Electrochemical synthesis of ammonia on Ru-doped perovskite type electrode and its thermal catalytic property for ammonia synthesis

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Abstract: We investigated the effect of Ru-doping to a cathode catalyst for electrochemical synthesis of ammonia using a proton conducting solid electrolyte and cermet electrodes of Ni and $BaCe_{0.9-x}Y_{0.1}O_{3-\delta}$ (Ni-BCY) at atmospheric pressure. Additionally, the performance of Ru-doped BCY perovskite (BCYR) for thermal catalytic synthesis of ammonia was evaluated; optimum reduction temperature of the catalyst was examined. The electrochemical synthesis was performed using dry nitrogen and wet hydrogen at 600 °C in a double chamber reactor. The maximum ammonia formation rate of 1.8×10^{-10} mol s^{-1} cm^{-2} and 0.3×10^{-10} mol s^{-1} cm^{-2} were obtained for Ni-BCYR and Ni-BCY electrodes, respectively.
Keywords: Ammonia, Electrochemical synthesis, Thermal catalytic synthesis.

1. Introduction

In recent years, it has been studied to generate hydrogen using electric power derived from renewable energy and further convert it to a chemical substance suitable for storing and transporting such as ammonia. As an alternative to the Harbor-Bosch method requiring high-temperature and high-pressure conditions, we focus on electrochemical synthesis of ammonia[1] from water and nitrogen with renewable electricity[2,3]. Schimatic diagram of the electrochemical synthesis of ammonia is shown in Fig.1. It is considered to be an effective process for ammonia synthesis from the renewable electricity at everywhere. However, the formation rate of electrochemical synthesis of ammonia has been inadequate to use the practical system. Recently, Kosaka *et al*. have reported the possitive effect of Ru doping for electrochemical ammonia synthesis[4]. In the present work, we have studied the electrochemical synthesis of ammonia using Ru-doping $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY) perovskite as a cathode material, and its performance for thermal catalytic ammonia synthesis has been evaluated.

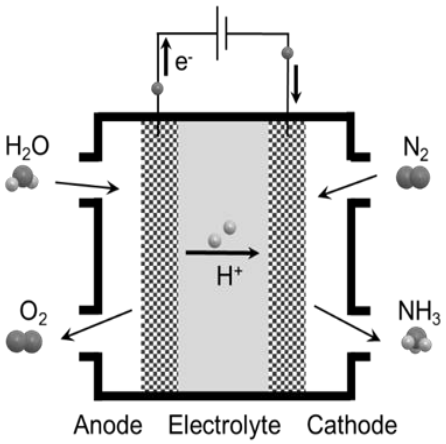

Figure 1. Schematic diagram of electrochemical synthesis of ammonia using a solid electrolytic cell.

2. Experimental

The Ru-doped perovskite type oxide, $BaCe_{0.9}Y_{0.1}Ru_{0.1}O_{3-\delta}$ (BCYR10) was prepared by the citric acid complex method. The obtained precursor powder was calcined at 1200 °C for 12 h. As a cermet type cathode, the composite powder of NiO and BCYR10 (Ni-BCYR10) was prepared by a wet ball milling method. Likewise, Ni-BCY anode powder was also prepared. The obtained electrode powders were pasted on BCY(NiO) electrolyte pellets and calcined at 1300 °C to fabricate a Ni-BCY (anode)|BCY(NiO)|Ni-BCYR10 or Ni-BCY (cathode) cell[2,3].

The thermal catalytic synthesis of ammonia was conducted using a fixed bed flow tube reactor at the temperature range of 350°C to 500 °C. The prepared BCYR10 was reduced in 100% H_2 for 2 h at 400 °C, 600 °C, and 800 °C. Subsequently, a gaseous mixture of N_2/H_2 (N_2:H_2 = 1:3) was fed into the catalyst bed at the total flow rate of 60 mL min^{-1}. The generated ammonia was trapped with dilute sulfuric acid and the ammonia formation rate was determined based on the difference of electrical conductivity of the solution.

Electrochemical synthesis of ammonia was carried out at 600 °C using a double chamber reactor. The 10% H_2/Ar gas was fed into cathode and anode at 800 °C for the reduction of the electrodes. And then, a gaseous dry N_2 was fed into the cathode and a gaseous mixture of 2.3% H_2O/H_2 was fed into the anode. The applied voltage was set to the range of 0 V to −4.0 V *vs*. open circuit voltage (OCV). The generated ammonia was collected with ultrapure water, and the ammonia concentration in the collecting solution was measured by an ion chromatography to determine the ammonia formation rate.

3. Results and discussion

Figure 2 shows the results of the thermal catalytic synthesis of ammonia over the BCYR10 reduced at 400 °C, 600 °C, and 800 °C. The BCYR10 catalyst reduced at 800 °C exhibited the highest ammonia formation rate among three catalysts. We thus conclude that the reduction treatment at 800 °C was the most optimal. Figure 3 shows the results of electrochemical synthesis of ammonia using the fabricated Ni-BCY (anode)|BCY(NiO)|Ni-BCYR or Ni-BCY (cathode) cell with the reduction treatment at 800 °C for both electrodes. Ammonia was hardly synthesized when the applied voltage was 0 V to −2.5 V (vs. OCV), but the ammonia formation rate increased drastically from the applied voltage of −2.8 V. The maximum ammonia formation rate was 1.8×10^{-10} mol s^{-1} cm^{-2} at the applied voltage of −3.3 V and the faraday efficiency was 0.019%. When a voltage was applied in a more negative side than −3.3 V, the ammonia formation rate decreased. This may be caused by that the electrode is hydrogen poisoned, because the hydrogen production reaction of protons conducted through electrolyte is more dominant compared to ammonia production reaction. Electrochemical synthesis of ammonia was also carried out in a cell using a Ni-BCY cathode, the maximum production rate of ammonia was as low as 0.3×10^{-10} mol s^{-1} cm^{-2}. Even when a high voltage was applied, no improvement of the ammonia formation rate was confirmed. This result indicates that the electrochemical synthesis of ammonia was improved by Ru doping to BCY perovskite. Namely, the Ru species were reduced and precipitated on the BCY surface, leading to the enhancement of the ammonia synthesis activity of electrode catalyst.

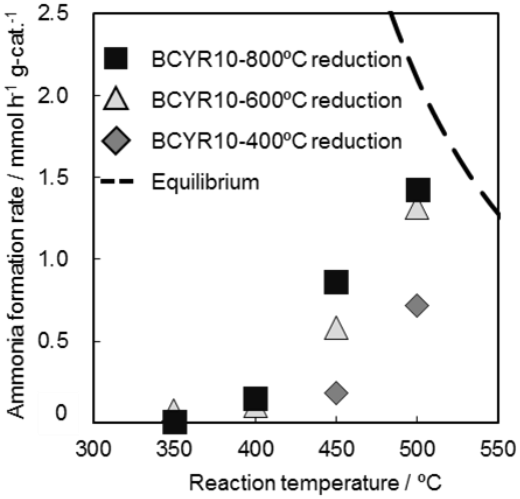

Figure 2. Performance of BCYR10 with the reduction at (■) 800 ºC and (▲) 600 ºC, and (◆) 400 ºC for thermal catalytic ammonia synthesis.

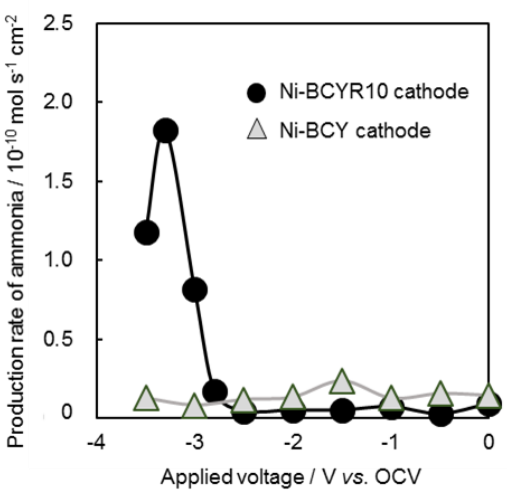

Figure 3. Performance of (●) Ni-BCYR10 and (▲) Ni-BCY cathodes for electrochemical ammonia synthesis at 600 ºC.

Acknowledgements

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References

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