

# Development of a New Technology for Energy Storage Material Using Atmospheric-Pressure Plasma

S. Zen

Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, Japan

**Abstract**—Recently, there is an increasing need for technology to store and transport unstable renewable energy in chemical energy due to environmental problems, depletion of fossil fuels and other factors. In this report, magnesium nitride ( $\text{Mg}_3\text{N}_2$ ) is proposed as a new reusable chemical energy carrier.  $\text{Mg}_3\text{N}_2$  is suitable for storage and transportation and reacts with water to produce  $\text{NH}_3$  as a hydrogen carrier. On the other hand, chemically active species generated by atmospheric pressure plasma have high chemical reactivity. Hence, the technique has been developed to synthesize  $\text{Mg}_3\text{N}_2$  with a dielectric barrier discharge (DBD) treatment.

**Keywords**—Atmospheric-pressure plasma, non-thermal plasma, dielectric barrier discharge, energy storage material

## I. INTRODUCTION

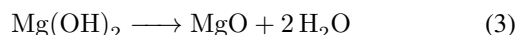
There is an increasing need for technology to store and transport unstable renewable energy in chemical energy due to environmental problems, depletion of fossil fuels and other factors. Since hydrogen is an ideal energy carrier, development of hydrogen storage material is a hot topic [1], [2]. Ammonia ( $\text{NH}_3$ ) is considered as a promising hydrogen storage material because of high hydrogen storage density and established mass production technology [3]. However, since ammonia is designated as a deleterious substance, there is a problem that it is necessary to pay attention to safety. Here, magnesium nitride ( $\text{Mg}_3\text{N}_2$ ) is proposed as a new reusable chemical energy carrier material.  $\text{Mg}_3\text{N}_2$  stores about  $43 \text{ GJ/m}^3$ , which is 10 times of 700 atm hydrogen gas tank.  $\text{Mg}_3\text{N}_2$  reacts with water to produce  $\text{NH}_3$  as shown in (1) [4].



In addition,  $\text{Mg}_3\text{N}_2$  can also be used as a fuel as follows:



$\text{Mg}_3\text{N}_2$  is suitable for storage and transportation because it is chemically stable under dry conditions. Hence  $\text{Mg}_3\text{N}_2$  can be considered as a new solid  $\text{NH}_3$  carrier. When magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ), which is a by-product, is heated up to about 600K, it changes to magnesium oxide ( $\text{MgO}$ ) as follows:



Once a technique to synthesize  $\text{Mg}_3\text{N}_2$  from  $\text{MgO}$  is developed, magnesium resources can be recycled. In this report, I report the key technology: synthesizing  $\text{Mg}_3\text{N}_2$  from  $\text{MgO}$  with a dielectric barrier discharge (DBD) treatment.

## II. EXPERIMENTAL APPARATUS AND PROCEDURE

Fig. 1 shows the coaxial cylinder type DBD treatment reactor filled with atmospheric-pressure dry nitrogen ( $\text{N}_2$ ),

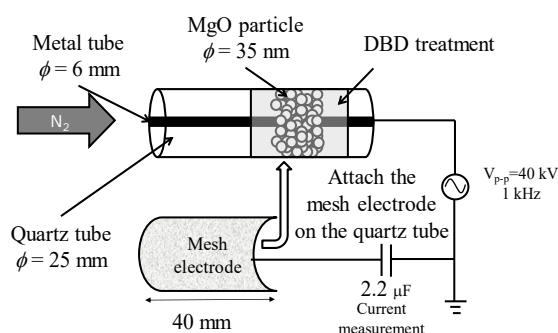


Fig. 1. Dielectric barrier discharge treatment reactor.

300K). The inside diameter and thickness of quartz tube were 25 mm and 2 mm, respectively. A metal tube and a metal mesh were used as each DBD electrode. DBD occurred between the closed quartz tube and the metal tube.  $\text{MgO}$  particles (3 g, Kanto Denka Kogyo Co. Ltd.) with an average particle size of 35 nm were placed in the DBD reactor. The gap between the glass surface and the metal tube was 9.5 mm. A high ac voltage of  $V_{p-p} = 40 \text{ kV}$  and 1 kHz was applied between the electrodes. The reactor temperature was measured using an infrared camera. After the DBD treatment,  $\text{MgO}$  samples (0.5 g) were reacted with ultrapure water (20 ml) to produce  $\text{NH}_3$ .

Then, a commercially available indophenol blue method (Kyoritsu Chemical-Check Lab. Corp., WAK-NH4, 0.2–10 mg/L) was used to measure the ammonium ion concentration in the solution.

## III. RESULTS AND DISCUSSION

Fig. 2 shows a typical 128 times average  $Q$ - $V$  Lissajous waveform during the DBD treatment.  $X$ -axis and  $Y$ -axis are applied voltage and charge, respectively. The area of the  $Q$ - $V$  Lissajous corresponds to the energy consumed during one voltage period. As a result, the power consumption of this DBD treatment can be calculated as 50 W. A photograph of infrared camera immediately after 10 min of DBD treatment

Corresponding author: Shungo Zen  
e-mail address: zen@ee.e.titech.ac.jp

Presented at the 5th East Asia Joint Symposium on Plasma and Electrostatic Technologies for Environmental Application (EAPETEA-5), in June 2017

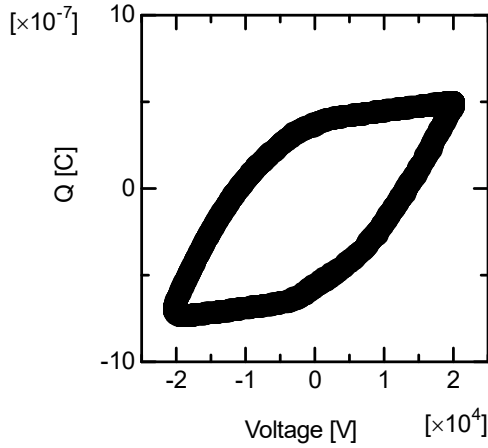


Fig. 2.  $Q$ - $V$  Lissajous during the DBD treatment.

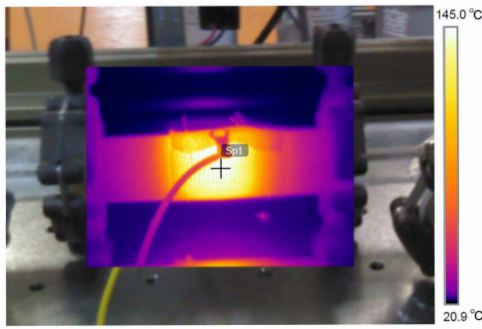


Fig. 3. Photograph of infrared camera immediately after 10 min of DBD treatment.

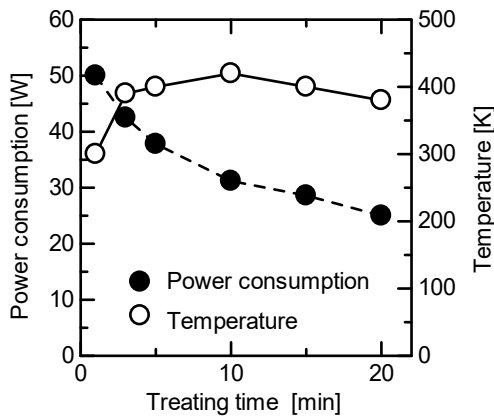


Fig. 4. Changes in power consumption and DBD reactor temperature during the DBD treatment.

is shown in Fig. 3. Since the quartz tube was placed at room temperature, the hot area was the DBD reactor. Fig. 4 shows the changes in power consumption and DBD reactor temperature during the DBD treatment.

The center of DBD reactor temperature was reached to  $150^{\circ}\text{C}$  and saturated after 10 min of DBD treatment. Traditionally,  $\text{MgO}$  reduction by heat is said to require a very high temperature (exceeding  $4000\text{K}$ ) [5]. This indicates that DBD

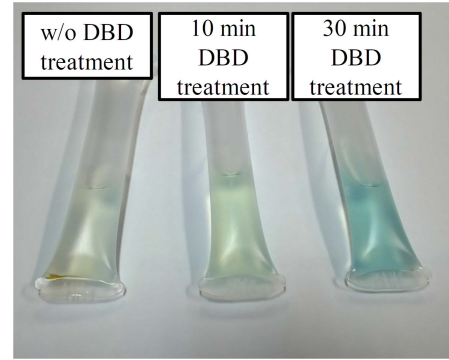


Fig. 5. The ammonium ion concentration in solution for different DBD treatment time.

treatment is a low-temperature process of  $\text{MgO}$  reduction. On the other hand, the power consumption of DBD treatment was decreasing from 50 W to 25 W. This result indicates that the conditions may be changed during DBD treatment.

Fig. 5 shows the results of the ammonium ion concentration in solution for different DBD treatment time. The absorption spectra of the solution were measured using a spectral photometer. As a result of analyzing the absorption ratio, the ammonium ion concentration of 10 min DBD treated sample and 30 min DBD treated sample were 0.5ppm and 1.5ppm, respectively. Although the energy efficiency is still low, this result indicates that synthesis of  $\text{Mg}_3\text{N}_2$  from  $\text{MgO}$  and  $\text{N}_2$  takes place via low temperature plasma chemical processes. Chemical active species are considered to promote this chemical reaction instead of heat. N radicals, which is known as a strong reducing agent [6], can be considered as one of the possible chemical active species for this synthesizing process. In the present experiment, a thorough optimization of the DBD treatment is not carried out. Further improvement in energy efficiency by DBD treatment is possible with further optimization of parameters.

#### IV. CONCLUSIONS

In this report,  $\text{Mg}_3\text{N}_2$  has been proposed as a new reusable carrier of chemical energy. Although the energy efficiency is still low,  $\text{Mg}_3\text{N}_2$  can be synthesized from  $\text{MgO}$  and  $\text{N}_2$  using a low temperature plasma generated by DBD. N radicals can be considered as one of the possible chemical active species for this synthesizing process. Further improvement in energy efficiency by DBD treatment is possible with further optimization of parameters.

#### ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI Grant Number 16H06790.

#### REFERENCES

- [1] B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, "Metal hydride materials for solid hydrogen storage: A review," *International Journal of Hydrogen Energy*, vol. 32, pp. 1121–1140, 2007.
- [2] Y. Kojima, H. Miyaoka, and T. Ichikawa, "Hydrogen storage materials," in *New and Future Developments in Catalysis*, S. L. Suib, Ed. Amsterdam: Elsevier, 2013, ch. 5, pp. 99–136.

- [3] A. Klerke, C. H. Christensen, J. K. Nørskov, and T. Vegge, "Ammonia for hydrogen storage: challenges and opportunities," *Journal of Materials Chemistry*, vol. 18, pp. 2304–2310, 2008.
- [4] G. E. Veitch, K. L. Bridgwood, and S. V. Ley, "Magnesium nitride as a convenient source of ammonia: Preparation of primary amides," *Organic Letters*, vol. 10, pp. 3623–3625, 2008.
- [5] T. Yabe, S. Uchida, K. Ikuta, K. Yoshida, C. Baasandash, M. S. Mohamed, Y. Sakurai, Y. Ogata, M. Tuji, Y. Mori, Y. Satoh, T. Ohkubo, M. Murahara, A. Ikesue, M. Nakatsuka, T. Saiki, S. Motokoshi, and C. Yamanaka, "Demonstrated fossil-fuel-free energy cycle using magnesium and laser," *Applied Physics Letters*, vol. 89, p. 261107, 2006.
- [6] A. C. Gentile and M. J. Kushner, "Reaction chemistry and optimization of plasma remediation of  $N_xO_y$  from gas streams," *Journal of Applied Physics*, vol. 78, pp. 2074–2085, 1995.