

# Multi-stage synthesis of magnesium nitride using an atmospheric-pressure dielectric barrier discharge

Shungo Zen\*, Yingwen Huang, Nozomi Takeuchi

Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, 2-12-1-S3-3, Ookayama, Meguro-ku, Tokyo, Japan

\* Corresponding author: [zen@ee.e.titech.ac.jp](mailto:zen@ee.e.titech.ac.jp) (Shungo Zen)

Received: 18 March 2021

Revised: 8 May 2021

Accepted: 20 May 2021

Published online: 22 May 2021

## Abstract

A multi-stage dielectric barrier discharge (DBD) was used to elucidate the reaction pathway for synthesizing  $Mg_3N_2$  from MgO, nitrogen, and hydrogen using atmospheric pressure plasma. Recently, ammonia has been considered as a promising carbon-free material for hydrogen storage and carrier owing to its high hydrogen density. However, the extensive use of ammonia as an energy carrier has problems with respect to transportation and storage because of its toxicity, odor, and combustibility. Therefore, we consider that  $Mg_3N_2$  can solve these problems and focus on  $Mg_3N_2$  synthesis by nitridation of MgO using a DBD in a  $N_2$  and  $H_2$  atmosphere instead of directly synthesizing ammonia. By investigating the  $Mg_3N_2$  synthesis pathway using a multi-stage atmospheric pressure plasma, it is considered that H atoms and NH radicals reduce MgO and promote nitriding.

**Keywords:** Ammonia carrier, dielectric barrier discharge,  $Mg_3N_2$  synthesis, non-thermal plasma.

## 1. Introduction

Owing to significant use of fossil fuel energy, environmental problems such as the greenhouse effect, acid rain, and smog are becoming severe [1]. Recognizing these issues has led to increased attention to renewable energy sources [2]. However, renewable energy output is not stable because it is usually affected by weather or location. To solve these disadvantages, energy carriers that can conveniently and safely transport and store energy have been studied. Ammonia is considered a good hydrogen storage material because it has a high hydrogen weight density of 17.6% wt. and ease of liquefaction [3–5]. However, ammonia gas has inconvenience and safety problems with transportation and storage owing to its pungent smell, flammability, and toxicity [6, 7]. Because  $Mg_3N_2$  can react with water and easily generate ammonia gas [8], we propose  $Mg_3N_2$  as a novel and safe ammonia carrier [9–11].  $Mg_3N_2$  is solid, so there is no compression step before storage. Under dry conditions, the  $Mg_3N_2$  chemical properties are very stable. Therefore,  $Mg_3N_2$  is considered a safer and more convenient ammonia carrier. However,  $Mg_3N_2$  synthesis efficiency has not yet been achieved for practical application. Synthetic pathway elucidation is indispensable for further synthetic efficiency improvement. In this study, to elucidate the nitriding reaction path of MgO by atmospheric-pressure plasma under a nitrogen-hydrogen mixed gas,  $Mg_3N_2$  was synthesized by multi-stage dielectric barrier discharge (DBD).

## 2. Experimental

Fig.1 shows a DBD reactor schematic. A stainless rod with a diameter of 10 mm acting as a high-voltage electrode was inserted in a quartz tube with inner and outer diameters of 25 and 30 mm, respectively. The lower portion of the quartz tube (50 mm) was immersed in 1 L of tap water, which was used as the ground electrode in generating a uniform DBD. The water electrode was also able to cool down the quartz tube during

the discharge process. The gap between the high-voltage electrode and quartz test tube was 7.5 mm. 3.5 g of MgO nanoparticles (average diameter: 35 nm) that were pretreated by heating in air at 300 °C for 10 min were placed at the bottom of the quartz tube. A ceramic plug with a 24 mm outer diameter was used to block the spread of the MgO nanoparticles during discharge. By filling the H<sub>2</sub>/N<sub>2</sub> background gas, the gas pressure inside the tube was adjusted to 1 atm. A 1 kHz sinusoidal high-voltage AC ( $V_{p-p} = 36$  kV) was applied to generate the discharge in the experiment. When the voltage was applied, a uniform DBD occurred because MgO nanoparticles spread at the bottom 50 mm portion of the closed quartz test tube, due to the electrohydrodynamic phenomenon [12–13]. The consumption power was measured using the voltage-charge curve (V-Q Lissajous diagram) of a capacitor (2.2 μF). After the MgO nitridation, 1 g of nanoparticles were completely reacted with 10 mL of pure water to generate NH<sub>3</sub> and then the NH<sub>3</sub> was dissolved in water for 10 min. Subsequently, the solution was filtered, and a commercially available indophenol blue colorimetric method was used to measure the total NH<sub>4</sub><sup>+</sup> concentration.

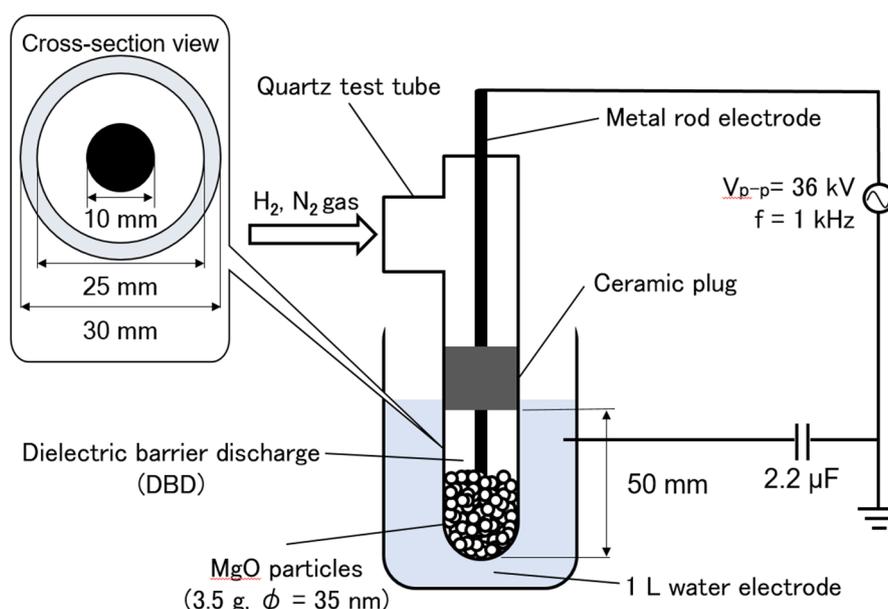


Fig. 1. Schematic diagram of a DBD reactor.

### 3. Results

#### 3.1. Influence of hydrogen gas proportion

Fig. 2 shows the results of the intermittent synthesis using the same reaction gas proportions. The horizontal axis represents the hydrogen proportion and the left vertical axis represents the NH<sub>4</sub><sup>+</sup> concentration. The total discharge time was 20 min. Each five minutes of discharging, the discharge was suspended and the system rested for 3 min to cool down the matter inside the quartz test tube. When the hydrogen proportion was zero, the NH<sub>4</sub><sup>+</sup> concentration was the lowest at approximately 3.53 ppm. The addition of hydrogen to the reaction gas significantly increased the NH<sub>4</sub><sup>+</sup> concentration. The NH<sub>4</sub><sup>+</sup> concentration was saturated with the addition of approximately 30% or more of hydrogen. This result showed the same tendency as in our previous study [11]. Fig. 2 also shows the average of consumption power during the discharge under each condition. The consumption power for all conditions was approximately 30 W.

#### 3.2. Effect of refreshing reaction gas

To eliminate the effects of by-products and moisture, gas refreshing was performed during intermittent synthesis. Each proportion was discharged four times, and each discharge lasted for 5 min. The interval between two adjacent discharges was 3 min. During each interval, the reactor reaction gas was evacuated, and

the same proportion of gases was introduced; simultaneously, the reactor was cooled. Fig. 3 combined the data of the reaction gas refreshing synthesis and 20 min of intermittent synthesis.

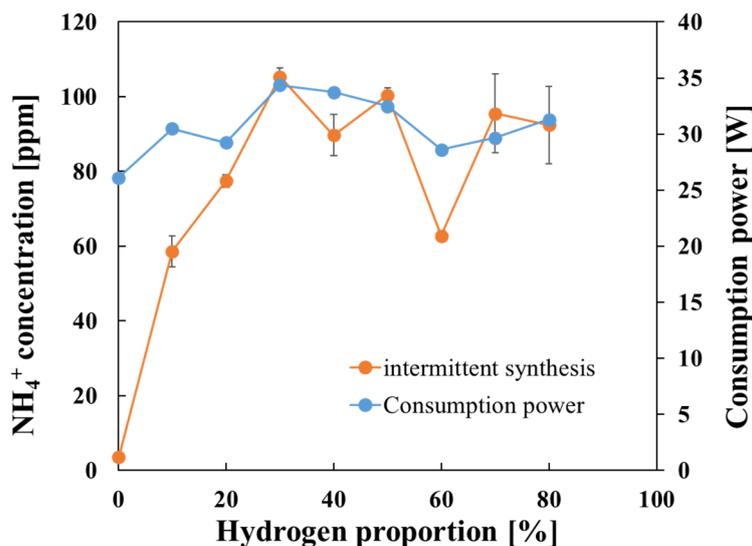


Fig. 2. NH<sub>4</sub><sup>+</sup> concentration and consumption power of different hydrogen proportion.

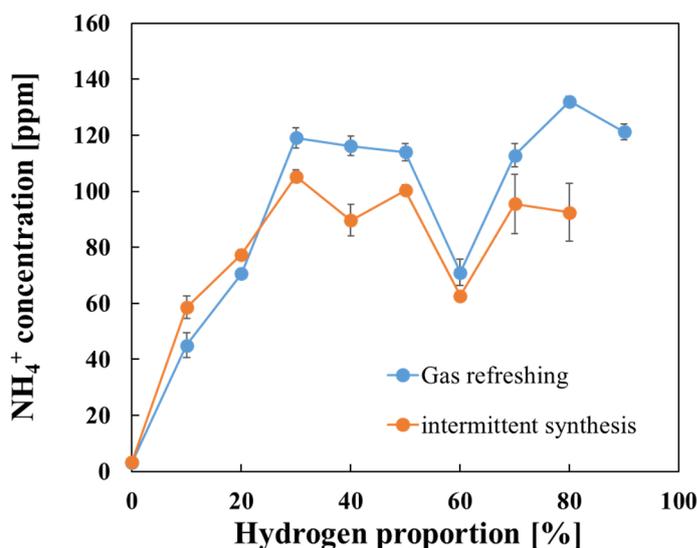


Fig. 3. NH<sub>4</sub><sup>+</sup> concentration of 20 min discharge and background gas renewal experiment.

### 3.3. Effect of discharge process number

Based on the gas refreshing experiment, an experiment was conducted to determine whether increasing the number of discharge processes could improve the ammonium ion concentration. A mixture of 80% H<sub>2</sub>, 20% N<sub>2</sub> was selected as the background gas proportion. Only the number of discharge processes was changed whereas the 3 min interval and gas refreshing procedure were the same. As shown in Fig. 4, the amount of ammonium ion concentration increased up to four discharge time processes. When the number of discharge processes was greater than four, even with increasing discharge process iterations, the ammonium ion concentration dropped instead of rising.

### 3.4. Effect of 100% hydrogen

To investigate the influence of 100% hydrogen gas on the MgO nitridation, two series of experiments were conducted. One was a mixed gas experiment, and the other was a multiple stage experiment that contained 100% hydrogen discharge. In the mixed gas experiment, a specific proportion of hydrogen and nitrogen mixed

gas ( $H_2 = 0\% \sim 75\%$ ) was input and discharged for 10 min. Subsequently, the remaining gas was pumped out, and the same proportion of gas was input to proceed with a 5 min discharge. In the multiple-stage experiment, 5 min of 100% hydrogen discharge was added between the 10 min and 5 min discharges described above. Fig. 5 shows the ammonium ion concentration variation by changing the hydrogen proportion. When the hydrogen proportion was zero, the ammonium ion concentration in the multiple-stage experiment was five times that of the mixed gas experiment. When the hydrogen proportion was greater than zero, the ammonium ion values of the two experiments did not differ significantly.

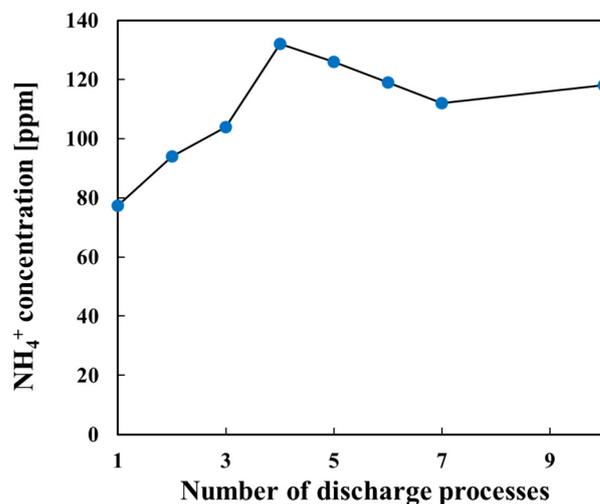


Fig. 4. Ammonium ions concentration in mixed gas and multiple stage experiments.

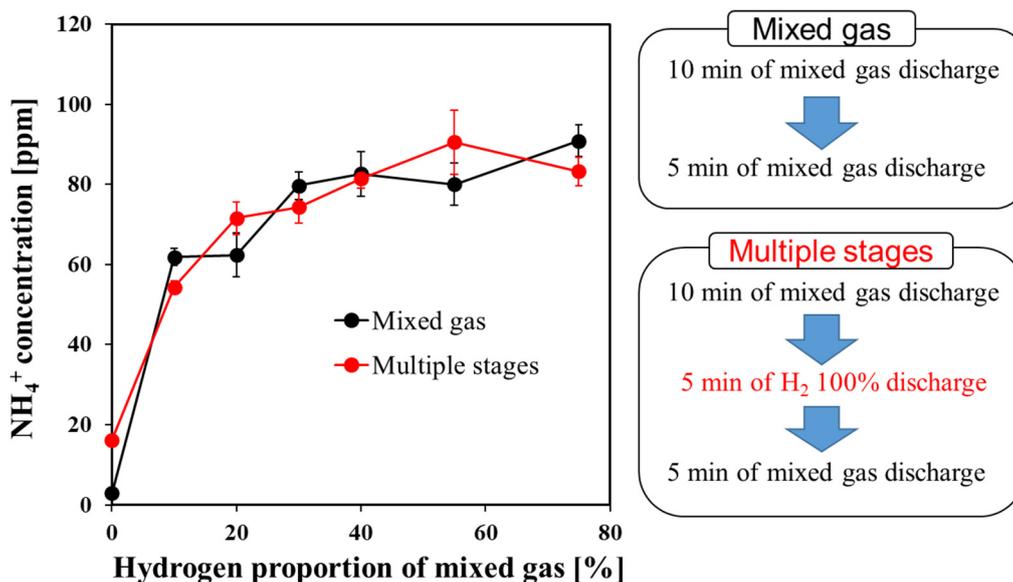


Fig. 5. Ammonium ions concentration in mixed gas and multiple stage experiments.

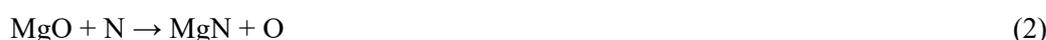
#### 4. Discussion

The reaction gas refreshing synthesis, as shown in Fig. 3, succeeded in nitriding at a higher concentration than the intermittent synthesis or our previous study [11] when the hydrogen proportion was greater than 30%. This suggests that by-products such as water may have an adverse effect on the nitriding process. Therefore, we can conclude that gas refreshment contributes to MgO nitridation.

The results, as shown in Fig. 4, suggested that when the number of discharge processes is less than four, the total discharge time may be too short; i.e., the nitridation reaction was insufficient. As a result, when the

number of discharge processes increased, the total discharge time also increased, which led to an ammonium ion concentration improvement. When the number of discharge processes reached four, the magnesium nitride formation reached saturation, so the ammonium ion concentration did not increase with additional discharge process iterations. Moreover, it is possible that an over-extended discharge may cause  $Mg_3N_2$  to decompose, owing to the long discharge time itself or the accompanying heat. In the most efficient case, about 80 ppm of ammonium ion was generated by the synthesis for 5 minutes. It can be calculated that about 2.8 mg of ammonia could be generated in the 3.5 g of nanoparticles. A power of 30 W was consumed for 5 min, thus an energy of 9 kJ was expended. The energy efficiency can be calculated as 0.7% from the input power and the heat of combustion of ammonia as  $22.3 \text{ kJ g}^{-1}$ .

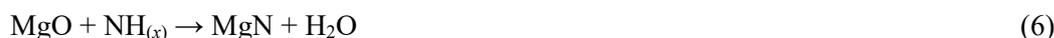
During the discharge process of the results shown in Fig.5, hydrogen and nitrogen molecules ionize and dissociate to H,  $H^+$ , N,  $N^+$  particles, and so on. At further discharge steps, these particles collided with each other and formed  $NH^+$ ,  $NH_2^+$ ,  $NH_3$ , and  $NH_4^+$  [14–15]. When the hydrogen proportion was zero, only N radicals should participate in the reaction with magnesium oxide to generate magnesium nitride. This process may be inefficient.



In the multiple-stage experiment, 100% of hydrogen discharge was introduced and produced H radicals that might reacted more easily than N particles so that MgO might react with H radicals and change to magnesium. Then, magnesium reacted with N radicals, and magnesium nitride might be generated. As a result, the concentration of the ammonium ions increased. The process can be described as follows:



When the hydrogen proportion was greater than zero, the difference between the two curves was not obvious. There are two possible explanations for this finding. One explanation is that owing to the introduction of hydrogen into the reaction gases, MgO might reacted directly with H radicals and reduce to magnesium. Subsequently, magnesium might be nitride during the discharge process. The other explanation is that MgO might reacted with  $NH_x$ ,  $NH_x^+$  formed by the interaction between hydrogen and nitrogen, generating  $Mg_3N_2$ . The process can be simply described as:



Therefore, it could be considered that MgO nitriding has occurred, but XRD and XPS analysis are indispensable to confirm the formation of  $Mg_3N_2$ .

## 5. Conclusion

The multi-stage DBD plasma succeeded in synthesizing  $Mg_3N_2$  at a higher concentration than in previous studies with a wide range of hydrogen ratios. However, when the number of gas refreshing discharge processes reached four, the magnesium nitride formation reached saturation, so the ammonium ion concentration did not increase with additional discharge process iterations. In addition, there are two possible pathways for nitriding magnesium oxide. One explanation is that MgO might have reacted directly with H radicals and reduce to magnesium, then might be changed to  $Mg_3N_2$ . The other explanation is that MgO might reacted with  $NH_x$ ,  $NH_x^+$  formed by the interaction between hydrogen and nitrogen, generating  $Mg_3N_2$ . In the future, these results and discussion might lead to further efficiency improvements in  $Mg_3N_2$  synthesis.

## Acknowledgment

This work was supported by the JSPS KAKENHI Grant Number 19K14958. This work was carried out by the joint usage / research program of center for Low-temperature Plasma Science, Nagoya University.

## References

- [1] Florinda, M., Felgueiras, C., and Smitková, M., Fossil fuel energy consumption in European countries, *Energy Procedia*, Vol. 153, pp. 107–111, 2018.
- [2] Bull, S.R., Renewable energy today and tomorrow, *Proc. IEEE*, Vol. 89 (8), pp. 1216–1226, 2001,
- [3] Wang, W., Herreros, JM, Tsolakis, A., and York, A.P.E., Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming, *Int. J. Hydrogen Energy*, Vol. 38 (23), pp. 9907–9917, 2013.
- [4] Patil, B.S., Wang, Q., Hessel, V., and Lang, J., Plasma N<sub>2</sub>-fixation: 1900–2014, *Catal. Today*, Vol. 256, pp. 49–66, 2015.
- [5] Kim, H. H., Teramoto Y., Ogata A., Takagi H., and Nanba T., Atmospheric-pressure nonthermal plasma synthesis of ammonia over ruthenium catalysts, *Plasma Process. Polym.*, Vol. 14, pp. 1–9, 2017.
- [6] Chakraborty, D., Petersen, H. N., Elkjer, C., Cagulada A., and Johannessen T., Solid ammonia as energy carrier: Current status and future prospects, *Fuel Cells Bulletin*, Vol. 2009 (10), pp. 12–15, 2009.
- [7] Checkel, M.D., Ting, D.S.K., and Bushe, W.K., Flammability limits and burning velocities of ammonia/nitric oxide mixtures, *J. Loss Prev. Process Ind.*, Vol. 8 (4), pp. 215–220, 1995.
- [8] Hu, J., Band, o Y., Zhan, J., Zhi, C., and Golberg, D., Carbon nanotubes as nanoreactors for fabrication of single-crystalline Mg<sub>3</sub>N<sub>2</sub> Nanowires, *Nano Lett.*, Vol. 6 (6), pp. 1136–1140, 2006.
- [9] Zen, S., Abe, T., and Teramoto Y., Indirect synthesis system for ammonia from nitrogen and water using nonthermal plasma under ambient conditions, *Plasma Chem. Plasma Proc.*, Vol. 38 (2), pp. 347–354, 2018.
- [10] Zen, S., Development of a new technology for energy storage material using atmospheric-pressure plasma, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 12 (1), pp. 12–14, 2018.
- [11] Zen, S., Abe, T., and Teramoto, Y., Atmospheric pressure nonthermal plasma synthesis of magnesium nitride as a safe ammonia carrier, *Plasma Chem. Plasma Proc.*, Vol. 39 (5), pp. 1203–1210, 2019.
- [12] Elagin, I., Samusenko, A., and Chirkov, V. A., Numerical study of the needle inclination angle effect on ionic wind direction, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 14 (1), pp. e01006, 2020.
- [13] Moreau, E., Souakri, S., and Benard, N., Ionic wind produced by a millimeter-gap DC corona discharge ignited between a plate and an inclined needle, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 15 (1), pp. e01001, 2021.
- [14] Zhu, X., Hu X., Wu X., Cai Y., Zhang H., and Tu X., Ammonia synthesis over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellets in a packed-bed dielectric barrier discharge reactor, *J. Phys. D: Appl. Phys.*, Vol. 53 (16), pp. 164002, 2020.
- [15] Peng, P., Li Y., Cheng Y., Deng S., Chen P., and Ruan R., Atmospheric pressure ammonia synthesis using non-thermal plasma assisted catalysis, *Plasma Chem. Plasma Process.*, Vol. 36 (5), pp. 1201–1210, 2016.