

Non-thermal plasma fixing of nitrogen into nitrate: solution for renewable electricity storage?

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Abstract The rapid deployment of solar and wind technology produces significant amount of low-quality electricity that calls for a better storage or usage instead of being discarded by the grid. Instead of electrochemical CO₂ reduction and/or NH₃ production, here we propose that non-thermal plasma oxidation of N₂ into nitrate or other valuable nitrogen containing compounds deserve more research attention because it uses free air as the reactant and avoids the solubility difficulty, and also because its energy consumption is merely 0.2 MJ/mol, even lower than the industrially very successful Haber–Bosch process (0.48 MJ/mol) for NH₃ production. We advocate that researchers from the plasma community and chemistry community should work together to build energy efficient non-thermal plasma setup, identify robust, active and low-cost catalyst, and understand the catalyzing mechanism in a plasma environment. We are confident that free production of nitrate with zero CO₂ emission will come true in the near future.

Keywords energy storage, nitrogen fixation, non-thermal plasma

Nowadays, renewable energy technologies such as wind, solar and other renewable energy sources have begun to replace fossil fuels for electric power generation. From the practical view, it is the time to consider how to deal with the fluctuations in energy output for wind and solar energy, if we want to integrate such energy with the rest of the grid. During peak seasons, there is even vast wastes of electricity for the renewable energy power station to avoid grid overload [1].

The long-term storage (or usage) of electricity has become one of the biggest challenges for renewable sources. Converting renewable power into chemical

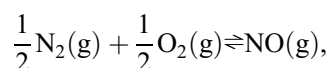
energy such as fuels or chemicals becomes a well-acknowledged solution. One of the most studied chemical energy storage method is carbon dioxide electrochemical reduction. This strategy converts the greenhouse gas CO₂ into valuable chemicals using low-cost renewable electricity, thus killing two birds with one stone. However, considering the rather low content of CO₂ in air (0.04% v/v) and the difficulty in gathering CO₂, it is challenging and might even be costly for the large scale (GW level or more) deployment, although the reported Faradaic efficiency is pretty high (~90%) [2].

Here we believe the use of electrical energy to fix the dominant gas in air—nitrogen, i.e., reduction or oxidation of N₂, is one of the most promising way to meet with the seasonal variability of renewable energy sources. Nitrogen-related chemicals play a significant role in our society, such as nitrogen fertilizer, raw materials for chemical industry, etc. Nitrogen fertilizer provides indispensable constitutes for plants and crops. And nitrate is highly demanded in various industry, the price of industrial HNO₃ analytical reagent being ~1800 RMB/ton and NaNO₃ analytical reagent 20000 RMB/ton.

Recently, some researchers start to utilize electrochemical method to conduct ammonia synthesis as a means to store renewable electricity. Although the reported Faraday efficiency even reach 45%, the production rate is rather low (14 mg · m⁻² · h⁻¹), mainly due to the very limited solubility of nitrogen in common electrolytes [3]. Gas phase reaction seems more reasonable for nitrogen reduction because high pressure could significantly increase the reactant concentration, boosting reaction speed and production yield. The current most widespread gas-phase nitrogen fixation method is Haber–Bosch process. Fritz Haber and Carl Bosch developed and scaled up the artificial nitrogen fixation into ammonia in the first half of the 20th century. They were later awarded Nobel prizes for two times, in 1918 and 1931 separately, demonstrating the great significance of nitrogen fixation [4]. Today, Haber–Bosch process has been reformed greatly and becomes the most

effective and universal nitrogen fixation method. The reaction converts atmospheric N_2 and H_2 to NH_3 at 150–250 atm¹⁾ and between 400°C and 500°C, utilizing Fe^{3+} as the catalyst. However, Haber–Bosch process consumes almost 2% of world's total energy supply and emits 300 million metric tons of CO_2 , which accounts for 3% of global CO_2 emission [5,6]. Moreover, hydrogen requires steam reforming of methane from natural gas, further increasing the energy consumption of the whole nitrogen fixation process.

Thereby the oxidation of nitrogen into nitrates, rather than reduction of nitrogen, comes into our view as nitrogen fixation method, based on the abundant sources of N_2 and O_2 (Eq. (1)). Moreover, the current mainstreaming nitrate production is via oxidation of NH_3 ; a direct reaction between N_2 and O_2 to form first NO and then NO_2 , and subsequently react with H_2O (or $NaOH$ solution) to produce nitrate would be more chemistry and energy efficient. However, the oxidation of N_2 is very difficult to occur both thermodynamically and kinetically: as shown in Eq. (1), in which $\Delta_r G_m^\ominus(T_l)$ means standard Gibbs free energy change under normal temperature T_l , and $\Delta_f G_m^\ominus[NO(g)]$ means standard molar free energy of formation for NO . This reaction is highly endothermic and requires 86.55 kJ/mol Gibbs free energy change (Eq. (1)); dissociation of triple N_2 bond (964 kJ/mol) also need to overcome a prohibitive energy barrier. Such reaction can only be observed in Nature under extreme conditions like lightning.



$$\Delta_r G_m^\ominus(T_l) = \Delta_f G_m^\ominus[NO(g)] = 86550 \text{ J} \cdot \text{mol}^{-1}. \quad (1)$$

The electronic configurations of N_2 and O_2 provide a simple illustration of how to make above reaction occur (Fig. 1). The highest occupied molecular orbital (HOMO) of N_2 is $2\sigma_g$ in anti-symmetry, while the lowest unoccupied molecular orbital (LUMO) of O_2 are half-filled π_g in symmetry. The different symmetries forbid the flow of electrons from N_2 to O_2 . On the contrary, the symmetry of LUMOs ($1\pi_g$) of N_2 matches with the LUMOs ($1\pi_g$) of O_2 . Electron density could flow from the half-filled $1\pi_g$ of O_2 to the LUMOs of N_2 , but this violates the electronegativity nature of atoms. Thereby we could expect the reaction to occur if the electrons are excited from HOMO of N_2 to LUMO, then flow into LUMO of O_2 (Fig. 1). Then the activation of N_2 becomes the key of this reaction.

Considering the strong $N \equiv N$ triple bond, high energy is required to excite N_2 . This is also the basic mechanism of lightning-driven NO formation, but poses significant challenge for electrochemical fixation of N_2 . Plasma, which is composed of ions and high-energy electrons,

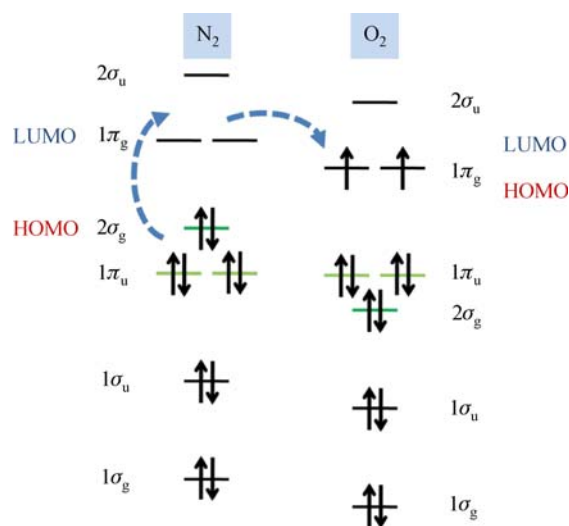


Fig. 1 Scheme of molecular orbitals of N_2 and O_2

however, can provide enough driving force to initiate the reaction. In addition, the energy consumption of plasma-driven nitrogen fixation is also advantageous. Figure 2 also summarizes the other nitrogen fixation method. Biological nitrogen fixation refers to the process of nitrogen fixing microorganisms reducing nitrogen into ammonia in the atmosphere, requiring energy consumption of approximately 0.77 MJ/mol NH_3 produced [7]. In biological nitrogen fixation process, nitrogenase enzyme is core while it is too complex and only particular nitrogen fixation bacteria can choose the most efficient ones. Cyanamide process uses calcium carbide, an intermediate product, to fix nitrogen into ammonia, while metalcomplex fixation produces ammonia with transition metal. Both these two methods is discarded by industry due to low yields and large $1/2N_2$ energy consumption, with theoretical limit of 2.7 MJ/mol [8]. Haber–Bosch process prevails in industrial nitrogen fixation currently, but it is focused on ammonia synthesis only and it almost reach its theoretical energy consumption limit (0.48 MJ/mol) [9]. In comparison, the theoretical energy consumption limit of non-thermal plasma (NTP) even reaches 0.2 MJ/mol [10,11], even lower than half of that of Haber–Bosch process, as shown in Fig. 2.

As stated previously, there are two kinds of plasma: thermal plasma and non-thermal plasma (NTP). For thermal plasma, the system is in a state of thermal equilibrium and the temperature is higher than 5×10^3 K, where the average kinetic energy of all kinds of particles (electrons and ions) is the same. According to existing reports on laboratory scale thermal plasma nitrogen fixation, energy consumption ranges from 10 to 1000 MJ/mol HNO_3 [12–15]. To make nitrogen fixation possible through thermal plasma, the reaction requires high pressure

1) 1 atm = 1.013×10^5 Pa

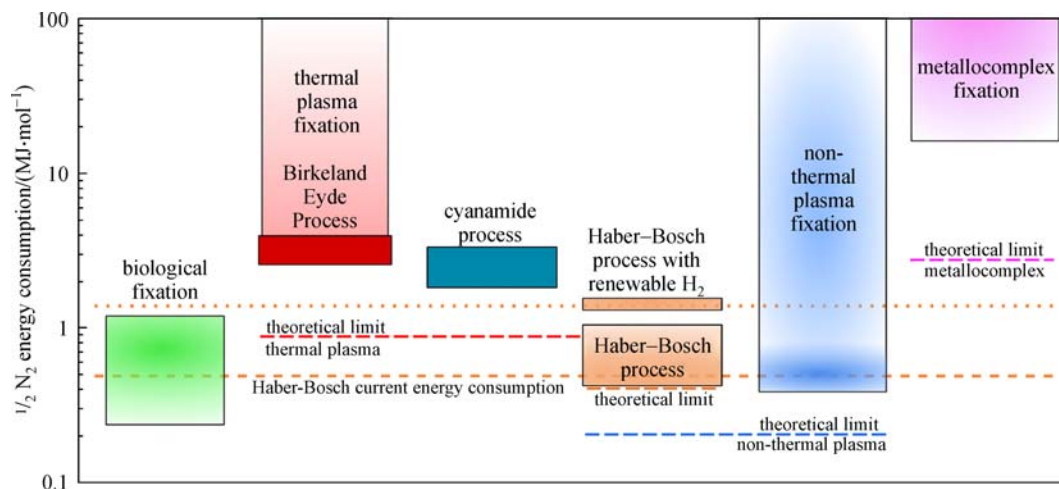


Fig. 2 Comparison of the energy consumption of nitrogen fixation [7]. The Haber–Bosch process now is close to its theoretical limits. Non-thermal plasma nitrogen fixation also demonstrates high efficiency and has even lower theoretical limit of power consumption

ranging from 20 to 30 atm and temperature above 3000 K [11]. This method is neither economic nor easily controllable in industrial nitrogen fixation.

NTP is in general any plasma which is not in thermodynamic equilibrium, either because the ion temperature is different from the electron temperature, or because the velocity distribution of one of the species does not follow a Maxwell–Boltzmann distribution. The biggest feature is that the temperature of the electrons can be several orders of magnitude higher than that of background gas. Thereby electrons in NTP are the promising candidates for high-energy species to activate the reactant, since the energy in the electronic vibration mode could be delivered to nitrogen fixation reaction to attain the huge activation energy. NTP could be acquired under atmospheric pressure by various technologies such as glow discharge, dielectric barrier discharge and gliding arc discharge, etc.

The possible reactions between N_2 and O_2 under plasma

are summarized in Fig. 3. The first step is the transformation from N_2 to $N_2(V)$ by the hot electrons presented abundantly in the plasma. $N_2(V)$ tend to combine with O^* (activated oxygen atom) to form NO and N^* (activated nitrogen atom). N^* can combine with O_2 to further produce NO and O^* , or following the other route to react back with NO to produce N_2 and O^* . Evidently, the feeding ratio of O_2 to N_2 should be high enough, and the reaction selectivity of N^* needs great precautions.

Suitable supports/catalysts are necessary to ensure efficient NO_x production, and this is the area calls for intensive research. Some preliminary investigation on the particle size, shape, surface area and dielectric constant of catalyst on the discharge and catalyzing behavior in plasma have been conducted by Patil [17]. Theoretically, small-particle catalysts presents higher surface area exposed in plasma, which is conducive to microdischarge, the essential role in plasma ionization. Here we suppose nano-scale particles show greater advantages than the

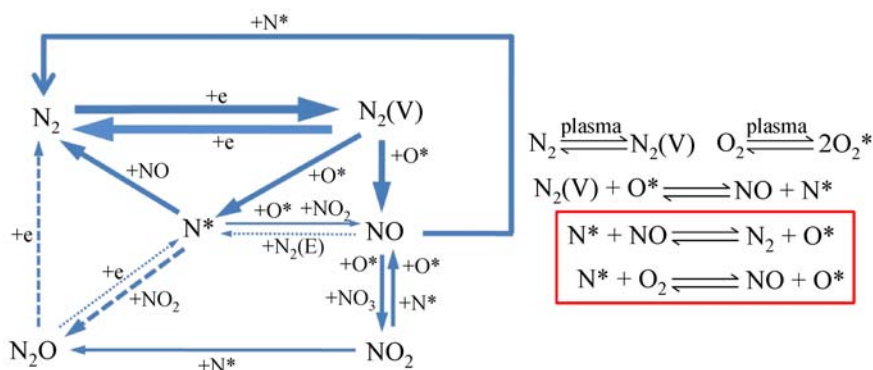


Fig. 3 Scheme of the conversion between molecules and atoms [16]. In plasma, the conversion is most strong between N_2 and $N_2(V)$. $N_2(E)$: electronically excited N_2 molecules. $N_2(V)$: vibrationally excited N_2 molecules. Thickness of the arrows is accord to the importance of the reactions. Dashed line means less important reaction

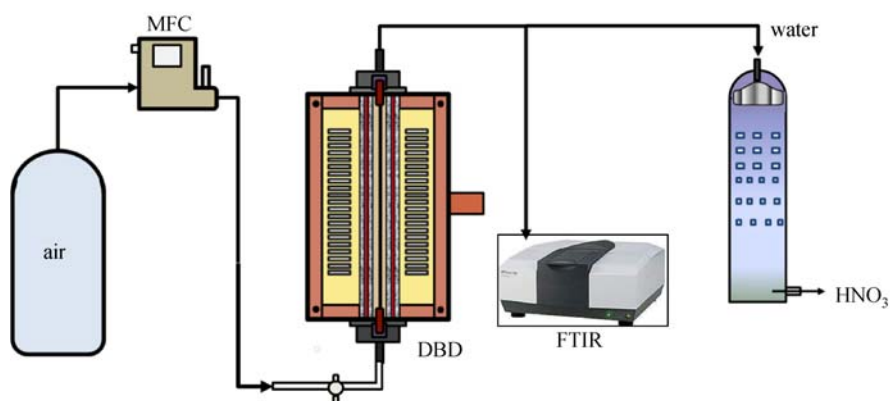


Fig. 4 Scheme of the ideal setup of plasma-assisted nitrogen fixation and simplified process. MFC stands for mass flow controller; DBD stands for dielectric barrier discharge setup; FTIR stands for Fourier transform infrared spectrometer

micron-scale ones studied by Patil. So far high valence metal oxide shows superiority which may attribute to their oxygen activation properties, but the mechanism is much more complex according to reported results. Moreover, low dielectric constant gives rise to higher voltage on the packing material and thus more intense plasma. Other rules should also be taken into considerations: the strong adsorption of N_2 or N^* , the easy desorption of NO and other NO_x , abundance of oxygen atoms. Thereby, WO_3 , MoO_3 , ZrO_2 , HfO_2 [18] nanoparticles etc, are promising catalysts due to the strong coordination between metals and nitrogen, plenty of active sites, as well as the abundance of oxygen. The desorption of NO and other NO_x should be further studied. It should be noted that reductive catalysts (C, metals, etc.) should be absolutely avoided, since excited nitrogen atoms can be easily reduced back to N_2 . The supposed reaction facility is shown in Fig. 4. Air (or with the extra supply of O_2 if necessary) are continuously injected into NTP equipment, with flow rate controlled by mass flow controller (MFC). The product can be monitored by Fourier transform infrared spectrometer (FTIR). Then the produced NO, N_2O and NO_x could further react with O_2 to form NO_2 . Later NO_2 could be collected by simple reaction with H_2O to form HNO_3 and NO; or reaction with NaOH to form $NaNO_3$ and NO. The surplus NO will be recollected and oxidized, serving as raw material to produce HNO_3 . The advantage of this idea is that we can make full use of N_2 and O_2 in the atmosphere as reactant.

To sum up, although not in the main stream, the oxidation of nitrogen seems a promising method to store redundant electricity from renewable energy power stations. Non-thermal plasma is environmental friendly because it only requires electrical power supply and can be realized at normal temperature and pressure. Considering the theoretical energy consumption limit of 0.2 MJ/mol nitrogen atom fixation, the equivalent electricity consumption is 0.56 kWh/mol nitrogen fixed and amounts to

approximately 476 RMB/ton (estimated using 0.5 RMB per kWh electricity), even less than half of the current cost of HNO_3 . Practically, the energy used for plasma nitrogen fixation is from surplus electricity generated by power plant, which indicates almost zero cost of this fixation. Finding a stable, efficient and low-cost catalyst for the non-thermal plasma N_2 oxidation is the key for its success, however this is still in its very infancy stage. We thus advocate intensive research efforts into this field, including setup optimization, catalyst identification and mechanism understanding. We hope the nearly free production of nitrate and related chemicals (using air and surplus renewable electricity) would come true in the near future.

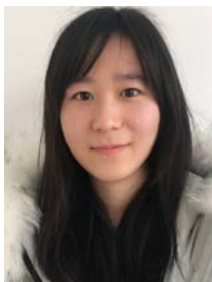
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References

1. Lund H, Munster E. Management of surplus electricity-production from a fluctuating renewable-energy source. *Applied Energy*, 2003, 76(1-3): 65-74
2. Lv W, Zhang R, Gao P, Lei L. Studies on the faradaic efficiency for electrochemical reduction of carbon dioxide to formate on tin electrode. *Journal of Power Sources*, 2014, 253: 276-281
3. Zhou F, Azofra L M, Ali M, Kar M, Simonov A N, McDonnell-Worth C, Sun C, Zhang X, MacFarlane D R. Electro-synthesis of ammonia from nitrogen at ambient temperature and pressure in ionic liquids. *Energy & Environmental Science*, 2017, 10(12): 2516-2520
4. Thomas H. *The Alchemy of Air: A Jewish Genius, A Doomed Tycoon, and The Scientific Discovery That Fed The World But Fueled The Rise Of Hitler*. 1st ed. New York: Harmony Books, 2008
5. Schrock R R. Reduction of dinitrogen. *Proceedings of the National Academy of Sciences of the United States of America*, 2006, 103

(46): 17087

6. Erisman J W, Sutton M A, Galloway J, Klimont Z, Winiwarter W. How acentury of ammonia synthesis changed the world. *Nature Geoscience*, 2008, 1(10): 636–639
7. Cherkasov N, Ibadon A O, Fitzpatrick P. A review of the existing and alternative methods for greener nitrogen fixation. *Chemical Engineering and Processing*, 2015, 90: 24–33
8. Kipouros G J, Sadoway D R. Toward new technologies for the production of lithium. *JOM*, 1998, 50(5): 24–26
9. Appl M. The Haber–Bosch heritage: the ammonia production technology. In: *Proceedings of 50th Anniversary IFA Technical Conference*, 1997, 25
10. Legasov V A, Rusanov V D, Fridman A A. Non-equilibrium plasma-chemical processes in heterogeneous media. *Plasma Chemistry*, 1978, 5: 222–241
11. Rusanov V D, Fridman A A, Sholin G V. The physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules. *Soviet Physics-Uspekhi*, 1981, 24(6): 447–474
12. Mccollum E D, Daniels F. Experiments on the arc process for nitrogen fixation. *Industrial & Engineering Chemistry*, 1923, 15(11): 1173–1175
13. Partridge W S, Parlin R B, Zwolinski B J. Fixation of nitrogen in a crossed discharge. *Industrial & Engineering Chemistry*, 1954, 46(7): 1468–1471
14. Rahman M, Cooray V. NO_x generation in laser-produced plasma in air as a function of dissipated energy. *Optics & Laser Technology*, 2003, 35(7): 543–546
15. Namihira T, Katsuki S, Hackam R, Akiyama H, Okamoto K. Production of nitric oxide using a pulsed arc discharge. *IEEE Transactions on Plasma Science*, 2002, 30(5): 1993–1998
16. Wang W, Patil B, Heijkers S, Hessel V, Bogaerts A. Nitrogen fixation by gliding arc plasma: better insight by chemical kinetics modelling. *ChemSusChem*, 2017, 10(10): 2145–2157
17. Patil B. Plasma (catalyst)-assisted nitrogen fixation: reactor development for nitric oxide and ammonia. Eindhoven: Technische Universiteit Eindhoven, 2017, 93–125
18. Holland P L. Metal–dioxygen and metal–dinitrogen complexes: where are the electrons? *Dalton Transactions (Cambridge, England)*, 2010, 39(23): 5415–5425



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