mmol·L⁻¹) was used to absorb for 40 min, and the concentration of NH₄⁺ was tested by cation chromatography. The collected ammonia rate was calculated using the following equation:

$$r_{\text{NH}_3} = \frac{V \times c_{\text{NH}_4^+}}{t \times A} \quad (1)$$

where V (mL) is the volume of HCl used to collect NH₃, c_{NH₄⁺} (mol·mL⁻¹) is the measured concentration of NH₄⁺, t (s) is the collection time of ammonia, and A (cm²) is the effective area of the cell cathode catalyst.

3 Results

3.1 Catalyst characterization

Fig. 1 shows the XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ materials prepared by three methods (traditional solid-phase method, sol-gel method, and freeze-drying method). The catalyst powders prepared by all three methods exhibit a standard single perovskite structure without any other impurity peaks, and the peak shapes are sharp, indicating that the crystallinity of the samples is good.

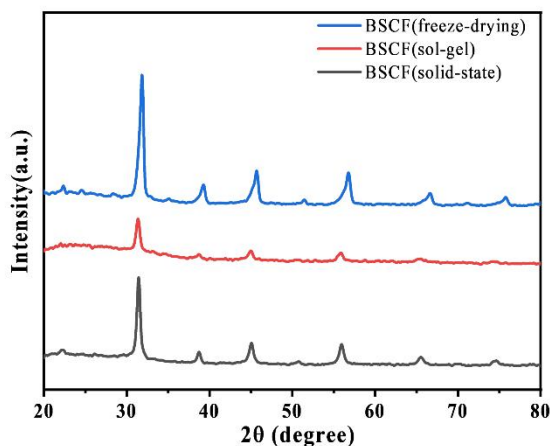


Fig. 1 XRD spectra of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ prepared by different methods

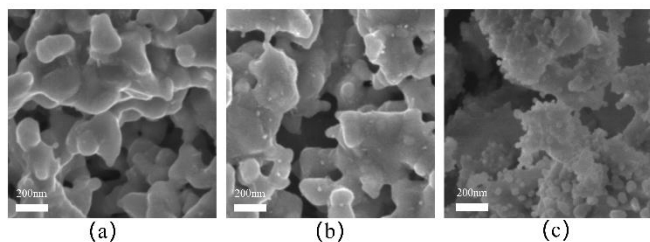


Fig. 2 SEM image of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ prepared by different methods. (a) solid-state method; (b) sol-gel method; (c) freeze-drying method.

Fig. 2 shows the SEM images of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ catalysts synthesized by three methods after being reduced at 600 °C at H_2 atmosphere for 4 h. In Fig. 2a, the catalyst exhibits a relatively smooth surface, whereas in Fig. 2b, distinct nanoparticles are clearly observed on the surface. Notably, Fig. 2c shows the highest density of nanoparticles. These observations suggest that, compared to the conventional solid-state reaction method, the powder synthesized via the sol-gel approach possesses a smaller particle size, which facilitates the exsolution of metallic nanoparticles. Furthermore, the incorporation of freeze-drying enhances the uniformity of material dispersion and results in smaller pore sizes, promoting the exsolution of a greater number of nanoparticles. Therefore, the material prepared by the freeze-drying method was selected for subsequent ammonia synthesis performance studies.

3.2 Performance of ammonia synthesis

Firstly, the catalyst with the highest NH_3 synthesis rate needs to be selected for the subsequent experiments. The ammonia synthesis performance of perovskites with varying Co contents was evaluated at 600 °C under an applied potential of 1.0 V. As shown in the Fig. 3, with increasing Co content, the ammonia synthesis rate initially increases and then decreases. This trend can be attributed to the fact that the introduction of Co facilitates nitrogen activation, while an excessive Co content reduces the Fe content in the material. The optimal performance, with an ammonia yield of $55.4 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, was achieved at a Co content of 0.3. Therefore, this composition was selected for subsequent ammonia synthesis studies.

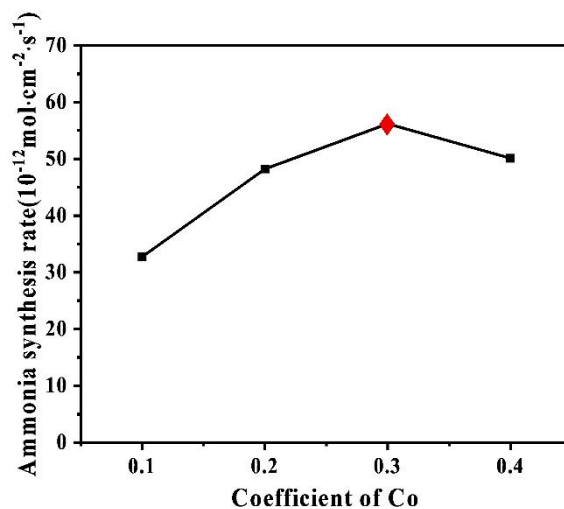


Fig. 3 The influence of Co content in perovskite on ammonia synthesis rate.

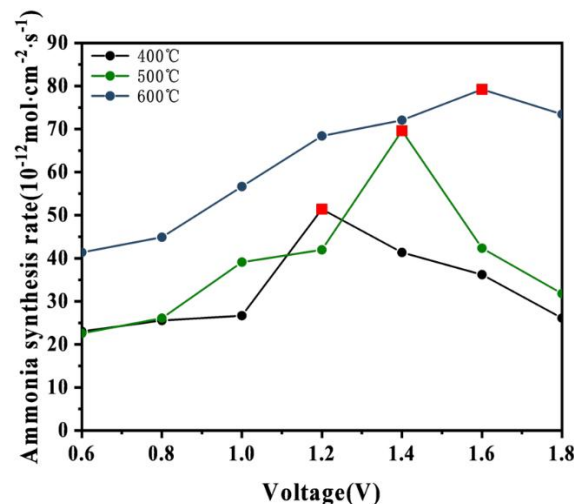


Fig. 4 Ammonia Production rate of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_3$.

Previous studies have revealed that the main reasons affecting the rate of ammonia synthesis are the temperature and the applied voltage. In order to further demonstrate the optimal performance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_3$, we conducted ammonia production performance tests under different reaction temperatures and different potentials. As shown in Fig. 4, at each temperature, the ammonia production rate

initially increases and then decreases with increasing applied potential, indicating the existence of an optimal potential for ammonia synthesis. Specifically, at 400 °C, the optimal potential is 1.2 V, achieving an ammonia production rate of $51.4 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. At 500 °C, the optimal potential shifts to 1.4 V, with a corresponding rate of $69.6 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. At 600 °C, the optimal potential is 1.8 V, yielding a rate of $79.2 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. This trend can be attributed to the fact that, at a fixed temperature, an increase in applied potential enhances the current, thereby promoting proton transport through the solid electrolyte. However, the increased proton flux leads to greater occupation of active sites by protons, which favors the competing hydrogen evolution reaction and consequently reduces the ammonia production rate. Furthermore, we conducted stability tests on the material under the optimal reaction conditions at three different temperatures, as shown in the Fig. 5. During the 5 h operation, the current density of the battery remained stable.

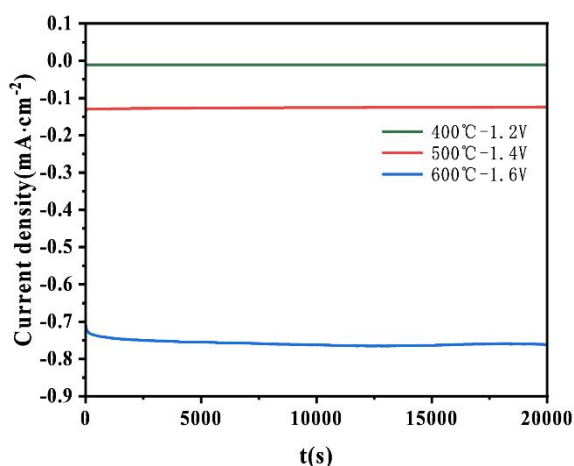


Fig. 5 Long-term stability test of general overview point.

4 Conclusion

In this study, the ammonia production performance of BSCF under high-temperature electrocatalytic conditions was investigated. Through a comparative evaluation of various perovskite preparation methods, the freeze-drying technique was ultimately employed to synthesize BSCF perovskite, which exhibited high porosity and fine particle sizes. By systematically regulating the B-site Co doping content, a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_3$ material with optimal ammonia production performance was obtained. Under a high-temperature hydrogen atmosphere, CoFe nanocrystals with catalytic activity for the NRR were in situ exsolved from the perovskite matrix. The results demonstrate that at 600 °C and an applied potential of 1.8 V, the catalyst achieves an ammonia production rate of $7.92 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$; even at a lower temperature of 400 °C, it maintains an ammonia production rate of $5.14 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. These findings indicate that the perovskite material prepared by freeze-drying, with in situ exsolved CoFe alloys, exhibits significant catalytic performance in high-temperature electrocatalytic nitrogen reduction.

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6 References

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