

RF plasma pulsing: an effective approach for the reduction of the energy cost of ammonia synthesis

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Abstract: In this contribution, we present detailed characterization of ammonia synthesis via a radio frequency-driven low-pressure nonthermal plasma reactor. We have extensively investigated two parameters affecting the nitrogen fixation efficiency and its energy cost: the H₂-N₂ molar ratio and the plasma pulse duration. Optical emission spectroscopy is also performed to estimate atomic hydrogen and nitrogen density. This work highlights the pulsed operation is a promising approach to reduce energy cost of ammonia synthesis.

Keywords: Ammonia, Synthesis, Nonthermal plasma, Pulse, Atomic density, Energy cost

1. Introduction

Ammonia production via a sustainable pathway has attracted significant attention in the plasma community. [1–3] Although ammonia is an essential feedstock for various synthetic products (e.g., fertilizers) as well as a promising candidate for a sustainable energy carrier due to its high hydrogen content (17.75 wt% by weight) [4], it is produced through a thermally driven heterogeneous catalytic method, Haber-Bosch (HB) process.[5] The centralized production of ammonia via the HB process has led to over-fertilization practices for local farmers, disrupting the natural nitrogen cycle on the earth. The massive emission of CO₂ from the HB process also threatens the sustainable future of mankind.[6,7] Nonthermal plasmas have the potential to relieve the environmental problems associated with the HB process. Plasma-based facilities at small scale are compatible with a distributed chemical infrastructure for the on-site production of feedstock ammonia.[3] They are also electrically driven process, which means the green-house gas emission from the HB process could be significantly reduced when they are operated via renewable energy resources. Moreover, nonthermal plasmas enable the activation of stable molecules, making it possible to overcome their activation energy barrier (e.g., CO₂, CH₄, and N₂) even at room temperature thanks to the presence of highly energetic electrons. While ammonia production through nonthermal plasmas coupled with heterogeneous catalysis could be promising alternative to the HB process, the inherent complexity of the interaction between nonthermal plasmas and the surface of metal catalysts has limited our fundamental understanding of the ammonia formation.

In this contribution, we comprehensively investigate process parameters such as hydrogen-to-nitrogen molar ratio in a RF-driven low pressure nonthermal plasmas to characterize the nitrogen fixation efficiency and its energy cost. A cone-shape fine stainless-steel mesh is utilized as a metal catalyst. We measure the highest nitrogen fixation efficiency reaching out 8.4% at the hydrogen-rich

condition (i.e., hydrogen-to-nitrogen ratio equal to 19). Although significant nitrogen fixation efficiency is achieved under hydrogen abundant conditions, it is confirmed that these conditions are unfortunately detrimental to the energy cost. A point that is often overlooked in the community is the fact that the dissociation energy for the N–H (3.7 eV) bond is lower than that of the N≡N (9.8 eV) and H–H (4.5 eV) bonds.[8] It means that the plasma in continuous wave (CW) mode rapidly dissociates the formed ammonia as soon as it leaves the surface of the catalyst and diffuses back into the plasma volume, resulting in a reduction of the nitrogen fixation efficiency as well as inducing a significant waste of electrical input energy. Operating the plasma in a pulsed mode can significantly alleviate these challenges.

2. Experimental details

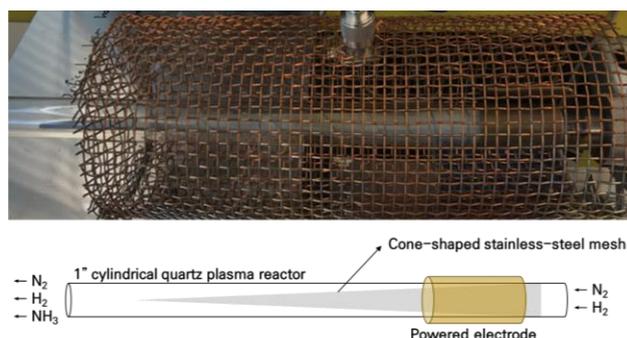


Fig. 1. Photograph and schematic of the RF-driven low pressure nonthermal plasma reactor with a mesh catalyst.

A schematic of the RF-driven nonthermal plasma system for ammonia synthesis is presented in Fig. 1. Nonthermal plasmas are formed in a 2.54 cm diameter cylindrical quartz tube reactor using a 13.56 MHz electrical signal supplied by a thick copper ring electrode. The copper electrode is powered by a power supply (RFPP RF-5S, Advanced Energy). The impedance is balanced through a

matching network (MFJ-989D, MFJ). The molar ratio of the nitrogen and hydrogen mixture is controlled by mass flow controllers (MKS 1179C, MKS Instruments). The total flow rate of the mixture keep constant as 20 sccm in this study. The pressure set to 0.5 Torr through an automated pressure control system (MKS 600 series, MKS Instruments). The reaction products are sampled downstream of the reaction zone via a 50 orifice and quantified through a residual gas analyser (RGA). The nitrogen fixation efficiency (η) is calculated by measuring the partial pressure of nitrogen and ammonia through the RGA and is defined as

$$\eta(\%) = \frac{P_{NH_3}}{P_{N_2} + P_{NH_3}} \times 100 \quad (1)$$

where P_{NH_3} and P_{N_2} are the partial pressures of ammonia and nitrogen. The energy cost (σ) to produce 1 mol of ammonia is calculated through

$$\sigma \left(\frac{MJ}{mol} \right) = [Measured\ power \times \left(\frac{MJ}{10^6 J} \right)] / \left[\left(\frac{2P_{NH_3}}{P_{N_2} + P_{NH_3}} \right) \times Flow\ rate\ of\ N_2\ (sccm) \times \left(\frac{0.001 L}{1 cm^3} \right) \times \left(\frac{1 mol}{22.4 L} \right) \times \left(\frac{1 min}{60 s} \right) \right] \quad (2)$$

where measured power is the actual power consumed to maintain the plasma. [9] Although the electrical input power is set to 60 W at the RF power supply, this power is not fully transferred to the copper electrode. Therefore, power measurements are carried out through an oscilloscope (TDS 2024C, Tektronix) coupled with a high-voltage probe (TEK-P6015A, Tektronix) and a current probe (2877, Pearson Electronics). The actual power (ω) to sustain the discharge is obtained through

$$\omega(W) = V_{rms\ plasma\ on} \times I_{rms\ plasma\ on} \times \cos \left[\phi_{plasma\ on} - \left(\phi_{plasma\ off} - \frac{\pi}{2} \right) \right] \quad (3)$$

where ϕ is the phase difference between current and voltage. The actual power is the one used here to estimate the energy cost of ammonia synthesis. Plasma pulsing is performed via the modulation function built into the RF power supply. This allows turning on and off the RF power with an arbitrary frequency and duty cycle. Number of pulses during the residence time set to 1 so that the frequency and duty cycle are controlled by that, meaning the nitrogen and hydrogen mixture is exposed to a single plasma pulse. The residence time calculated through the total flow rate and the plasma volume is 40 msec. The experimental conditions are summarized in Table 1.

We also estimate the density of atomic nitrogen and hydrogen to correlate them with our results (e.g., nitrogen fixation efficiency and energy cost) as function of hydrogen-to-nitrogen molar ratio via Optical Emission

Spectroscopy (OES) measurements. A small flow of Ar is flowed to the reactor as an actinomer. The following emission lines are used to estimate the atomic densities: the hydrogen line at 656.2 nm (transition 3d2 D_j to 2p2 P₀), the nitrogen line at 744.2 nm (transition 3p4 S₀ to 3s4 P), and the Ar line at 750.4 nm (transition 2p1 to 1s2). They are estimated through the relation summarized by Tatarova et al. using the line intensity ratio from our OES spectrum. [10,11] We obtain electron impact-induced excitation rates to the selected excited states of argon, nitrogen, and hydrogen via the BOLSIG+ that is designed to solve Boltzmann equation for electron kinetics. [12] The collision cross-section for Ar, N, H, N₂, H₂, and NH₃ are obtained from the LXCat database. The excitation rates are estimated by balancing the total ionization frequency derived from the BOLSIG+ calculation and the wall loss coefficients (K_w) for the dominant ions to the wall in the N₂-H₂ plasma. K_w is based on the cylindrical geometry and uniform density discharge model for low pressure and is defined as

$$K_w = 2.75 \frac{u_B h_R}{R} \quad (4)$$

where u_B is the Bohm velocity, R is the radius of the reactor, and h_R is defined as

$$h_R = 0.8 \left(4 + \frac{R}{\lambda_i} \right)^{-1/2} \quad (5)$$

where λ_i is the ion mean free path, which is estimated as:

$$1/\lambda_i = \sum_{j,k} \sigma_k n_j \quad (6)$$

where n_j is the background density of species j , and σ_k means the cross section for the collision of the ion with the background gas molecule j . We assume N₂H⁺ and NH₄⁺ ions are dominant in the case of CW plasma. N₂H⁺ is assumed to be the dominant ion in the case of a pulsed plasma. [13,14] Total cross sections for collisions between the dominant ions i (N₂H⁺ and NH₄⁺) with background gas molecules j (N₂, H₂, and NH₃) are referred from the work by Sode et al. [13]

Table 1. Experimental conditions for ammonia synthesis using RF-driven nonthermal plasmas.

Experimental conditions	
Total flow rate [sccm]	20
Pressure [Torr]	0.5
Temperature [K]	300
Hydrogen-to-nitrogen ratio ^a	0.1–19
Residence time [msec]	40
Number of pulses during residence time	1
Plasma on time in the pulsed mode [msec]	2–30
Plasma on time/residence time	0.05–0.75
Duty cycle [%] ^b	5–75

$$^a \text{Hydrogen-to-nitrogen ratio} = \frac{\text{flow rate of } H_2 \text{ [sccm]}}{\text{flow rate of } N_2 \text{ [sccm]}}$$

$$^b \text{Duty cycle} = \frac{\text{Plasma on time [msec]} \times 100}{1/\text{frequency [msec]}}$$

3. Results and discussion

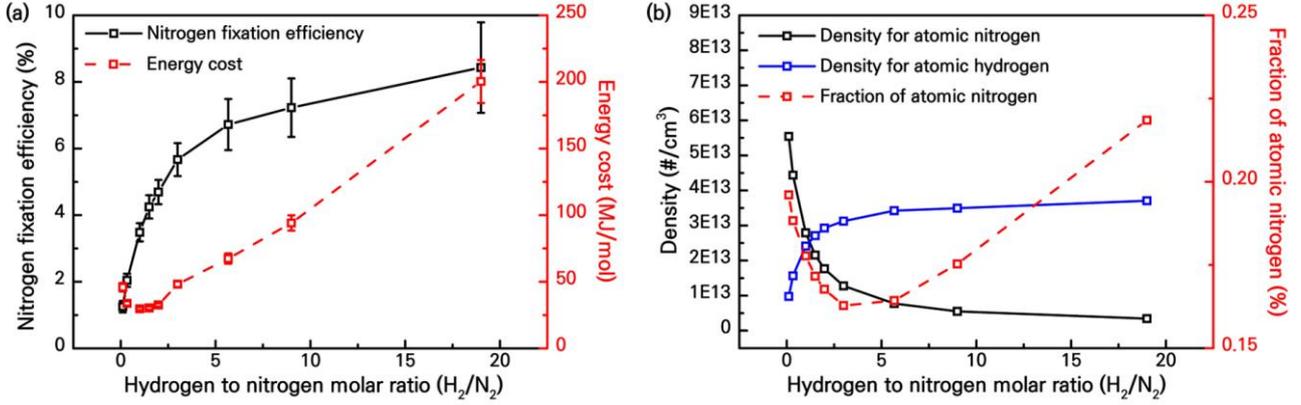


Fig. 2. (a) Measured nitrogen fixation efficiency and energy cost and (b) the atomic nitrogen and hydrogen density and nitrogen dissociation fraction as function of hydrogen to nitrogen molar ratio.

Fig. 2(a) shows nitrogen fixation efficiency and its energy cost as function of the hydrogen to nitrogen molar ratio. Nitrogen fixation efficiency improved as hydrogen to nitrogen ratio increased, reaching 8.4% at the hydrogen-rich condition (Flow rate of N_2 : 1 sccm and H_2 : 19 sccm). However, the corresponding energy cost at that condition was around 200 MJ/mol (~ 2000 eV/molecule and ~ 0.3 g/kWh) that was quite high. The lowest energy cost being 30 MJ/mol (~ 300 eV/molecule and 2 g/kWh) was achieved at the equal flow rate of nitrogen and hydrogen. At the slightly hydrogen-rich conditions (e.g., hydrogen to nitrogen molar ratio is equal to 1.5 and 2), the energy cost remained close to the lowest energy cost. For understanding these experimental results better, we carried out BOLSIG+ calculations coupled with OES measurements to estimate the atomic hydrogen and nitrogen density. Once the electron temperature and the corresponding electron energy distribution function is obtained through BOLSIG+, it is possible to calculate the excitation rates for argon, nitrogen, and hydrogen from the ground state to the specified excited state. The atomic nitrogen and hydrogen density at the condition leading to the lowest energy cost was roughly 2.8×10^{13} (N) and 2.4×10^{13} (H), and the corresponding nitrogen dissociation fraction was 0.18%. The degree of nitrogen fixation largely exceeds the degree of nitrogen dissociation (κ) that defined as

$$\kappa(\%) = \frac{[N]}{[N_2]} \times 100 \quad (7)$$

where $[N]$ is the atomic nitrogen density and $[N_2]$ is the molecular nitrogen density. While fraction of atomic nitrogen was around 2.2% at the hydrogen-rich condition, the nitrogen fixation efficiency was 8.4% that highly exceeds the atomic nitrogen fraction. We have used the rate of electron impact-induced dissociation of molecular nitrogen to estimate the fraction of atomic nitrogen when integrating over the residence time in the plasma (40

msec). Assuming that all the dissociated atomic nitrogen is converted to ammonia, at least an electron density of 1.1×10^{10} cm⁻³ is needed to convert 8% of molecular nitrogen into ammonia, but this value is significantly higher than the actual plasma density in our reactor. Yamijala et al. figured out that atomic nitrogen abstracts rapidly atomic hydrogen on the surface of metal catalyst, forming ammonia through an Eley-Rideal (ER) mechanism. [11] Van't Veer et al. found that atomic hydrogen is the main adsorbate on the metal surface, implying that surface saturation through atomic hydrogen is critical for ammonia formation. The authors suggested that ER reactions led to the formation of NH moieties on the catalyst surface. [15] Engelmann et al. compared a noble metal (Ag) to a non-noble metal (Ru), concluding that ER reactions are the time-limiting step for both metals. [16] However, the measurements reported here suggest that ER reactions alone cannot account for the ammonia produced in the reactor. Other pathways, such as vibrational excitation and enhanced dissociated adsorption, must also play a role in ammonia formation. Moreover, nitrogen fixation efficiency is highly improved under hydrogen abundant conditions that shows high atomic hydrogen density in Fig. 2(b). This implies that a sufficient flux of atomic hydrogen to the metal surface is also essential for the ammonia formation.

Fig. 3(a) shows instantaneous nitrogen fixation efficiency via the plasma in a pulsed mode. Our mass spectroscopy (RGA) measures a time-averaged nitrogen fixation efficiency. Assuming that there is no ammonia formation during the plasma-off phase due to the pulsed mode, the instantaneous nitrogen fixation efficiency is derived as dividing the nitrogen fixation efficiency by the duty cycle. It was observed that the instantaneous nitrogen fixation efficiency highly improved as plasma on time get shorter, showing the maximum point with the shortest pulse duration (2 msec). Moreover, the energy cost with the plasma pulsing was significantly reduced compared to that of the CW plasma as shown in Fig. 3(b). It decreases

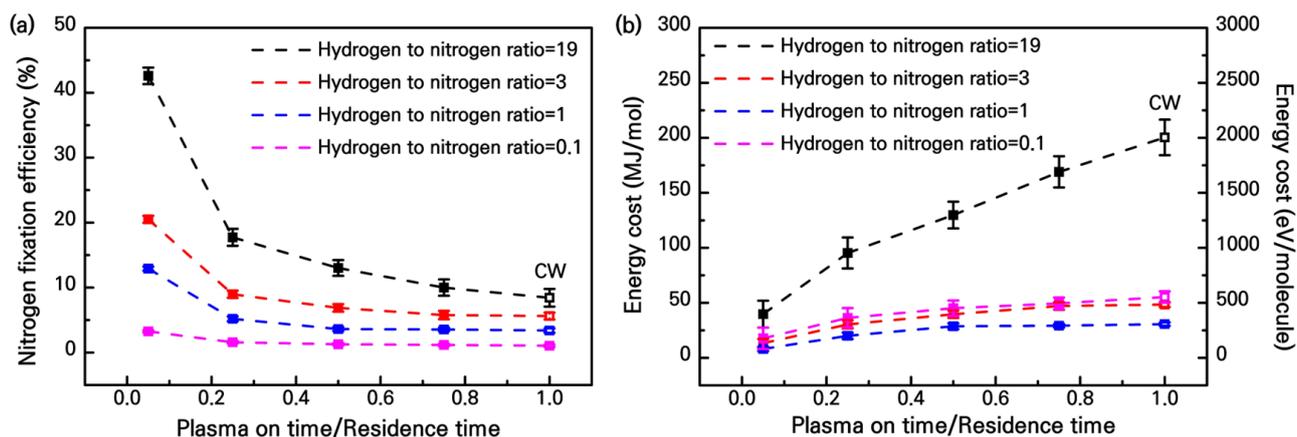


Fig. 3. (a) Instantaneous nitrogen fixation efficiency and (b) energy cost according to the plasma on time/residence time. Residence time is 40 msec, and plasma on time is varied from 2 to 30 msec (see Table 1).

by roughly a factor of 4 when the plasma on time is 2 msec. The lowest energy cost was 8 MJ/mol (~ 80 eV/molecule and ~ 8 g/kWh) when flow rate of hydrogen and nitrogen was same as 10 sccm. We interpret these results as following: the plasma in a pulsed mode is extinguished before the ammonia diffuses back into the plasma volume, but any ammonia produced at the surface of metal catalyst in the continuous mode has sufficient time to diffuse back into the plasma volume. While re-dissociation of ammonia occurs in the continuous plasma, operation in a pulsed mode prevents the synthesized ammonia from re-dissociating in the plasma.

4. Conclusions

The approach described in this contribution provides insights into the parameters affecting both the nitrogen fixation efficiency and its energy cost via the RF-driven low pressure nonthermal plasma reactor. While the nitrogen fixation efficiency was improved at the hydrogen abundant conditions, these conditions showed low fraction of atomic nitrogen. It highlights the importance of other activation pathways (e.g., vibrationally excited nitrogen molecules and enhanced dissociative adsorption) since nitrogen dissociation alone cannot account for the high nitrogen fixation efficiency that highly exceeds the fraction of atomic nitrogen. Moreover, hydrogen rich conditions also led to an increase of energy cost for the ammonia synthesis. We noted the bond energy for N–H is relatively lower than that of N \equiv N and H–H, therefore, we introduced the pulsed plasma operation to prevent ammonia dissociation in the continuous plasma. We found out that operation in the pulsed mode is a promising approach to reduce the energy cost, decreasing the energy cost by roughly a factor of 4 at the 2 msec of pulse duration compared to the continuous case. The lowest energy cost (8 MJ/mol) was achieved at 2 msec of plasma on time when equal flow rates of nitrogen and hydrogen were flown into the reactor. Under the pulsed mode, the plasma is extinguished before a significant fraction of synthesized ammonia on the surface of the metal catalyst

diffuses back into the plasma volume, resulting in a significant saving in energy consumption.

5. Acknowledgements

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