Membrane Technology
ISSN (online): 1873-4049

Research Status and Prospect of Nitrogen Fixation Technology: A Brief Review

Ying Zhao*, Ling Zhu, Xiaoxin He, Junqi Quan, Wenbo Peng, Ali Tao*
School of Pharmacy, Anhui Xinhua University, Hefei 230088, People's Republic of China
**Corresponding Authors.*

Abstract:
The energy consumption of nitrogen fixation industry accounts for 2% of the world. The development of new nitrogen fixation technology based on renewable energy is of great significance for realizing energy conservation and emission reduction. The synthesis of ammonia by H-B method has low energy consumption and large scale, but the reaction conditions of high temperature and high pressure with catalysts and the high requirements for the stability of the power system make it incompatible with the regional and instability properties of renewable energy such as photovoltaic and wind power. The new nitrogen fixation technology represented by plasma technology and photoelectric catalytic nitrogen fixation technology has made remarkable progresses, with the advantages of mild conditions and environment friendliness, which provides a new direction for the future development of nitrogen fixation technology. The review of nitrogen fixation technology development, e.g. photoelectric catalytic nitrogen fixation and the photoelectric catalytic nitrogen fixation are presented. The analysis of the nitrogen fixation mechanism, energy consumption are introduced, which is expected to reduce the feasibility of nitrogen fixation energy consumption. This paper systematically summarizes the research status and looks forward the future development trend. It's proposed that the coordinated nitrogen fixation by non-equilibrium plasma and catalyst will be the key to reduce the energy consumption and improve the yield of plasma nitrogen fixation, which has a broad development prospect.

Keywords: nitrogen fixation technology; oxidized nitrogen fixation; low temperature plasma technology.

INTRODUCTION

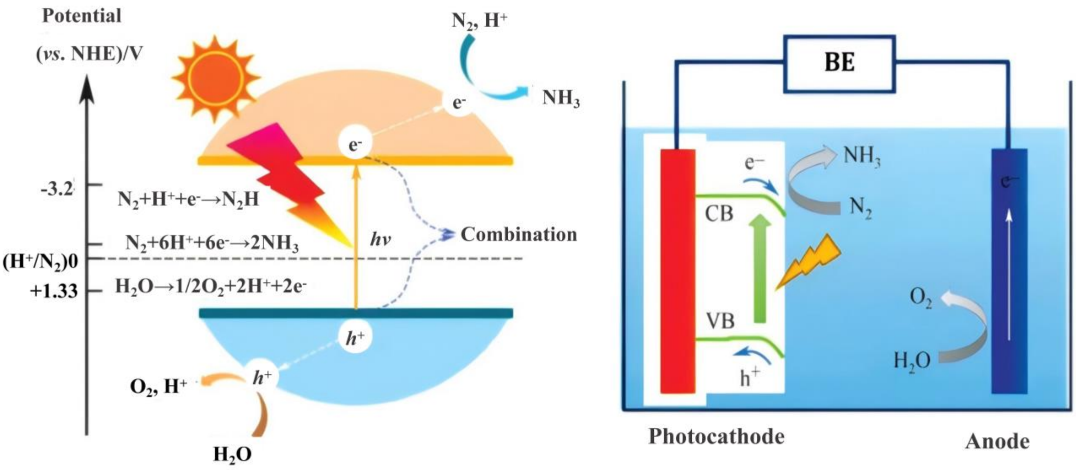
Nitrogen fixation is an important process to solve the global population survival problem. Biological nitrogen fixation and lightning nitrogen fixation in nature cannot meet the growing demand of human beings. Artificial nitrogen fixation technologies, e.g. Birkeland-Eyde (B-E) oxidizes nitrogen fixation [1-3] and Haber-Bosch (H-B) for synthetic ammonia [4], are a typical representative of the current large-scale industrial nitrogen fixation technology and have been greatly developed. In 1903, Birkenland and Eydem produced the first nitric acid factory in Notodden using a thermal plasma arc method [3]. The air through the thermal plasma reaction chamber is discharged to generate high concentration NOx. Then the reaction gas is quickly been cooled to "freeze" the desired product, and finally enters the tower system to be absorbed by water or dilute nitric acid to produce nitric acid. The energy consumption of Birkeland-Eyde oxidized nitrogen fixation is about 2.4-3.8 MJ/molN. However, the high energy consumption, difficult production control and short plasma electrode life become important factors limiting the development of B-E oxidized nitrogen fixation technology.

H-B ammonia synthesis nitrogen fixation process is the synthesis of ammonia using nitrogen and hydrogen at high temperature (400-600℃), high pressure (about 30 MPa) and catalyst (iron), which is the most important synthetic ammonia nitrogen fixation technology in the world [5]. For more than 100 years since the beginning of the 20th century, H-B process synthetic ammonia-nitrogen fixation technology has supported more than 40% of the worlds population [6-7]. As one of the world's basic industries, China accounts for 27% of the ammonia production. Hydrogen is the main raw material supporting the synthetic ammonia industry, still coming from coal, natural gas and coke oven gas. Its annual energy consumption accounts for 2% of the world's energy, and causes serious air pollution and a large amount of CO2 and other greenhouse gas emissions [8]. In recent years, with the rapid development of photovoltaic, wind power technology, large-scale green renewable energy electrolysis water hydrogen synthesis ammonia process brought great opportunities for traditional ammonia industry. However, H-B process containing high temperature, high pressure, catalyst and harsh reaction conditions, and the intermittent and instability of photovoltaic, wind power and other renewable energy are still difficult to reconcile the contradiction. In the short term to achieve large-scale green transformation has great difficulties [9-11]. Therefore, seeking a green and sustainable nitrogen fixation technology that is environmentally friendly, milder, less energy consumption, more efficient and easy to large-scale production has become an urgent pursuit of researchers all over the world. Based on this, this paper systematically reviews the new nitrogen fixation technology and research progress, analyzes the mechanism and energy consumption of nitrogen fixation technology, and finally summarizes the future development prospect of new nitrogen fixation technologies, so as to provide reference for the design of large-scale nitrogen fixation technology with lower energy consumption.

NEW NITROGEN-FIXATION TECHNOLOGY AND ITS RESEARCH PROGRESS

Research Progress of Photoelectric Catalytic Nitrogen Fixation Technology

Scholars from all over the world are actively exploring photo-catalysis [12-17], photo-electrocatalysis [18-21], electro-catalysis [22-31] for N_2 reduction to make NH_3. Schrauzer et al [16] found that under UV light irradiation, the semiconductor TiO_2-based photo-catalyst shows the abilities to induce the nitrogen reduction for ammonia synthesis. As shown in figure 1 (a), the basic principle of the photo-catalytic synthesis of ammonia is that the photo-catalyst absorbs photons which can produce pair of photo-electron-hole. The carriers diffuse and transfer from the inside of the catalyst to the surface. The photoelectron reacts with the nitrogen adsorbed on the surface of the catalyst, which gradually hydroodize and protonate nitrogen and eventually generate ammonia. The process of photo-catalytic nitrogen reduction is limited by the diffusion and separation of photo-electrons and charge carriers. Most studies of photo-catalysts is to shorten the diffusion distance of charge carriers and reduce the composition probability of photo-electron and hole. Therefore, the researchers attempted to introduce external electric field to suppress the photo-catalytic electron and hole in the diffusion process which was called photoelectric catalysis as shown in figure 1(b). Three electrodes were adopted to achieve photoelectric catalytic nitrogen reduction with catalyst working as photo-cathode and water decomposition occurs on the anode reverse electrode.



(a) Photocatalysis (b) Photoelectric catalysis

Figure 1. Basic principles of the photocatalysis (a) and photoelectric-catalysis reaction processes(b)

Photoelectric catalysis can directly convert solar energy into chemical energy, which is of positive significance to reduce the energy consumption of the synthetic ammonia industry. However, the critical challenge is the lack of NRR catalyst with high Faraday efficiency. Previous research has focused on how to enhance the adsorption and activation capacity of nitrogen on catalysts. Although a variety of catalytic materials have demonstrated electro-catalytic NRR properties, however the NH_3 yield and Faraday efficiency are still unsatisfactory. In heterogeneous catalytic system, it is much complex due to the complexity of the phase interface and mutual transfer process of electron in the catalyst and reactant between delocalized/localized state. The proton transfer process also need to consider the phase interface and solvent chemical environment factors, which lead to the complexity of the reaction process and difficulty to clearly define. Proton transfer has a significant influence on the kinetic characteristics and the reaction path of the photo-catalytic reactions [19]. Vasileios Kyriakou et al. designed an integrated $BaZrO_3$ matrix proton ceramic membrane reactor (PCMR) with the reactor inner wall as the first catalyst (nickel-based catalyst) [25]. Steam and methane mixed in the reactor and produced hydrogen ions, electrons and CO_2 on the surface of the catalyst. The resulting electrons are transmitted to the surface of the second catalyst (vanadium, nitrogen and iron) on the outer wall of the reactor. Thus the adsorbed positively charged hydrogen ions transferred to the outer wall. Hydrogen ions, electrons and nitrogen molecules form ammonia on the surface of the second catalyst. The whole reaction is carried out at atmospheric pressure and at the temperature of 600°C, and the energy consumption is only 1/2 of that of the water vapor recombination method. The exhaust gas produced by the reaction is CO_2. The method combines the mechanism of the electro-catalytic reaction to reduce the energy consumption and exhaust emissions. However it's still hard to meet the actual production demand due to the slow synthetic ammonia reaction rate and high reaction temperature. The key to solve the problem is to improve the catalytic activity of catalyst under mild conditions.

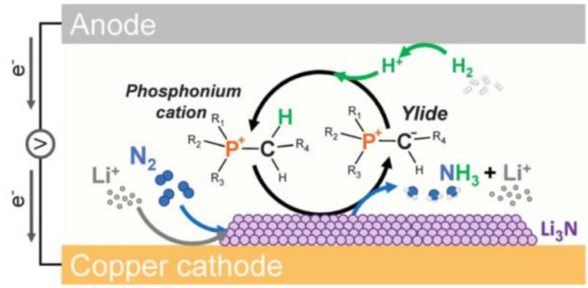


Figure 2. Schematic diagram of the electrocatalytic ammonia synthesis reaction

Suryanto et al. attempted to produce NH3 by N2 at room temperature and atmosphere as shown in figure 2 [32]. The reaction is based on the electro-chemical nitrogen reduction reaction (NRR), fully considering the influences of solvent type on the solubility of nitrogen in solvent, the type and concentration of proton carrier on the NRR reaction, and the side reaction products during the NRR reaction. Although this study achieved good results in terms of ammonia yield and running stability, it is difficult to find the electrode anode region to avoid solvent oxidation. More appropriate and stable solvent is needed to improve reliability. Therefore, to achieve high selectivity, high energy efficiency and high yield in the process of electro-chemical synthesis of ammonia will mainly depend on the combined design of electrode, catalyst and electrolyte. The conventional methods require high electron energy of 15.6 eV to make the N_2 ionization yield N_2^+, or 9.75 eV to isolate N atoms. In contrast, the excitation of the N_2 requires only 6.17 eV of electron energy. To excite N_2 to N_2^* only needs 0.29 eV of energy by particle collision. However, given that the dissociation energy of the first N-N bond in the bond is 410 kJ mol^{-1}, the electron energy in photo-catalysis and electro-catalysis is not sufficient to directly break the bond under mild conditions. It is common to undergo an alternating or end-association process, where the $N \equiv N$bond breaks only after the N-H bond is formed, which makes the reaction rate relatively slow.

Photo-catalytic nitrogen fixation technology simulates the principle of biological nitrogen fixation and directly converts solar energy into chemical energy. Using nitrogen and water as raw materials, it is an effective way for sustainable ammonia synthesis under mild reaction conditions. The carrier of photoelectron-hole pair generated in the process will be transferred from the inside of the catalyst to the surface. The nitrogen is gradually transferred to the surface of the catalyst through dissolution, diffusion process before ammonia synthesis through processes of activation, decomposition, dissociation, desorption and deattachment [33-35]. In the heterogeneous reaction system, promoting the nitrogen dissolved diffusion, adsorption and activation is the key to improve the reaction rate and efficiency. The catalyst material of two-dimensional structure helps to reduce the possibility of recombination of electron and hole in migration. By the introduction of nitrogen atoms and Ru active sites on TiO_2 with nanosheet structure, the separation efficiency of the carriers and thus the activity are significantly improved. The doping treatment of the catalyst can generate the defect sites and enhance the reducing performance of the nitrogen gas [36-37]. Although photoelectric catalysis can realize the direct transition from sunlight to nitrogen fixation products, the high energy required for dissociation leading to the low photo-catalytic efficiency results in the uncertainty of the industrialization prospect. Researchers have used a variety of methods to design highly active photo-active nitrogen fixation catalysts. However, the activity of the existing photo-catalytic nitrogen reduction and synthesis of ammonia is still low. At present, the catalyst with high activity, high selectivity and high stability are still explored. The catalyst system designed by doping and adding additives, as well as the optimization of reaction speed control, are still expected to combine with renewable energy technology to achieve industrial production of ammonia.

Research Progress in Plasma Nitrogen-Fixing Technology

Compared with H-B synthetic ammonia under high temperature, high pressure and catalyst conditions, plasma nitrogen fixing method for the reaction conditions are relatively mild, which is easy to realize the distributed production of ammonia. More importantly, the stability requirement of the external power is relatively low. In the background of the rapid development of green sustainable energy, plasma nitrogen fixing technology has been paid increasingly extensive attentions and in-depth studies [38-42]. To achieve nitrogen fixation reaction is inevitably accompanied by high energy consumption and other problems [9] because nitrogen molecules are extremely stable with bond energy of 946 kJ/mol. Low-temperature plasma is rich in high energy electrons and high concentration of free radicals, which can break the bond through the collision of high energy electrons at mild pressure and temperature and then fix the nitrogen to NOx or NH3 through oxidation or hydrogenation. Theoretically, the process has lower energy consumption for nitrogen fixation [5,43-45]. Plasma has non-equilibrium characteristics and excellent reactivity.

According to the different discharge device and excitation mode, the low-temperature plasma technology used for nitrogen fixation mainly includes spark discharge [46,47], corona discharge [48-49], glow discharge [50], dielectric barrier discharge (DBD) [51-56], radio-frequency discharge [57], arc [1-3,58], microwave [59-63], pulsing controlled plasma [64-65], and the plasma system coupled with catalyst [52,59,66]. Figure 3 lists the typical reactors of B-E structure, sliding arc structure, sliding arc-DBD structure and microwave structure, which have been studied and applied in the field of plasma oxidation and nitrogen fixation.

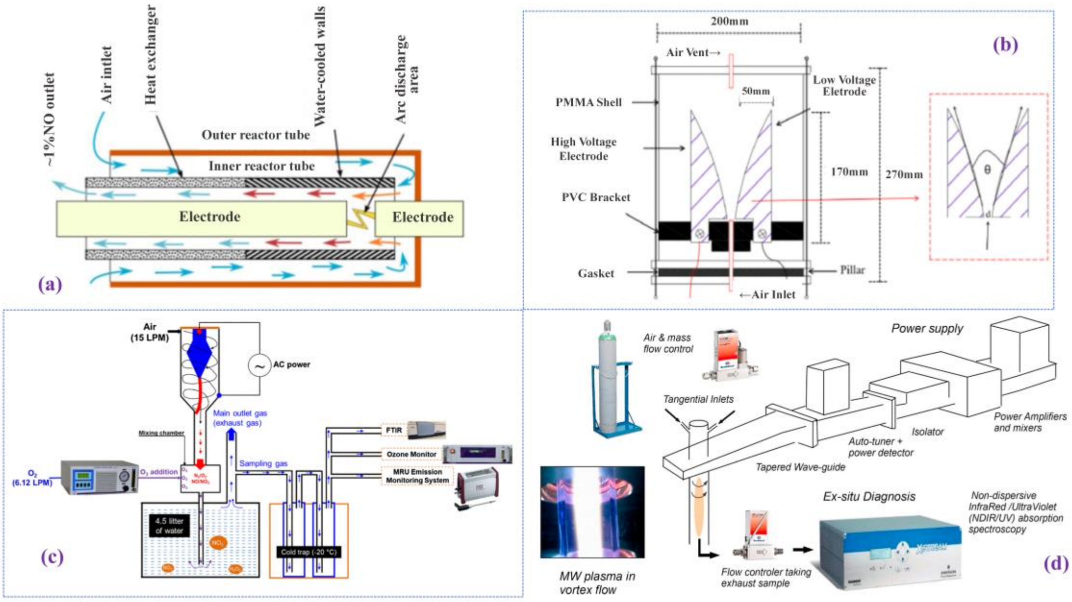


Figure 3. Typical plasma structure. (a) B-E thermal plasma; (b) sliding arc plasma structure; (c) Arc plasma at elevated pressure; (d) Microwave plasma

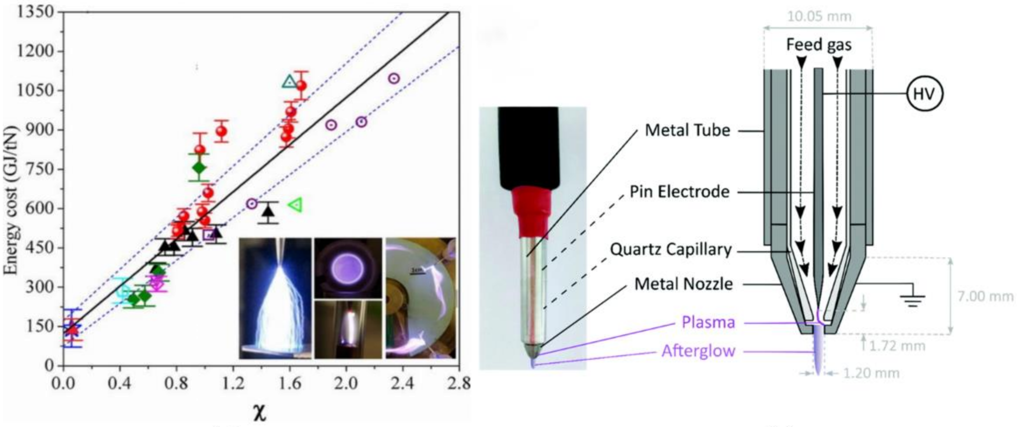
Low-temperature plasma can be mainly divided into thermodynamic equilibrium (quasi-equilibrium) and non-equilibrium states [67], according to the difference of the electron temperature Te and the gas temperature Th. In the thermodynamic equilibrium or quasi-equilibrium states, Te is close to Th and the gas temperature is high. While in the non-equilibrium plasma, Te is much greater than the Th and the gas temperature is low or even close to room temperature. The DC thermal plasma used in the B-E nitrogen oxidation fixation process belongs to the former. Although the energy loss generated by high temperature gas can be reduced by efficient heat transfer, how to achieve a more efficient nitrogen fixation process at lower gas temperature is still the unremitting pursuit of domestic and foreign researchers. Numerous research works have been carried out on the type of plasma generation. The types of plasma generation mainly include spark discharge, DC glow, dielectric barrier discharge, radio frequency plasma, pulse discharge, arc plasma, microwave plasma, laser-induced plasma and plasma generated by liquid phase environment. As can be seen from Table 1, the sliding arc, dc arc and microwave plasma in quasi-thermodynamic equilibrium plasma get more attention, and the energy consumption of nitrogen fixation of 2.4-4.8 MJ/molN is comparable to that of B-E process. The energy consumption of RF plasma is 24-108 MJ/molN [57] which may be attributed to the lower plasma conversion efficiency of the RF plasma and the inefficient energy recovery in the experiments. Sliding arc plasma is a structure that the plasma discharge state frequently starts and stops through air flow. The schematic structural diagram can be found in Figure 3 (b). Because of the rapid transfer of arc roots and the rapid cooling of air flow, the plasma gas temperature is lower than the conventional thermal arc plasma and higher than the cold plasma. Sliding arc plasma can utilize vibration dynamic nitrogen particles at atmospheric pressure, known as a more promising mode of nitrogen fixation. The best reported NOx yield and energy consumption were respectively about 5.5% and 2.5 MJ/molN, which is equivalent to the lowest energy consumption of the B-E process [43]. In non-thermodynamically equilibrium plasma, nitrogen fixation energy consumption has a large span ranging from 0.28 to 1673 MJ/molN. The highest NO yield of microwave plasma with low pressure magnetic confinement reaches 14%, which still maintains the lowest record of 0.28 MJ/molN [42]. The reason may be that the low pressure magnetic confinement microwave plasma can obtain good electron resonance heating effect, and the electron temperature can reach more than 10eV which is slightly higher than the NN bond energy 946 kJ/mol, i.e. 9.8eV. However, the maintenance of magnetic field confinement microwave plasma requires expensive vacuum equipment, which is difficult to realize the promotion and application in industry [39]. The reason for the high energy consumption of nitrogen fixation in the pulse corona plasma type may be the low plasma density and electron temperature, and the plasma energy is more dissipated in the form of sound, light and heat, and fails to effectively form NOx by stimulating nitrogen through electrons. DBD plasma is a common way to produce cold plasma with high density plasma at a lower gas temperature by placing a single or multiple dielectric plate between two electrodes to limit the rapid growth of current. The temperature of DBD plasma gas is low which results in the lower energy loss caused by temperature rise. But in general, the rate of the ionization rate of DBD plasma is 1-2 orders of magnitude lower than that of thermal plasma, which leads to a reduction of nitrogen fixation efficiency of electron excited nitrogen molecules and high energy consumption of nitrogen fixation ranging from 56 to 140 MJ/molN [5,53].

Table 1. Several typical low-temperature plasma nitrogen fixation techniques

Discharge type		NOx potency/%	Energy consumption/(MJ·mol-1·N-1)	Thermodynamic equilibrium states	Reference
Spark		—	20.27-40	Non-equilibrium	[68,69]
DC glow	Needle plate electrode	—	7	Non-equilibrium	[50]
	Needle electrode	0.7	2.8	Non-equilibrium	[51]
DBD	DBD	0.36	56-140	Non-equilibrium	[5]
	Al2O3-DBD	0.5	18	Non-equilibrium	[53]
RF		—	24-108	Quasi-equilibrium	[57,69]
Impulsive	ns spark	—	5-7.7	Non-equilibrium	[50]
	Pulse corona	—	180	Non-equilibrium	[48]
	Negative pulse corona		1673	Non-equilibrium	[66]
	Positive pulse corona		1057	Non-equilibrium	[66]
	Pulse sliding arc	1-2	2.8-4.8	Quasi-equilibrium	[64,65]
Microwave	Conventional	0.6	3.76	Quasi-equilibrium	[59]
	Magnetic confinement	14	0.28	Non-equilibrium	[43]
	MoO3 Collaborative coupling	6	0.84	Quasi-equilibrium	[59]
Arc	DC thermal arc	2	2.4-4.1	Quasi-equilibrium	[1-3]
	Propeller arc plasma	0.4	4.2	Quasi-equilibrium	[50]
	Sliding arc	1.5	3.6	Quasi-equilibrium	[70,71]
laser-produced plasma		—	8.9	Non-equilibrium	[72]
Plasma-phase liquid nitrogen fixation		—	13.35-50.25	Non-equilibrium	[73-75]

A large number of theoretical and experimental studies show that the synergistic effect of catalyst and plasma is expected to reduce nitrogen fixation energy consumption due to a synergistic effect [8, 53, 59]. N2 at the lower vibration level under the coupling between the plasma and the catalyst. The particle reaction rate will be significantly increased to achieve the massive decomposition of nitrogen molecules on the surface of the catalyst. Liu K [53, 54] developed the monary, binary and ternary composite catalysts of different components Mn/Co/W elements coupled with DBD plasma. The results showed that the catalyst provided a large amount of oxygen vacancies for full oxidation of NOx including Mn3WCo/γ-Al2O3. The maximum total nitrogen concentration of cooperative nitrogen fixation was increased by 71.6%, and the energy consumption was reduced by 21.7%. Kim [59] developed a microwave plasma system coupling with the MoO3 catalyst with the nitrogen fixation energy and the NOx concentration of 0.84 MJ/molN and 6%, respectively.

Pulse power technology and power supply technology are constantly developing. The pulse-modulate spark discharge [50], slide arc discharge [64,65], magnetron glow discharge were used to study the transition of NOx. Luo [76] investigated the effect of pulse modulation on nitrogen fixation efficiency of air discharge in RF air plasma. As shown in figure 4(a), it is found that the nitrogen fixation efficiency decreases with the increase of pulse frequency. NOx concentration gradually increases with the duty cycle, and the nitrogen fixation efficiency reaches 5.22 MJ/molN. Pei [50] achieved a minimum energy consumption of 2.9 MJ/molN using pulse modulation rotating spark plasma. Vervloessem [77] reached 0.42 MJ/molN by using high-speed airflow coupled pulse spark oxidation (shown in Figure 4 (b)). Britun [78] reached minimum energy consumption of 0.34 MJ/molN by pulse spark plasma which is similar to the theoretical value of 0.29 MJ/molN. Although the pulsed spark plasma has the advantages of low energy consumption, compact and easy extension, the NOx concentration and yield still need to be optimized.



(a) (b)

Figure 4. Pulse power technology on oxidation nitrogen fixation. (a) nitrogen fixation energy consumption of pulse modulated rotating spark discharge plasma; (b) schematic diagram of nitrogen fixing device coupled with high-speed airflow.

Plasmonium synthesis by direct nitrogen fixation is another important method of nitrogen fixation [9,39,79-83] using N2 and H2 as the reactants to synthesize NH3. In the traditional H-B ammonia synthesis process, high temperature, high pressure and catalyst are required. N_2 and H_2 in the low temperature plasma environment can react under milder conditions, which need to bring N2 and H2 to form the NH and NH2 by electron dissociation and excitation. And finally NH2 and H react to generate ammonia in which electrons need to break N and H-H bonds to form more active reactive species. However, the electron temperature of low plasma is about 1-2 eV at constant pressure. As a result, using the appropriate catalyst is promising to reduce the reaction barrier, energy consumption and improve the ammonia yield [5]. Synthetic ammonia reaction is volume increase and exothermic reaction. In order to reduce energy consumption, it tends to use the non-equilibrium characteristics of low temperature plasma. Although it is easier to obtain a plasma environment with lower temperature and higher electron temperature at low pressure, the researchers mostly used DBD plasma structure in order to avoid using expensive vacuum system, which is easy to operate and scale at atmospheric pressure, and also conducive to achieve synergistic nitrogen fixation in combination with catalysts. The catalysts including MgO, α-alumina, feroelectric material, Rh/γ-alumina, and Ru-Mg/γ-alumina [79-83], for cooperative DBD plasma ammonia synthesis has a wide energy consumption span ranging from 1.7 to 576 MJ/molN. Numerous findings suggest that catalyst-carrier and promoter systems are more conducive to reducing the dissociation barrier of N2, which improves the catalytic activity of the heterogeneous catalyst system and improves the efficiency and conversion rate of ammonia synthesis. The complex chemical reaction in the plasma system leads to the diversity of the plasma catalytic reaction products, so choosing the appropriate plasma type and the catalyst type adapted to this environment will be the key to improve the synthesis efficiency.

ANALYSIS of the Plasma Nitrogen Fixation Mechanism and Energy Consumption Analysis

NOx synthesis depends on decomposition. Electron excitation reactions are divided into five main types [7]: direct decomposition of electron collision (1), electron excitation decomposition (2-4), electron and ion composite decomposition (5), excited state collision decomposition (6) and vibrational decomposition (7).

$$e+N_2 \rightarrow e+2N, T_e>9.75\text{eV} \tag{1}$$

$$e+N_2 \rightarrow e+N_2^*(v=1),\ T_e>0.29\ \text{eV} \tag{2}$$

$$e+N_2^* \rightarrow e+2N \tag{3}$$

$$e+N_2 \rightarrow 2e+N_2^+, T_e>15.6eV \tag{4}$$

$$2e+N_2^+ \rightarrow e+2N \tag{5}$$

$$N_2^*+N_2^* \rightarrow N_2+2N \tag{6}$$

$$N_2(v)+M \rightarrow 2N+M \tag{7}$$

The theoretical energy consumption of plasma nitrogen fixation is as low as 0.2 MJ/molN, which is the minimum energy required for $N_2+O_2 \rightarrow 2NO$, with ΔH_m=180 kJ/mol. The reaction energy barrier of the Zeldovich reaction is the key to determine the energy consumption of plasma nitrogen fixation [7,12,84]. Wang [23] found that the reduced electric field can regulate the vibration excitation level of nitrogen molecules, and then carry out the Zeldovich reaction more efficiently. Different plasma types have different characteristics, such as the low temperature of the plasma source gas represented by the discharge structure and discharge form of DBD, electric spark and corona discharge, and low pressure glow discharge. The reaction between gas components mainly depends on the electron energy, while the electron temperature at atmospheric pressure plasma is generally 1-2eV, i.e., 0.09-0.19 M J/mol, which is far lower than the dissociation energy of nitrogen and oxygen. Although the electron energy has a certain distribution in the high energy region, the proportion is very low and can be ignored. Therefore, the yield of nitrogen fixation obtained from atmospheric pressure plasma is generally only about 1%, while for low pressure microwave plasma can reach 14% [43]. In the reaction process of oxidation and nitrogen fixation, the collisions between electrons, active particles and other particles produce nitrogen atoms and oxygen atoms, and then the desorption process will release NO. Therefore, increasing the electron temperature and the concentration of active free radicals will also be the key to achieve lower nitrogen fixation energy consumption.

$$e+O_2 \rightarrow O+O+e, T_e>5.12 \text{ eV} \tag{8}$$

$$O+O_2+M \rightarrow O_3+M \tag{9}$$

In the process of atmospheric pressure plasma with high-frequency electron collisions, the gas temperature similar to the electron temperature while its energy transfer to neutral particles after sufficient collision of electrons. Atmospheric pressure microwave plasma, dc thermal arc plasma represented by the quasi equilibrium plasma, the gas temperature can reach to 1000-3000 degrees or even higher. Thermal NOx formation mechanism will dominate [59]. The generation of thermal NOx is closely related to temperature. N2 reacts with O2 under high temperature combustion conditions, which is the main generation way of NOx in high temperature combustion equipment (e.g., combustion chamber). It is mainly affected by three factors: flame temperature, nitrogen and oxygen ratio, and the residence time of the gas in the high temperature area. It has been shown that the generation of thermal NOx has a critical temperature of 1800 K. When the temperature is below this limit, the generation of NOx is less. Once the temperature exceeds this limit, the production of NOx will increase sharply with the rise of temperature, showing almost exponential growth trend. Whenever the temperature increases by 100 degrees from the limit, the generation of NOx increases by 6 to 7 times. Different from the thermal NOx generation mechanism, electronic action and temperature effect and synergistic effect in low temperature plasma, the NOx generation mechanism in low temperature plasma still needs a lot of experimental and theoretical research [85].

In the mechanism of ammonia and nitrogen fixation in plasma synthesis, the main reaction processes include[5]:

$$N_2 \rightarrow 2N^* \tag{10}$$

$$H_2 \rightarrow 2H^* \tag{11}$$

$$N^*+H^* \rightarrow NH \tag{12}$$

$$NH+H^* \rightarrow NH_2^* \tag{13}$$

$$NH_2^*+H^* \rightarrow NH_3 \tag{14}$$

It can be seen that the NH radical is the precursor in the NH_3 synthesis system. In plasma, NH groups are formed by N and H atoms which are essential species. The dissociation energy of hydrogen molecules (4.52 eV) is relatively low, while the ionization energy (15.6 eV) and dissociation energy (9.75 eV) of nitrogen molecules are both high. In order to obtain more precursors, N2 is reduced through the assistance and synergy of plasma and catalyst. Dissociation barrier promotes the surface adsorption reaction, and then the synthesis of ammonia and nitrogen fixation have become the focus of current research. Hong [86, 87] found that free radicals react with vibrational excitation molecules and are a key factor affecting the synthesis of ammonia.

In the context of the vigorous development of renewable energy, although the price of electricity has been greatly controlled, the development of nitrogen-fixing technology with low energy consumption and high efficiency is still the direction pursued by researchers worldwide. According to the theoretical estimates, the energy consumption of non-thermal plasma nitrogen fixation is about 0.2 MJ/molN. Based on the $N_2+O_2\rightarrow 2NO$ reaction (i. e., the enthalpy of NO formation), the theoretical energy consumption of thermal plasma and the H-B process is 0.72 MJ/molN and 0.35 MJ/molN, respectively. However, the current energy consumption for non-thermal plasma nitrogen fixation, thermal plasma and the H-B process, is about 2.4 MJ/molN, 2.4-3.1 MJ/molN and 0.6-0.7 MJ/molN, respectively. At present, the H-B method is the most mature ammonia synthesis process with an annual output of nearly 200 million tons. Up to now, the nitrogen fixation technology by non-thermal plasma and plasma coupling with catalyst is still attracting much attention and been developed to further reduce the nitrogen fixation energy consumption.

CONCLUSIONS AND PROSPECTS

This paper summarizes the characteristics, mechanisms, advantages and key problems of photoelectric catalytic nitrogen fixation and plasma oxidation nitrogen fixation/synthetic ammonia nitrogen fixation technology. Plasma nitrogen fixation and photoelectric catalytic nitrogen fixation technology has obvious advantages compared with traditional H-B method, such as easier modular structure, relatively mild reaction conditions, lower demand for power stability. Through the use of mature and stable photovoltaic, wind power and other renewable energy, nitrogen fixation, synthetic ammonia energy-resources and large-scale energy storage, it has gathered worldwide attention in the realization of energy independence and zero green-house gas emission. However, the energy consumption of new nitrogen fixation technology represented by plasma nitrogen fixation technology is still very high. Although there are reports showing that the energy consumption of plasma nitrogen fixation is close to the lowest theoretical nitrogen fixation energy consumption, the concentration and output of nitrogen fixation products need to be greatly improved, and the possibility of replacing H-B ammonia synthesis process is low in the short term. Although photoelectric catalysis is expected to directly use light energy to fix nitrogen, but the nitrogen fixation efficiency is still very low compared with the plasma nitrogen fixation technology which has a higher development potential. However, how to reduce the energy consumption of nitrogen fixation and improve the concentration and yield of plasma nitrogen fixation products is the focus of current domestic and foreign research. The deep understanding of the reaction mechanism of plasma nitrogen fixation and photoelectric catalytic nitrogen fixation, and the exploration of catalyst synergistic nitrogen fixation mechanism is help to promote the development of nitrogen fixation technology. Plasma catalytic ammonia synthesis process uses hydrogen as raw material, which will still be unable to get rid of the dilemma of difficult hydrogen storage and transportation in the short term. Since 1908, the thermal plasma nitrogen fixing technology based on the B-E process route has been developed, and the nitrogen fixing energy consumption is the lowest to 2.4 MJ/molN. However, the process is difficult to large-scale promotion due to the limited service life of thermal plasma equipment. It is estimated that the theoretical energy consumption of 0.72 MJ/molN is still twice of that of H-B theoretical value. Based on the non-equilibrium plasma nitrogen fixation technology through NO synthesis key process Zeldovich reaction has higher prospects for development. The development of new low temperature plasma technology to effectively control the plasma density, electron temperature and free radical energy in active gas distribution, and promote the synergy effect of non-equilibrium plasma and efficient catalyst, will be the key to improve the efficiency of nitrogen fixation and reduce the energy consumption of nitrogen fixation.

ACKNOWLEDGMENTS

This project was partially supported by University Synergy Innovation Program of Anhui Province (No. GXXT-2022-026), Natural Science Research Project of Anhui Educational Committee (Nos. KJ2021A1168 and 2024AH050620), Quality Engineering Projects of Anhui Educational Committee (No. 2022sx061), Quality Engineering Projects of Anhui Xinhua University (Nos. 2022jy010, 2022jxtdx03, 2023jy027 and 2022xqjdx04), Natural Science Research Project of Anhui Xinhua University (No. 2023zr019), Industry-Academia-Research Collaborative Projects of Anhui Xinhua University (Nos. 2024cxy137, 2024cxy138 and 2024cxy14*0).*

REFERENCES

[1] Birkeland K, On the Oxidation of Atmospheric Nitrogen in Electric Arcs. Trans Faraday Soc., 1906, 2(2): 98-116.

[2] Eyde S. Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway. Ind Eng Chem, 1912, 4(6): 771-774.

[3] Gross B, Grycz B, and Miklossy K. Plasma Technologies. Science Press, 1980, 23(8): 69-69.

[4] Gorbanev Y, Vervloessem E, Nikiforov A, et al. Nitrogen Fixation with Water Vapor by Nonequilibrium Plasma: Toward Sustainable Ammonia Production. ACS Sustain Chem Eng, 2020, 8(10): 2996-3004.

[5] Lu XP, Lei XY, Cheng H, et al. Nitrogen fixation applications for plasma technology. Journal of Nanchang University (Science edition), 2021, 45 (4): 511-519.

[6] Cherkasov N, Ibhadon AO, Fitzpatrick P. A Review of the Existing and Alternative Methods for Greener Nitrogen Fixation. Chem Eng Process, 2015, 90: 24-33.

[7] Rouwenhorst KHR, Fatme J, Bogaerts A, et al. From the Birkeland-Eyde process towards energy-efficient plasma-based NOx synthesis: A techno-economic analysis. Energy Environ Sci, 2021, 14(9): 2520-2534.

[8] Lv XJ, Chen H, Wu AJ, et al. Direct air oxidation of nitrogen fixation based on magnetic separation. Journal of Zhejiang University (Engineering Edition), 2022, 56 (6): 1206-1211.

[9] Zhou D, Zhou R, Zhou R, et al. Sustainable Ammonia Production by Non-Thermal Plasmas: Status, Mechanisms, and Opportunities. Chem Eng J, 2021, 421(1): 129544.1-13.

[10] MacFarlane DR, Cherepanov PV, Choi J, et al. A. N. A Roadmap to the Ammonia Economy. Joule, 2020, 4(6): 1186-1205.

[11] Wang H, Seemakurthi RR, Chen GF, et al. Laser-induced nitrogen fixation. Nat Commun, 2023, 14(1): 5668..

[12] Dong GH, Ho W, Wang C. Selective Photocatalytic N2 Fixation Dependent on g-C3N4 induced by Nitrogen Vacancies. J Mater Chem A, 2015, 3(46): 23435-23441.

[13] Hirakawa H, Hashimoto M, Shiraishi Y, et al. Photocatalytic Conversion of Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. J Am Chem Soc, 2017, 139(31): 10929-10936.

[14] Li CC, Wang T, Zhao ZJ, et al. Promoted Fixation of Molecular Nitrogen With Surface Oxygen Vacancies on Plasmon-Enhanced TiO2 Photoelectrodes. Angew Chem Int Edit, 2018, 57(19): 5278-5282.

[15] Bao T, Xi Y, Zhang C, et al. Highly efficient nitrogen fixation over S-scheme heterojunction photocatalysts with enhanced active hydrogen supply, National Science Review, 2024, 11: nwae093.

[16] Schrauzer GN, Guth TD, Photolysis of Water and Photoreduction of Nitrogen on Titanium Dioxide. J Am Chem Soc, 1977, 99(22): 7189-7193.

[17] Li S, Chen X, Hu S, et al. Infrared Ray Assisted Microwave Synthesis: A Convenient Method for Large-Scale Production of Graphitic Carbon Nitride with Outstanding Nitrogen Photofixation Ability. Rsc Adv, 2016, 6(51): 45931-45937.

[18] Shi L, Li Z, Ju LC, et al. Promoting Nitrogen Photofixation Over a Periodic Ws2@TiO2 Nanoporous Film. J Mater Chem A, 2020, 8(3): 1059-1065.

[19] Khadijeh P, Aziz HY, Alireza K, Outstanding photocatalytic nitrogen fixation performance of TiO2 QDs modified by Bi2O3/NaBiS2 nanostructures upon simulated sunlight, J Coll Interf Sci, 2023, 641: 1000-1013.

[20] Ali SA, Sadiq I, Ahmad T, Flatland materials for photochemical and electrochemical nitrogen fixation applications: from lab-door experiments to large-scale applicability, Sus Energ Fuels, 2024, 8: 3476-3495.

[21] Guo K, Yang J, Yu N, et al. Biological nitrogen fixation in cereal crops: Progress, strategies, and perspectives, Plant Comm, 2023, 4(2): 100499.

[22] Li X, Xie HT, Mao J. Ag Nanoparticles-Reduced Graphene Oxide Hybrid: An Efficient Electrocatalyst for Artificial N2 Fixation to NH3 At Ambient Conditions. J Mater Sci, 2020, 55(12): 5203-5210.

[23] Wang ZQ, Li YH, Yu HJ, et al. Ambient Electrochemical Synthesis of Ammonia from Nitrogen and Water Catalyzed by Flower-Like Gold Microstructures. Chem Sus Chem, 2018, 11(19): 3480-3485.

[24] Lv XW, Wang L, Wang GC, et al. ZIF-Supported AuCu Nanoalloy for Ammonia Electrosynthesis from Nitrogen and Th in Air. J Mater Chem A, 2020, 8(18): 8868-8874.

[25] Kyriakou V, Garagounis I, Vourros A, et al. An Electrochemical Haber-Bosch Process. Joule, 2019, 4(1): 142-158.

[26] Adeosun S, Thorn JRP, Lin C, et al. Direct Nitrogen Oxidation via Pd-nanoparticle Electrocatalysis. ChemRxiv. 2024, 2(10): 1-9.

[27] Ashida PH, Muraliraj A, Sreekuttan MU, Electrochemical nitrogen fixation on single metal atom catalysts. Chem Commun, 2023, 59, 10689-10710.

[28] Jin H, Kim SS, Venkateshalu S, et al. Electrochemical Nitrogen Fixation for Green Ammonia: Recent Progress and Challenges. Adv Sci, 2023, 10: 2300951.

[29] SanthoshCR, Sankannavar R, A comprehensive review on electrochemical green ammonia synthesis: From conventional to distinctive strategies for efficient nitrogen fixation. Appl Energ, 2023, 352: 121960.

[30] Wang YF, Zhao CR, Yuan SD, et al. One-step fabrication of Cu-doped Bi2MoO6 microflower for enhancing performance in photocatalytic nitrogen fixation. J Coll Interf Sci, 2023, 638: 427-438.

[31] Omain T, Alexander B, Olivia W, et al. Searching for the Rules of Electrochemical Nitrogen Fixationp. ACS Cataly 2023, 13(22):14513-14522.

[32] Suryanto B, Matuszek K, Choi J, et al. Nitrogen Reduction to Ammonia at High Efficiency and Rates Based on a Phosphonium Proton Shuttle. Science, 2021, 372(6547): 1187-1191.

[33] Li ZP, Guo W. Advances in photocatalytic nitrogen fixation. Henan Chem Industry, 2023, 40(10): 10-15.

[34] Ren XL, Yan XQ, Gong XJ. Research progress in the synthesis of ammonia by photo(electric) reduction of nitrogen. Chem Prog, 2020, 39 (12): 4856-4865.

[35] Liu S, Wang Y, Wang S, et al. Photocatalytic Fixation of Nitrogen to Ammonia by Single Ru Atom Decorated Tio2 Nanosheets. Acs Sustain Chem Engin, 2019, 7(7): 6813-6820.

[36] Yang J, Guo Y, Jiang R, et al. High-Efficiency "Working-In-Tandem" Nitrogen Photofixation Achieved by Assembling Plasmonic Gold Nanocrystals on Ultrath in Titania Nanosheets. J Am Chem Soc, 2018, 140(27): 8497-8508.

[37] Lamichhane P, Veerana M, Lim JS, et al. Low-Temperature Plasma-Assisted Nitrogen Fixation for Corn Plant Growth and Development. Int J Mol Sci, 2021, 22(10): 5360.1-5360.20.

[38] Chen H, Yuan D, Wu A. Review of Low-Temperature Plasma Nitrogen Fixation Technology. Waste Dispos Sus Energ, 2021, 9(3): 201-217.

[39] Liu J, Nie L, Liu D, et al. Plasma for nitrogen fixation by using N2/O2 mixture: Reaction pathway, energy flow, and plasma reactor, Plasma Process Polym, 2024, 21: e2300153.

[40] Sun J, Zhang TQ, Hong JM, et al. Insights into plasma-catalytic nitrogen fixation from catalyst microanalysis and chemical kinetics modelling, Chem Eng J, 2023, 469: 143841.

[41] Lamichhane P, Pourali N, Rebrov EV, et al. Energy Intensified Nitrogen Fixation Through Fast Modulated Gas Discharge from Pyramid-shaped Micro-electrode. Plasma Chem Plasma Process, 2024, 44: 1369-1392.

[42] Rusanov VD, Fridman AA, Sholin GV. The Physics of a Chemically Active Plasma with Nonequilibrium Vibrational Excitation of Molecules. Sov Phys Usp, 1981, 6(24): 447-474.

[43] Takeshi S, Takashima K, Sasaki S, et al. Plasma nitrogen fixation for plant cultivation with air-derived dinitrogen. Plasma Process Polym, 2024, 21: e2400096.

[44] Zhang S, Shao T. Status and challenges of energy conversion from pulsed spark discharge plasma. J Petro Sci (Petrochem Indus), 2023, 39 (05): 963-976.

[45] Zhao SW, Zhang L, Fang Z, Pulse-bubble discharge plasma nitrogen fixation, J Ato Molec Phys, 2025, 42: 063002.

[46] Rehbein N, Cooray V. NOx production in Spark and Corona Discharges. J Electrostat, 2001, 5(51): 333-339.

[47] Bogaerts A, Neyts EC. Plasma Technology: An Emerging Technology for Energy Storage. ACS Energy Lett, 2018, 3(4): 1013-1027.

[48] Shen S, Chai Y, Shen Q, et al. Gas-Phase Amination of Aromatic Hydrocarbons by Corona Discharge-Assisted Nitrogen Fixation. Sci Rep-UK, 2021, 11(1): 2841.1-2841.9.

[49] Pei X, Gidon D, Yang YJ, et al. Reducing Energy Cost of NOx Production in Air Plasmas. Chem Eng J, 2019, 362: 217-228.

[50] Pei X, Gidon D, Graves D. Specific Energy Cost for Nitrogen Fixation as NOx using DC Glow Discharge in Air. J Phys D Appl Phys, 2019, 53(4): 044002.1-044002.12.

[51] Cheng H, Ma M, Zhang Y, et al. The Plasma Enhanced Surface Reactions in a Packed Bed Dielectric Barrier Discharge Reactor. J Phys D Appl Phys, 2020, 53(14): 144001.

[52] Patil BS, Cherkasov N, Lang J, et al. Low Temperature Plasma-Catalytic NOx Synthesis in a Packed DBD Reactor: Effect of Support Materials and Supported Active Metal Oxides. Appl Catal B-Environ Energy, 2016, 194: 123-133.

[53] Liu K, Yin Y, Geng WQ, et al. The influence mechanism of transition metal oxide catalyst on nitrogen fixation by medium blocking discharge. Journal of Chemistry of Higher Education, 2022, 43 (11): 181-191.

[54] Liu K, Yin Y, Geng WQ, et al. Study on nitrogen fixation performance and mechanism analysis of dielectric barrier discharge under different operating parameters. Journal of Chemical Industry, 2022, 73 (11): 4045-4053.

[55] Zhu MC, Wang FQ, Xia WD. Based on emission spectrum analysis of medium blocking discharge nitrogen fixation path. laser optoelectro progress, 2024, 61: 0930002

[56] Nepal CR, Nicolas M, Cédric P, et al. Mechanisms of reducing energy costs for nitrogen fixation using air-based atmospheric DBD plasmas over water in contact with the electrode, Chem Eng J, 2023, 461: 141844.

[57] William SP, Ransom BP, Bruno JZ. Fixation of Nitrogen in a Crossed Discharge. Ind Eng Chem, 1954, 46(7): 1468-1471.

[58] Ivan T, Colin OM, Annemie B, et al. Nitrogen Fixation by an Arc Plasma at Elevated Pressure to Increase the Energy Efficiency and Production Rate of NOx. ACS Sustainable Chem Eng, 2023, 11(5): 1888-1897.

[59] Kim T, Song S, Kim J, et al. Formation of NOx from Air and N2/O2 Mixtures Using a nonthermal microwave plasma system. Jpn J Appl Phys, 2010, 49(12): 126201.

[60] Mutel B, Dessaux O, Goudmand P. Energy Cost Improvement of the Nitrogen Oxides Synthesis in a Low Pressure Plasma. Rev Metaphys Morale, 1984, 19(6): 461-464.

[61] Jun D, Wenyi L, Qingqing C, et al. Sustainable Ammonia Synthesis from Air by the Integration of Plasma and Electrocatalysis Techniques. Inorg Chem Front, 2023, 10(19): 5762-5771.

[62] Li W, Zhang S, Ding J, et al. Sustainable Nitrogen Fixation to Produce Ammonia by Electroreduction of Plasma-Generated Nitrite. ACS Energy Lett, 2023, 11(3): 1168-1177.

[63] Seán K, Annemie B. Nitrogen fixation in an electrode-free microwave plasma, Joule, 2021, 5(11): 3006-3030.

[64] Wang W, Patil B, Heijkers S, et al. Nitrogen Fixation by Gliding Arc Plasma: Better Insight by Chemical Kinetics Modelling. Chem Sus Chem, 2017, 10(10): 2235-2245.

[65] Patil BS, Peeters FJJ, Rooij GJV, et al. Plasma Assisted Nitrogen Oxide Production from Air: Using Pulsed Powered Gliding Arc Reactor for a Containerized Plant. Amer Inst Chem Eng, 2018, 64(2): 526-537.

[66] Yu Y, Wei X, Chen W, et al. Design of Single-Atom Catalysts for Electrocatalytic Nitrogen Fixation. Chem Sus Chem, 2024, 17: e202301105.

[67] Xu XJ, Zhu DC. Gas Discharge Physics. Fudan University Press, 1996.

[68] Abdelaziz AA, Teramoto Y, Nozaki T, et al. Toward Reducing the Energy Cost of NOx Formation in a Spark Discharge Reactor through Pinpointing Its Mechanism. ACS Sus Chem Eng, 2023, 11(10): 4106-4118.

[69] Pavlovich MJ, Ono T, Galleher C, et al. Air Spark-Like Plasma Source for Antimicrobial Nox Generation. J Phys D Appl Phys, 2014, 47(50): 505202.1-505202.10.

[70] Vervloessem E, Aghaei M, Jardali F, et al. Plasma-Based N2 Fixation into NOx: Insights from Modeling toward Optimum Yields and Energy Costs in a Gliding Arc Plasmatron. ACS Sus Chem Eng, 2020, 8(14): 9711-9720.

[71] Jardali F, Alphen S, Creel J, et al. NOx Production in a Rotating Gliding Arc Plasma: Potential Avenue for Sustainable Nitrogen Fixation. Green Chem, 2021, 23(4): 1748-1757.

[72] Mahbubur R, Vernon C. NOx Generation in Laser-Produced Plasma in Air as a Function of Dissipated Energy. Opt Laser Techno, 2003, 35(7): 543-546.

[73] Joseph RT, Nabiel HA, Daniel JL, et al. A Plasma-Water Droplet Reactor for Process-Intensified, Continuous Nitrogen Fixation at Atmospheric Pressure. ACS Sus Chem Eng, 2020, 8(39): 14845-14854.

[74] Volkov AG, Bookal A, Hairston JS, et al. Mechanisms of Multielectron Reactions at the Plasma/Water Interface: Interfacial Catalysis, Rons, Nitrogen Fixation, and Plasma Activated Water. Electrochim Acta, 2021, 385: 138441.

[75] Zhang C, Kuang Y, Huang BD, et al. Factors of pulse liquid plasma, J Wuhan University (Eng Edi), 2023, 56 (11): 1327-1335.

[76] Luo Yi, Liu MY, Wang CX, et al. Pulse-modulated RF air plasma nitrogen fixation study. J Wuhan University (Eng Edi), 2023, 56 (10): 1405-1412.

[77] Vervloessem E, Gorbanev Y, Nikiforov A, et al. Sustainable NOx Production from Air in Pulsed Plasma: Elucidating the Chemistry Behind the Low Energy Consumption. Green Chem, 2022, 24(2): 916-929.

[78] Britun N, Gamaleev V, Hori M. Evidence of Near-the-limit Energy Cost no Formation in Atmospheric Spark Discharge. Plasma Sources Sci T, 2021, 30: 08LT02.1-10.

[79] Chen H, Wu A, Mathieu S, et al. Highly Efficient Nitrogen Fixation Enabled by an Atmospheric Pressure Rotating Gliding Arc. Plasma Processes Polym, 2021, 18(7): 2000200.1-13.

[80] Gómez-Ramírez A, Montoro-Damas AM, CotrinoJ, et al. About the enhancement of chemical yield during the atmospheric plasma synthesis of ammonia in a ferroelectric packed bed reactor. Plasma Processes Polym, 2017, 14(6): 201600081.1-201600081.8.

[81] Gómez-Ramírez A, Cotrino J, Lambert RM, et al. Efficient Synthesis of Ammonia from N2 And H2 Alone in a Ferroelectric packed-bed DBD reactor. Plasma Sources Sci T, 2015, 24(6): 065011.1-065011.8.

[82] Mizushima T, Matsumoto K, SugohJI, et al. Tubular Membrane-like Catalyst for Reactor with Dielectric Barrier Discharge Plasma and its Performance in Ammonia Synthesis. Appl Catal A-Gen, 2004, 265(1): 53-59.

[83] Iwamoto M, Akiyama M, Aihara K, et al. Ammonia Synthesis on Wool-Like Au, Pt, Pd, Ag, or Cu Electrode Catalysts in Nonthermal Atmospheric-Pressure Plasma of N2 and H2. Acs Catalysi, 2017, 7(10): 6924-6929.

[84] Hao Y, Dong X, Zhai S, et al. Hydrogenated Bismuth Molybdate Nanoframe for Efficient Sunlight-Driven Nitrogen Fixation from Air. Chem- Eur J, 2016, 22(52): 18722-18728.

[85] Xu T. Combustion science. Beijing: Machinery Press, 2010.

[86] Hong J, Prawer S, Murphy AB. Production of Ammonia by Heterogeneous Catalysis in a Packed-Bed Dielectric-Barrier Discharge: Influence of Argon Addition and Voltage. IEEE T Plasma Sci, 2014, 42(10): 2338-2345.

[87] Hong J, Aramesh M, Shimoni O. Plasma Catalytic Synthesis of Ammonia Using Functionalized-Carbon Coatings in An Atmospheric-Pressure Non-Equilibrium Discharge. Plasma Chem Plasma P, 2016, 36(4): 917-934.