

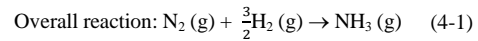
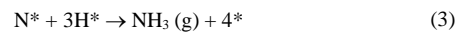
## 論文の内容の要旨

**論文題目** Electrode design and reaction analysis of electrochemical promotion of ammonia synthesis using protonic ceramic fuel cells  
(プロトン伝導性セラミック燃料電池を用いたアンモニア合成の電気化学的促進に対する電極設計と反応解析)

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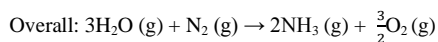
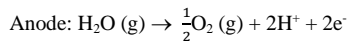
### Introduction

Nowadays, renewable energy has been developed and built in many countries. However, the instability of power supply has become a big issue because it depends on whether or atmospheric condition. To reduce the influence of the disadvantage, the storage for excess renewable energy is necessary. One of the solutions is transferring renewable energy to the energy carriers, such as hydrogen, methane, methanol, and ammonia. Considering the energy density and chemical stability, ammonia is a good candidate as an energy carrier. The artificial way for ammonia production is mainly the Haber–Bosch process, in which  $N_2$  and  $H_2$  react to  $NH_3$  over Fe-based catalysts at high temperature and pressure, as described by Eqs. 1 – 4-1. However,  $H_2$  in the Haber–Bosch process is mostly produced by the steam methane reforming method, which releases a large amount of  $CO_2$ . It is estimated that the Haber–Bosch process releases  $1.5 t_{CO_2} t_{NH_3}^{-1}$ , which contributes to 1.2% of the global  $CO_2$  emission every year. To reduce the carbon emission during ammonia synthesis, scientists proposed an electrochemical process to replace the Haber–Bosch process.



The process of electrochemical ammonia formation can be divided into two types: 1) direct electrochemical reaction of ammonia synthesis using a dual compartment reactor with  $N_2$  and  $H_2O$  (case 1) and 2) indirect electrochemical reaction of ammonia synthesis using a single compartment reactor with  $N_2$  and  $H_2$  (case 2). The reactions are described by the following equations:

Case 1

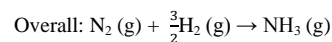
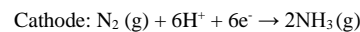
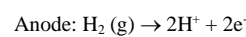


(5)

(6-1)

(7)

Case 2



(8)

(6-2)

(4-2)

In case 1, the reactor must be dual compartment, where  $N_2$  and  $H_2O$  are flowed into the cathode and the anode, respectively. In the anode,  $H_2O$  decomposed to protons, oxygen, and electrons. The protons pass through the proton-conductor electrolyte to the cathode and react with nitrogen molecule to form  $NH_3$  via a charge-transfer reaction at the triple phase boundary (TPB) between gas, proton-conductor, and electrical conductor. In case 2, a gaseous mixture of  $N_2$  and  $H_2$ , which is produced by an extra water

electrolysis device, is supplied into a single compartment reactor. The required voltage for electrochemical ammonia formation in case 2 is lower than that in case 1. Also, with supplying H<sub>2</sub> in the cathode, ammonia can be formed via not only the charge-transfer reaction but also the surface reaction, in which N<sub>2</sub> and H<sub>2</sub> react to form NH<sub>3</sub>. According to the previous studies, the ammonia formation rate in a gaseous mixture of N<sub>2</sub> and H<sub>2</sub> is higher than that in pure N<sub>2</sub>. However, the detailed reaction mechanism is unclear for the electrochemical ammonia formation in a gaseous mixture of N<sub>2</sub>-H<sub>2</sub>.

In this thesis, the reaction mechanism of electrochemical ammonia formation was discussed using proton-conductive fuel cells by using different cathode structures, i.e., cermet structure with long TPB length and metal structure with short TPB length, kinetic analysis, and deuterium isotope analysis using FTIR. Then, to achieve a highly efficient electrochemical process of ammonia formation, the energy efficiency for the electrochemical process was discussed using the single compartment reactor and the dual compartment reactor. The single compartment reactor, operating with a gaseous mixture of N<sub>2</sub> and H<sub>2</sub>, was considered to achieve a higher ammonia formation rate as compared to the dual compartment reactor. The results presented in this thesis can help for cathode design and reactor design in the electrochemical process for ammonia synthesis.

## Experimental

Fe-BCY and W-Fe-BCY cathodes were prepared by the impregnation method, and porous pure Fe cathode was prepared by the doctoral blade method. The properties and structures of the three cathodes are summarized in Table 1.

Table 1 Structures and properties of cathode catalysts

Cathode	Electrode structure	Property
Fe-BCY	Cermet electrode	Relatively long TPB length and high $i_{0,H_2}$
W-Fe-BCY	Cermet electrode	Relatively long TPB length and low $i_{0,H_2}$
Fe	Porous pure Fe electrode	Relatively short TPB length (active site: Fe surface) and low $i_{0,H_2}$

The device for electrochemical ammonia formation is shown in Fig. 1. A single cell is set between two quartz tubes in a furnace. Pyrex glass rings are used to seal the quartz tubes at 900°C. Then, the temperature decreases to operating temperatures (550 – 700°C). The produced ammonia is either flowed into a capture solution of 0.01 mM H<sub>2</sub>SO<sub>4</sub> for high performance liquid chromatography (HPLC) measurement or into a long optical cell for Fourier-transform infrared spectroscopy (FTIR) measurement.

## Results and discussion

The mechanism of electrochemical ammonia formation was discussed using proton-conductive fuel cells by using different cathode structures, i.e., cermet structure with long TPB length and metal structure with short TPB length, kinetic analysis, and deuterium isotope analysis using FTIR. The results are summarized in Table 2.

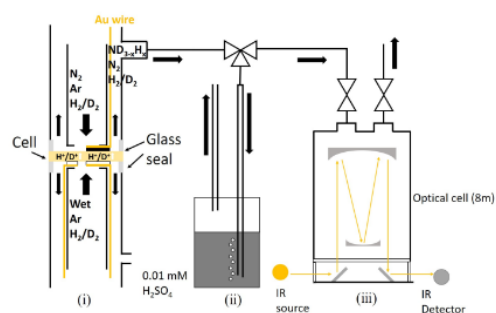


Fig. 1 A schematic of (i) the device for electrochemical ammonia formation, (ii) gas flow into a capture solution, and (iii) FTIR with an optical cell.

Table 2 List of experimental results

Cathode structures (Porous pure Fe cathode shows higher ammonia formation rate than cermet cathodes)	Not charge-transfer reaction
W addition (W-Fe-BCY cathode shows higher ammonia formation rate but lower current density than Fe-BCY cathode)	Promotion of ammonia formation is dominated by electrode potential.
Kinetic analysis: reaction orders of hydrogen ( $\alpha$ ) and nitrogen ( $\beta$ ) ( $\alpha$ and $\beta$ do not change after applying a negative voltage)	Surface reaction
The effect of H <sub>2</sub> partial pressure in the cathode on the ammonia formation (Ammonia formation rate is dependent on H <sub>2</sub> partial pressure)	Not charge-transfer reaction
Deuterium isotope analysis (NH <sub>3-x</sub> D <sub>x</sub> composition has a strong correlation to H <sub>2</sub> (D <sub>2</sub> ) species in the cathode)	Large contribution of surface reaction in the cathode

With a comparison of the performance of electrochemical ammonia formation using different cathode structures, porous pure Fe cathode, which is with short TPB length, shows the highest ammonia formation rate. The result indicates that the reaction is not followed by the charge-transfer reaction. Also, W addition into Fe-BCY improves the ammonia formation rate and reduces the current density, which suggests that the effect of applied voltage/electrode potential on promotion of ammonia formation is more significant than that of current density. Besides, the kinetic analysis was conducted to investigate the reaction mechanism. The values of hydrogen reaction order and nitrogen reaction order at the rest potential do not change after applying a negative voltage, which shows that the reaction is followed by the surface reaction with cathodic polarization. Additionally, as increasing H<sub>2</sub> partial pressure, the ammonia formation rate significantly increased, which implies that the reaction is not followed by the charge-transfer reaction. In deuterium isotope analysis, through the observation of ammonia product (NH<sub>3</sub> or ND<sub>3</sub>), a high correlation between the ammonia product and the H<sub>2</sub>/D<sub>2</sub> species in the cathode was observed, i.e., NH<sub>3</sub> formation in N<sub>2</sub>-H<sub>2</sub> and ND<sub>3</sub> formation in N<sub>2</sub>-D<sub>2</sub>. This result indicates that the reaction is followed by the surface reaction with cathodic polarization.

Through the investigation of reaction mechanism, it is found that the electrochemical ammonia formation is dominated by the surface reaction rather than the charge-transfer reaction. Based on the results, EPOC mechanism is proposed to explain the behavior of electrochemical ammonia formation. The promotion of ammonia formation is caused by an effective double layer which formed via H<sup>+</sup> spillover on the Fe surface. Decreasing the work function of Fe, i.e., increasing an electric field in the effective double layer, can promote the electron backdonation, which will induce electron transfer from the Fe Fermi level to the N<sub>2</sub> antibonding orbital of  $\pi_{2p}^*$ , as shown in Fig. 1. Furthermore, to explain the behavior of ammonia formation in this study, a new parameter, proton diffusion length,  $h$ , was proposed, which represented the area of effective double layer in porous pure Fe cathode. With combining the results of electrochemical ammonia formation and SEM/BET, the proton diffusion length was estimated between sub-micrometers to several micrometers. This result indicates that the thickness of Fe electrode

can be reduced to the proton diffusion length.

Finally, to estimate the energy consumption in electrochemical process using a dual compartment reactor (case 1) and a single compartment reactor (case 2), the continuous stirred-tank reactor (CSTR) is considered, as shown in Fig. 2. Fig. 2a shows that the energy consumption in case 2 using  $H_2$  and  $N_2$  as reactants in a single compartment reactor is mostly similar to that in the Haber–Bosch process when the current efficiency is over 50%. Besides, the ammonia formation rate and required Fe mass were estimated for a production rate of 100 tons ammonia per day, as shown in Fig. 2b. In this study, the highest ammonia formation rate and current efficiency were around  $1800 \mu\text{g mg}^{-1} \text{h}^{-1}$  and 65% at 0.1 MPa and  $550^\circ\text{C}$ , respectively. The ammonia formation rate was estimated around  $5500\text{--}7000 \mu\text{g mg}^{-1} \text{h}^{-1}$  at 0.2 MPa and  $550^\circ\text{C}$  by kinetic and thermodynamic analyses, which is comparable to that in the Haber–Bosch process at 10 MPa and  $450^\circ\text{C}$ . Considering the reactor integrated with renewable energy, the electrochemical process is more suitable than the Haber–Bosch process because of its low operating pressure, flexible operation (adjustment of production rate, quick start-up, and shut-down), and high ammonia formation rate.

## Conclusions

In this thesis, the reaction mechanism, performance of ammonia formation, and energy consumption were investigated. Through the investigation of reaction mechanism in the electrochemical process, the reaction is considered as surface reaction rather than charge-transfer reaction. Furthermore, a possible reaction mechanism, EPOC, was proposed to explain the behavior of electrochemical ammonia formation. Besides, based on the estimation of ammonia formation rate at high operating pressure and energy consumption, the performance in the electrochemical process can be comparable to that in the Haber–Bosch process. This result indicates that the electrochemical process can replace the Haber–Bosch process for the ammonia synthesis. We believe that our research can significantly help designing new reactors and has the potential of implementation.

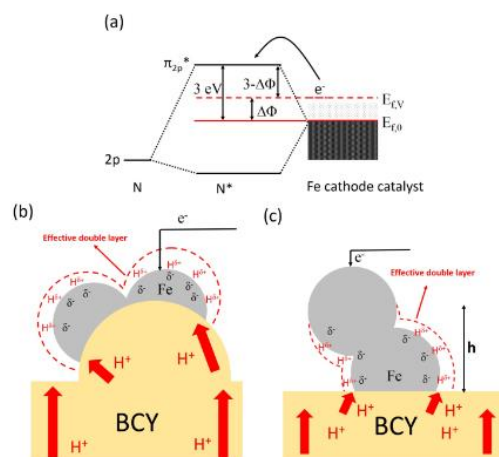


Fig. 1 (a) Energy diagram about N–N bonding is weakened by increasing the metal Fermi level as applied a negative voltage. Schematic images of effective double layer on Fe surface in (b) 10Fe–BCY and (c) porous pure Fe cathodes.

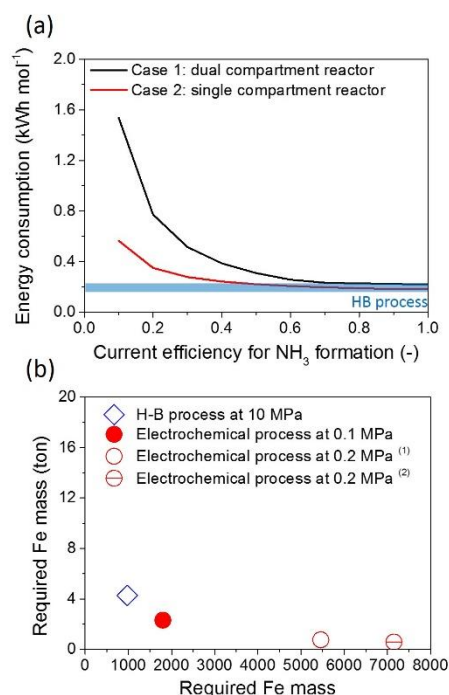


Fig. 2 (a) Energy consumption for case 1, case 2, and Haber-Bosch process. (b) Required Fe mass in electrochemical process and Haber-Bosch process with a production rate of 100 tons ammonia per day. <sup>(1)</sup> and <sup>(2)</sup> are estimated by kinetic analysis and thermodynamic analysis, respectively.