



Abstract Book

*Solvay Workshop on
“Plasma Technology and Other Green
Methods for Nitrogen Fixation”*

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INVITED TALKS

Electrocatalytic nitrogen fixation: perspectives, challenges and recent advances

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Nitrogen fixation is one of the most important processes on Earth, leading to the production of ammonia which is an essential building block for fertilizers, commodity chemicals and energy carriers. Currently the production of ammonia is completely dependent on fossil fuels. The Haber–Bosch process, the major source of the world's NH_3 nowadays, contributes to 90% of the annual production. However, the prospect of continued and growing use of this process for future supplies of NH_3 creates serious environmental concerns, as NH_3 synthesis constitutes 1.5% of global CO_2 emissions from the fossil fuels source (the global average is 2.86 tons of CO_2 per ton of NH_3).

Electrochemical methods offer the possibility to directly convert renewable electricity for the production of ammonia. This approach takes place under environmentally benign conditions (low temperatures, atmospheric pressure and aqueous conditions), can easily be controlled, and may enable decentralized production of ammonia. Moreover, the combination of plasma N_2 activation and electrochemical NH_3 synthesis is also shown to be promising.¹ However, there are still some challenges that need to be overcome in order for this electrochemical technology to become economically competitive or industrially relevant.

In this talk, several electrochemical pathways to form ammonia will be discussed from a fundamental and applied perspective. The focus will be on the electrocatalytic reduction of dinitrogen, nitrates and nitrites. First, I will zoom in on the small scale and will discuss the activity and selectivity of various electrocatalysts as well as the effects of process parameters (e.g. electrolyte composition, pH and membranes).^{2,3} Moreover, the development of our online and quasi-online spectroscopic- and chromatographic techniques during electrochemical analysis will be highlighted.^{3,4} Lastly, utilization of gas diffusion electrodes for electrosynthesis within the nitrogen cycle will be touched upon.⁵ I will present the activities of our group at VITO on this topic, which unveil important parameters to be considered in the electrochemical nitrogen fixation research, crucial to bring this technology closer to implementation.

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Cold plasma ammonia synthesis: the search for a suitable catalyst

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Plasma catalytic ammonia production at atmospheric pressure holds great promise due to its small scalable design, easy intermittent operation, and use of renewable energy. To meet the ammonia production, plasma-catalytic systems need intelligent design of catalytic materials with specific properties compared to traditional catalysts. Plasma helps to dissociate N₂ through vibrational excitations and produces H* radicals. Based on our recent preliminary results from experiments and DFT calculations, one of **our starting hypotheses** is that an optimal catalyst for plasma-assisted ammonia synthesis is one that delays the recombination of *adsorbed* hydrogen radicals (H*) into molecular hydrogen (H₂) as to allow them to instead bind to *adsorbed* nitrogen plasma activated species (N^{activated}) to form NH*. **We postulate that** such delay in recombination of hydrogen radicals can be achieved with catalysts that dissolve hydrogen more easily. However, under some conditions (e.g. “overabundance” of radicals) some metal catalysts we previously studied could slow down NH* formation due to its tendency to “trap” N to form nitrides, **we propose to** promote NH* formation (an essential step in ammonia synthesis) by using “nitrophobic” materials.

The extent of the interaction of the proposed catalysts with nitrogen, a pivotal chemical precursor for this reaction, can lead to a possible demarcation of the two regimes: “active site regime” and “pore size regime”, where better catalytic performances are observed respectively. And where the dominant reaction pathways may change with the catalytic surface identity. In this presentation, I will discuss the possibility that certain discharge conditions can lead to separate regimes, potentially as a result of different interactions of plasma generated species with metals and porous materials, respectively. To gain an initial understanding we have employed optical emission spectroscopy (OES), Fourier transform infrared absorption spectroscopy (FTIR-AS), and electrical measurements to characterize selected plasma-catalytic packed bed dielectric barrier reactors (PB). The possible existence of different reaction mechanisms when employing different packing materials due to the change in the interactions between plasma generated species and the catalytic surfaces will be discussed.

It is expected that a detailed understanding of the plasma conditions can aid in the intelligent design of the catalysts used in plasma catalysis, specifically in PB reactors for ammonia synthesis. This will result in the design of economical plasma intermittent small-scale decentralized systems to produce ammonia.

Electrocatalytic direct nitrogen fixation: perspectives and gaps

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Direct nitrogen fixation to ammonia using renewable energy sources is one of the key technologies to reach net-zero emissions (NZE) target by year 2050, as planned for EU. Ammonia is already a large commodity, particularly for fertilizers area, but its potential market can largely further grow for its use as chemical energy vector to transport H₂ or renewable energy. While already a two-step process of production of green H₂ by electrolysis following by a nearly conventional step of thermal catalytic production of ammonia from N₂ and H₂ is at a pilot stage, the challenge is the direct electrocatalytic production from N₂ (and H₂O), which overcome the energy losses of the two step-process, but especially has two additional crucial advantages: it allows i) to develop a very-compact process suitable for distributed production (a kind of artificial-leaf design) and ii) to avoid (in principle) a step of N₂ separation (from air) with high purity (even traces of O₂ are not compatible with the pyrophoric ammonia synthesis catalysts). Both aspects are crucial to enable the development of a distributed production of NH₃ (for use as H₂ or energy vector) and cost reduction.

There are, however, many scientific and technology gaps requiring to rethink (electro)catalysis from the fundamental viewpoint. Although electrochemistry is an old technology, several new challenges are posed by addressing the challenging route of the direct nitrogen fixation.

This lecture will first introduce a general perspective and status of the direct nitrogen fixation to ammonia by electrocatalytic methods, to discuss then briefly the question of the need to rethink (electro)catalysis in terms of fundamental approach to make a breakthrough change toward more industrial-relevant performances, presenting also, as an example, the need to consider in a more detail the indications from enzymatic mechanisms, finally concluding with some remarks on area requiring research attention, particularly how to operate directly with air rather than pure N₂.

Nitrogen fixation in plasma assisted catalytic reactor systems

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Nitrogen is one of the most important elements on Earth since it is essential to all life forms in many different ways. 78% of air contains diatomic nitrogen (N₂) which is chemically inert. Therefore, nitrogen needs to be fixated to different forms such as NH₃ and NO_x. Conventional nitrogen fixation is done by the Haber-Bosch process, which operates under severe process conditions. It consumes 1-2% of the world total energy production and emits million tons of CO₂. Plasma assisted nitrogen fixation can be a potential solution towards more sustainable nitrogen products and derivatives. NH₃ and NO_x can be synthesized applying different plasma types in different plasma reactors under different process conditions. Common factor is that they both are synthesized with non-thermal plasma (NTP) under ambient conditions.

For the NH₃ synthesis a dielectric barrier discharge (DBD) reactor is used, packed with a Ru-based catalyst, inducing plasma-surface interactions between highly excited gaseous species and an active catalytic surface. Different phenomena are observed with comparison to conventional thermal heterogeneous catalysis, among an increase of productivity and a decrease in energy consumption. Distinction has been made between plasma and catalytic contributions, to develop new plasma-enhanced catalysts.

NO_x is synthesized using a gliding arc reactor (GAR), providing a warm plasma with higher currents and power inputs compared to the DBD. The investigation of spatial development of NO_x along the reactor, NO and NO₂ selectivity and applied process parameters will result in a more optimized small-scale localized production plant for the in-situ formation of sustainable fertilizer. Post-plasma catalytic processing and novel process and reactor designs will increase the process efficiency and increase process sustainability all over the world, including remote and less fortunate areas in Africa.

Together with international project partners the aim of both processes is to enhance the sustainability and availability of localized-produced fertilizer and reduce the environmental footprint of nitrogen-fixation based processes.

Plasma Technology and Nitrogen Fixation at Scale

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I address two potential applications of plasma to largescale chemical processing associated with nitrogen fixation: air plasma to treat organic waste and plasma pyrolysis of natural gas to make H₂ and solid C. Industrial scale nitrogen fixation via Haber-Bosch was arguably the most important technological advance of the 20th century if the metric includes enabling human population growth. The main environmental problems with the current system of N-based fertilizers are CO₂ emitted during steam reforming to make H₂ and N-pollution caused by low N utilization efficiency (NUE). The latter problem is not as well-known as the former but is arguably more insidious and serious. From application of N fertilizer to the field to the ‘food on the fork,’ a huge amount of N is lost to the environment. This creates multiple, serious environmental problems and must eventually be addressed.

One way to improve NUE was first suggested by the founders of N₂Applied (Rune Ingels and Grete Sønsteby): use air plasma effluent to treat aqueous organic waste to trap bacterially produced and otherwise fugitive gaseous NH₃ as NH₄NO₂. This can be done locally – where organic waste is created – and by utilizing renewably generated electricity. The process has been demonstrated as technically feasible. However, the path to achieving globally significant scales using this process remains an open question.

The use of plasma to pyrolyze CH₄ to form H₂ and solid C has been demonstrated for many years and it offers a potentially CO₂ emission-free technology to replace methane steam reforming to generate H₂ for use in NH₃ synthesis. If globally significant quantities of H₂ are to be formed this way, however, enormous amounts of solid C will be created as well. One of the few markets that could utilize this much C is for building or structural materials.

Recent research has shown that CH₄ pyrolysis combined with suspended heterogenous catalyst allows the formation of carbon nanotubes (CNTs). CNTs can be spun into C fibers and these could be valuable as building materials. To grow CNTs from pyrolysis products, catalyst particles are suspended in the flowing gas – typically downstream from the plasma. Although this basic idea has been demonstrated by multiple groups at relatively small scales, there are multiple open challenges associated with scaling to be solved before this technology will be globally significant.

In both cases, the available evidence suggests that the most effective way to operate plasma for endothermic processes that require high T is in a ‘warm’ mode, rather than non-thermally. This may have implications for the optimal coupling of plasma with catalyst. In the wider context of electrification of the chemical industry, electrification via plasma can efficiently heat the reactant gas, thus replacing natural gas fired furnaces and the associated CO₂ emissions or the need for carbon capture. Perhaps ‘warm’ plasma will be of widest utility in electrifying other parts of a future ‘circular chemical economy’ with minimal environmental impacts.

Economic and Environmental Assessment of Small-scale Plasma-Assisted Ammonia Production Pathways – ‘at-Farm’

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Ammonia synthesis using the Haber-Bosch (HB) process is one of the most important inventions of the last century due its contribution to agriculture. Yet, this process requires a lot of energy and releases carbon emissions since hydrogen input is obtained by steam methane reforming and the reaction performed in harsh conditions. In addition, given that this process highly depends on non-expensive natural gas, ammonia production is concentrated in few countries at large-scale plants, adding emissions due to transportation. Distributed plants next to farmers can reduce these impacts, as well as reduce large storage needs, shortage risks and price volatility of imported fertilizers, promote local employment and bespoke production. Mini HB plants have been proposed, but they still need high pressure and heat, mainly produced by fossil sources. A proposed alternative is a non-thermal (NT) plasma reactor operating under ambient conditions, using only electricity. Yet, this technology has only reached energy efficiencies below 20%, whereby its high electricity consumption makes it more expensive than the conventional pathway. The feasibility of these emerging technologies can be promoted by the internalization of environmental benefits of its products life cycles in their economic analyses. In this sense, a life cycle assessment of different ammonia production pathways is performed in order to quantify, from cradle-to-utilization, credits of avoided emissions in the production, storage and transportation phases, by-products utilization, use of local renewable resources, reduction of product wastes, and soil beneficiation. Different scenarios are analysed for centralised and distributed ammonia production in Australia for the conventional large-scale HB process, alternatives using mini-HB reactor supplied by hydrogen from water electrolysis and thermal plasma methane pyrolysis, and the NT plasma-assisted synthesis supplied by water electrolysis, using different renewable energy sources according to the location. The best energy sources and plant configurations for each environmental impact category would be identified and their characterized results monetized and internalized in costing analyses for each alternative, which can contribute to the deployment of green ammonia distributed production.

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Can we manage without Haber Bosch?

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The Haber Bosch (HB) technology is the synthesis of ammonia from the pure components, hydrogen, and nitrogen. The HB process is today synonymous with the production of ammonia from any source of energy, predominantly the fossil fuels, gas or coal. Ammonia is both an energy carrier and a raw material for the fertilizer and chemicals industry.

Until recently, the fertilizer industry has thought that HB process, which is their backbone in production of nitrogen fertilisers, would not be challenged, since it is feeding about 48% (1) of the world's population and only using less than 1,5% of the global fossil fuels consumption.

The presentation will however focus on the vulnerability of the food-chain and its dependence on a low global warming footprint limited by cost and public opinions. The paradigm shift from fossil to renewable may be more dramatic than previously expected.

Ammonia is a very good CO₂ free energy carrier as well as being a potential energy resource for the shipping industry and on land mobility. The latter one is already challenged by electricity and battery technology which is already getting a foothold in the car industry. The strength of ammonia technology is its energy efficiency of 65% in combination with low carbon fossil fuels and its ability to separate and sequester a concentrated flow of CO₂. The cost of investing in new ammonia technology requires an ammonia price of 2-3 times more than the historic market price, before the cost of the CO₂ sequestration.

There are alternatives to the Haber Bosch, but most of them are based on inefficient 120 years old technology, like plasma fixation of nitrogen from air. The history books indicate an energy consumption of 60-65kwh/kgN, and no recent development has to my knowledge been able to reduce the energy consumption at industrial scale. N2 Applied we have developed a technology being able to produce 2-4% NO_x in air with a plasma energy consumption of 50-55 kwh/kgN. The NO_x is absorbed into livestock slurry and is neutralizing the free ammonia and stopping the methane formation. The total process is consuming 65-75 kwh/kgNO₃-N and has the potential of stopping the loss of 1-2kgNH₃-N for each kgNO₃-N produced in the plasma process. The energy consumption when the process is properly applied is 25-38kwh/kgN produced, recovered and applied to the field. The GWP reduction is equal to 1000kg CO₂-eq. per dairy cow per year.

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Reaction Pathways in Plasma-Catalytic Ammonia Synthesis

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Ammonia synthesis is a versatile probe reaction for studying plasma-catalytic conversion of N₂ and H₂ to form ammonia, because the reaction is relatively simple, forms no byproducts, whereas catalytic synthesis has been studied in detail.

Our work over the last few years will be summarized, showing that the dominant reaction pathways vary with the energy intensity of the plasma as well as with temperature of operation. Furthermore, the consequences of surpassing the thermodynamic equilibrium will be discussed as well as the effect changing the active metal in the catalyst.

Pulsed plasma discharges in air as an efficient strategy of nitrogen fixation and (H)NO_x transport into water

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The use of plasma discharges for nitrogen fixation from atmospheric air into nitrogen oxides and nitrites/nitrates in water is an emerging topic with great application potential in sustainable agriculture. Pulsed air transient spark (TS) discharge can efficiently generate as much as 7×10^{16} NO_x molecules/J [1]. In dry air, TS generates high concentrations of NO and NO₂, increasing with increasing input energy density, reaching 1200 and 180 ppm of NO and NO₂, at 400 J/L, respectively. In humid air, the concentration of NO₂ decreased to 120 ppm in favor of gaseous HNO₂ that reached approximately 100 ppm at 400 J/L. TS plasma can be simultaneously generated with microdroplets of water by the electrospray directly inside the discharge zone. Plasma activated water (PAW) is then generated, which contains high concentrations of H₂O_{2(aq)}, NO_{2⁻(aq)} and NO_{3⁻(aq)}, since water microdroplets significantly increase the plasma-liquid interaction interface [2]. This enables a fast transfer of NO, NO₂, HNO₂ from the gas into water. Our results show that gaseous HNO₂ generated in humid air TS or TS with water aerosol, rather than NO or NO₂, plays a major role in the formation of NO_{2⁻(aq)} in PAW that reaches concentrations up to 2.7 mM [3].

Another way of applying air plasma discharges for nitrogen fixation into water is using a water electrode in running or batch treatment with TS or atmospheric glow discharge. Various types of PAW prepared by the TS with electrospray, TS with water electrode and TS or glow discharge in batch water demonstrate different chemical composition of H₂O₂, NO_{2⁻} and NO_{3⁻}. In a closed chamber, nitrogen fixation rate and thus the production of NO_x and NO_{2⁻} and NO_{3⁻} in PAW is further increased, as opposed to open air system. Such PAWs have the potential to improve the plant early-stage development and later growth, and influence their physiological parameters, while causing no harmful DNA damage. Imbibition of seeds in PAW may lead to significant improvement of the agricultural plant yield, as investigated on barley, wheat, lettuce, maize and pea [4-7]. Interestingly, plasma treated weak ammonia solutions resulting in increased ammonium nitrate did not lead to any substantial improvements of the plant growth.

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Green ammonia synthesis on a NO_x trap fed with NO_x from plasma-driven nitrogen gas oxidation from air (PNOCRA Process)

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Lean NO_x traps are established technology in the automotive industry. These catalytic filters eliminate NO_x molecules from exhaust gas of an internal combustion engine running in lean mode. Periodically the engine is run in rich mode for a short time to produce gaseous reductants to reduce trapped NO_x selectively to N₂. We adapted the catalytic function of the Lean NO_x trap to produce NH₃ instead of N₂. NO_x is produced with a plasma process fed with ambient air. This PNOCRA process (Plasma Nitrogen Oxidation and Catalytic Reduction to Ammonia)¹, combining plasma-assisted nitrogen oxidation and Lean NO_x Trap technology, is a new, energy-efficient route of plasma-driven green NH₃ synthesis in a two-phase cyclic process. To achieve continuous ammonia production, at least two LNT units alternating between NO_x trapping and chemical reduction mode are needed. PNOCRA achieves low energy consumption. PNOCRA has no intrinsic CO₂ footprint and runs on air, water and renewable electricity. The energy performance of PNOCRA is significantly better than for plasma-based NH₃ production, directly from N₂ and H₂. The new process is attractive especially for small and medium-scale decentralized ammonia synthesis.

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Plasma catalytic production of ammonia: prospects, problems and possible solutions

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Ammonia is an attractive medium for the storage and transportation of hydrogen. The development of ammonia production methods that are compatible with renewable energy sources is an important goal. Plasma-enhanced catalytic production of ammonia offers important advantages, including the ability to operate at relatively small scales and be turned on and off as required. However, the process is still far from commercial viability, despite considerable research. While the best ammonia yields achieved are approaching those required, energy efficiencies are still over an order of magnitude too low to be competitive with other processes.

Most experimental studies have used a conventional coaxial dielectric-barrier discharge (DBD) reactor combined with various metal catalysts on oxide supports. Such a reactor has fundamental limitations. First, the electron energies in a DBD are typically above 10 eV, which leads unavoidably to significant dissociation and ionisation of nitrogen and hydrogen. Too many of these reactions preclude reaching competitive energy efficiencies for ammonia production. Second, kinetic modelling suggests that hydrogen adsorption on surfaces can inhibit reactions, such as dissociative adsorption of nitrogen molecules, that can provide energy-efficient production of ammonia.

We propose several strategies to overcome these limitations. These involve:

- (1) Using in-situ monitoring of surface-adsorbed species and computational modelling to understand the critical reactions and species and their dependence on the catalyst;
- (2) Introduction of novel catalysts to promote the occurrence of desirable surface reactions;
- (3) Use of water as the hydrogen feedstock, which dispenses with the substantial energy cost of producing hydrogen from methane or water;
- (4) Implementation of novel reactor designs that give greater control over the introduction of reactants.

We present examples of measurements and modelling from our work and the literature that demonstrate the value of such approaches. Further, we assess their potential to improve the performance of ammonia production.

Electrochemical nitrogen activation

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The current industrial ammonia synthesis based on the Haber-Bosch process has a substantial carbon footprint, and an alternative process based on the energy input from sustainable sources, solar or wind, would be highly desirable. Such a process could even open the possibility of using ammonia for chemical energy storage. I will introduce a model to describe electrochemical dinitrogen reduction. In particular, I will discuss a Li mediated process showing that we can now obtain up to 80% selectivity towards ammonia in this process. I will also discuss the possibility of an electrochemical dinitrogen oxidation process.

Mechanistic Aspects of Dinitrogen Cleavage and Hydrogenation to Ammonia in Catalysis and Organometallic Chemistry

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Molecular complexes, solid-state Haber-Bosch catalytic systems, silica-supported tantalum hydrides and nitrogenase display distinctive mechanisms for N₂ splitting. Some mechanistic critical steps and in particular in the key role played by metal hydride bonds and by dihydrogen in such reactions, will be discussed and contrasted to some molecular aspects of plasma driven dinitrogen dissociation and hydrogenation.

Plasma assisted synthesis of plasmonic titanium nitride nanoparticles and thin films

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A combination of non-thermal plasma and plasmonic catalysts is a promising approach to produce required products at relatively low temperature. Titanium nitride possesses similar plasmonic properties to gold; this is characterised by comparable absorption peaks, but with a broader width, and plasmonic resonance in the visible and infrared region. It is an attractive alternate plasmonic material useful in many applications, such as photo thermal conversion, photocatalysis, chemical sensing, photonics. Despite the plethora of methods to produce titanium nitride, it remains challenging to control the optical properties in an efficient way. Also, the optical behavior of ultrathin films (<10 nm) remains different from that of nanoparticles and a bulk material. Hence, to move toward the realization of practical plasmonic catalysts and plasma reactors utilizing TiN materials, developing methods to synthesis TiN nanoparticles and thin films with desired properties are of great interest. Scalability of the process is equally important to break into mass-production markets.

As the optical properties of a nanomaterial depend on both its composition and morphology, synthesis conditions can significantly affect the quality of the resulting material. Especially a prolonged annealing step often required in wet chemical processes (800°C for at least 5 h) could densify the structure and change the optical properties in an undesirable way. Alternative methods, such as nitrogen plasma synthesis, can mitigate the aforementioned issues by utilising high purity precursors coupled with a very short heating times. Non-thermal plasma synthesis of nanoparticles is characterized by high chemical reactivity, by the uniform charging of particles in the plasma, and by a high rate of heating induced by the interaction between the particles and the plasma radicals. This translates into the capability of producing powders and thin films composed of a wide range of morphologies, with a narrow particle size distribution, and with a high-quality crystalline structure. In this presentation we overview the suitability of different plasma methods for producing plasmonically active TiN nanoparticles and also the effects of varying reaction conditions on the properties of the materials obtained and the different factors contributing to their thickness dependent properties.

Catalyst-free, electrolytic synthesis of ammonia from nitrogen and water by atmospheric-pressure plasma processes

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There have been substantial efforts to develop a sustainable alternative to the Haber-Bosch process for the synthesis of ammonia from nitrogen gas in air that could be distributed and has a lower carbon footprint. In particular, electrified approaches have been studied that can electroreduce nitrogen in the presence of water at atmospheric pressure and near room temperature. However, most electrocatalyst materials studied to date have exhibited a preference for the competing hydrogen evolution reaction, leading to low yields and low selectivities for ammonia.

Our group has recently studied a catalyst-free, electrolytic process characterized by a plasma formed in contact with a liquid water surface. Critically, electrons in the plasma excite or even dissociate nitrogen molecules in the gas phase, and solvate in liquid water to produce one of the strongest reducing species known. Remarkably, we find that for certain configurations and certain processing conditions, ammonia is synthesized with 100% charge-transfer efficiency, meaning that the hydrogen evolution reaction is almost completely suppressed. In addition, the oxidation of nitrogen to nitrites or nitrates which is possible in a plasma-liquid process is also absent. The energy cost of the process is high and I will discuss recent efforts both by my group and others to address this issue. In addition, to make the process continuous and overcome mass transport issues, we have developed a plasma-droplet reactor in which the reactions occur between plasma species and aerosolized liquid water droplets. Potential reaction mechanisms in both approaches will also be presented.

Models and Opportunities in Plasma Catalysis

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Heterogeneous catalysis is essential to industrial chemical processes, from those that transform petroleum into fuels and chemicals to those, like the Haber Bosch process, that create fertilizers to feed the planet. The first heterogeneous catalysts were discovered empirically and improved through Edisonian experimentation. Within the last twenty years or so, however, the field has been transformed through the advent of catalysis science, which, using high fidelity synthesis and characterization coupled with molecular-level models, is able to understand and predict catalytic function. Catalysis science has revealed that the most common heterogeneous catalysts present a tableau of reactivity limited by intrinsic correlations between the various reaction steps that make up a surface catalytic reaction. Coupling of heterogeneous catalysts with non-thermal plasmas offers the potential to break these constraints. While empirical evidence suggests that such combinations can enhance apparent catalytic function relative to plasmas or catalysts alone, the absence of basic models to rationalize this behavior and guide material and plasma selection has limited progress. In this talk I will describe recent work to bridge this gap through the development of models that highlight the potential origins and consequences of combining non-thermal plasmas and catalysts, all in the context of nitrogen fixation.

Synergistic combination of plasma activation and electrocatalysis for nitrogen fixation by water

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Thermal catalysis has a central role in chemical industries, however due to the carbon dioxide emissions caused by the combustion of fossil fuels involved in such processes the electrification of these chemical transformations is a necessary response to climate change. Plasma catalysis and electrocatalysis have attracted high interest due to their potential to drive sustainable chemical processes.

Plasma catalysis can activate and selectively transform a variety of stable molecules to desired products. High energy electrons generated in plasmas can excite ground state gas-phase molecules, allowing them to react on catalytic materials at milder conditions than possible thermally. In electrocatalysis electrons are exchanged between electrodes/electrocatalysts and reactants to modify the rate of electrochemical reactions by altering the reaction pathways and decreasing the activation barriers.

In this contribution we will present an innovative combination of the two fields for the case of nitrogen fixation by water. We employ electrochemical systems with proton or oxygen ion conducting membranes for providing reacting species on electrocatalysts while radiofrequency plasmas are used to increase the reactivity of nitrogen. The spatial separation of nitrogen activation and water dissociation provides true independent parameters for performance optimization. Concentration of products is orders of magnitude higher than equilibrium and high selectivities towards desired products are observed.

Plasma catalysis: An emerging technology for decentralized ammonia synthesis

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Ammonia is one of the most important chemicals used in modern society, produced through the industrialized Haber-Bosch (H-B) process, which is typically carried out at high temperatures (450 – 600 °C) and high pressures (150 - 300 bar). This process emits over 300 million metric tons of CO₂ each year and is highly energy-intensive, consuming 1 - 2% of the world's primary energy supply.

Non-thermal plasma (NTP) has been considered as a promising and emerging technology for ammonia synthesis under mild conditions¹. NTP can generate highly energetic electrons and reactive species that can significantly enhance reaction kinetics and enable thermodynamically unfavorable reactions to proceed under ambient conditions. NTP process can be switched on and off instantly, offering the flexibility to be combined with intermittent renewable energy such as wind and solar power for small-scale decentralized ammonia production. Moreover, the synergistic coupling of NTP with heterogeneous catalysis has great potential to produce a significant process intensification to enhance the energy efficiency of the plasma-catalytic ammonia synthesis process. Although a variety of catalysts have been tested for plasma-catalytic ammonia synthesis, compared to thermal catalysis, relatively limited efforts have been made to the rational design highly active and stable catalysts for plasma catalysis.

We have reported a novel plasma-catalytic process for the synthesis of ammonia over metal (Ni, Fe and Cu)-based catalysts at room temperature and ambient pressure in a dielectric barrier discharge (DBD) reactor with a specially designed water ground electrode². In this talk, we will demonstrate how to enhance surface catalytic ammonia synthesis whilst limiting the reverse reaction to boost ammonia production in the plasma-catalytic ammonia synthesis through the finely designed mesoporous silica-supported Ni catalysts with controllable Ni nanoparticle distributions. *In situ* FTIR combined with catalyst characterization and plasma diagnostics will be used to understand the plasma-assisted surface reaction and to elucidate the reaction mechanism in the plasma-catalytic ammonia synthesis.

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Plasma-electrochemical conversion processes using ion conducting membrane: a playground for detailed studies on the role of surface charge and electric fields on plasma-electrocatalytic processes

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The use of ion conducting membranes in combination with plasma's for nitrogen fixation processes [1,2] poses new research questions on the influence of surface charge and electric fields on the plasma-electrocatalytic processes taking place on the membrane surface. Possible processes such as the exchange of electrons between electrodes/electrocatalysts and reactants can alter reaction pathways and decrease activation barriers, opening routes to modify the rate of electrochemical reactions.

In this contribution I will present an overview of the possible plasma-electrocatalytic mechanisms which can occur during the plasma-membrane interaction. This overview is mainly aimed to provide an inspiration for further experimental and modeling studies of this novel combination of plasma's and ion conducting membranes. These insights might provide novel pathways to higher conversion rates and higher selectivity of the desired chemical products.

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Electrifying nitrogen transformations: Decarbonizing ammonia using plasma catalysis and electrochemical reduction of nitrate in wastewaters

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Nitrogen fixation in fertilizers forms the basis of modern agriculture and mediates global food insecurity. However, conventional thermally-activated nitrogen conversion processes consume substantial amounts of fossil fuels as materials and energy inputs, leading to an unsustainable energy and carbon footprint. Furthermore, inefficiencies in reactive nitrogen management lead to energy losses as well as hazardous environmental pollution. Therefore, electron-driven approaches are needed to establish fossil-free nitrogen interconversions. Electrochemical and plasma-activated reactions operate under mild conditions, enabling facile coupling to intermittent renewable energy sources to reduce CO₂ emissions and reactive nitrogen pollution, facilitate storage and transportation of renewable energy in nitrogen-based fuels, and improve the global distribution of fertilizer to promote food security.

Non-thermal plasma has been used to synthesize ammonia under mild conditions, but the dearth of fundamental understanding of plasma catalytic reactions handicaps the development of efficient plasma catalytic N₂ conversion. Therefore, an in situ FTIR reactor is employed in combination with steady-state flow reactor experiments and plasma kinetic modeling to elucidate the surface reaction mechanisms and plasma-catalyst interactions. A techno-economic analysis reveals the threshold efficiency required for a plasma process to become environmentally and economically competitive.

Beyond electrification of N₂ fixation for ammonia synthesis, existing waste streams containing fixed nitrogen as nitrate may be mined for fertilizer or carbon-free renewable energy storage, via selective nitrate electroreduction to ammonium. The release of nitrate to the environment from wastewater effluent and agricultural runoff contributes to groundwater contamination, harmful algal blooms, and disruption of biogeochemical nitrogen flows. Therefore, electrochemical membranes are employed as porous flow-through electrodes for selective nitrate transformation to ammonium. These multifunctional electrified membranes for reduction of nitrate in wastewaters have the potential to partially displace carbon-intensive industrially synthesized ammonia while simultaneously accomplishing water decontamination. The prospects for reactive nitrogen recovery based on nitrate electrochemical conversion to ammonium are analyzed for various potential source waters.

CONTRIBUTED TALKS

N₂ fixation in ns-discharge above water: from kinetics to energy costs

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Electrical discharges operating in non-equilibrium conditions at atmospheric or even higher pressure attract increasing attention in many fields as a green and sustainable technology in comparison with conventional chemical energy-demanding processes. Recently, atmospheric nitrogen conversion or nitrogen fixation (NF) by non-thermal plasma has got renovate attention. Nitrogen fixation is a process of converting molecular nitrogen into valuable chemicals, such as NH₃ or NO_x. Nowadays, industrial Haber-Bosch (HB) catalytical NH₃ production is associated with high energy consumption and dramatic environmental impact. On the other hand, plasma-assisted NF can be a good alternative and, with the support of renewable energy sources, can bring many benefits and reduce industry impact on the environment. The obvious challenge on the way of high-energy efficiency is the energy-expensive process of molecular nitrogen dissociation which can be achieved effectively only in non-equilibrium conditions. The theoretical limit of scuh plasma-assisted NF is estimated at 2.5 times lower than the HB process, however, it still has not been yet achieved experimentally.

Here we overview the kinetics of nitrogen fixation in pulsed discharge in presence of plasma/liquid interface. The effect of liquid interface on the kinetics of N₂ fixation is still not fully investigated and the impact of water on the production of NO radicals, as the primary product of N₂ fixation from air plasma, is not yet understood. The non-thermal conditions at atmospheric pressure are achieved through ignition of the plasma discharge by an application of nanosecond pulses with a duration of 10 ns in the pin-to-liquid reactor. For oxidation pathways investigation, temporal-spatial dynamics of the key species was studied by using laser-induced fluorescence and optical emission spectroscopies. The kinetics of the species was studied at different operational conditions of the discharge: input energy and operational frequency. A low repetition frequency of 10 Hz was compared with a burst regime of 100 kHz frequency, to examine if a high repetition rate can improve the energy efficiency and increase the yield of the products. Kinetics of O atoms and NO radicals shown that reactions involving O atoms cannot explain the NO formation processes reaching the maximum at 60 us after the plasma pulse. The mechanism explaining NO formation on a long time scale of microseconds has been proposed and it is shown that NO formation takes place through the reactions involving OH radicals. The validation of the proposed mechanism has been performed by measurement time-resolved 2D profiles of OH radicals. Based on time and space resolved absolute density determination, the role of plasma/liquid interface as a source of OH radicals in NO production is determined. The Extended Zeldovich mechanism is proven to be the main pathway of NO production. The current study gives insights on the future development of research of nitrogen fixation in conditions realized by high power pulsed plasmas.

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Process considerations for plasma-catalytic ammonia synthesis with an outlook toward the ammonia economy

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Plasma-catalytic processes are considered as an alternative to electrify the chemical industry, in part due to its promise to enable intermittent operation [1]. In this context, plasma-catalytic ammonia synthesis has recently gained traction in academic research [2]. Most research focuses on enhancing the synergy between the plasma and the catalyst, and improving the understanding of the reaction mechanisms involved. Ammonia synthesis is a good example reaction for plasma-catalysis, due to the strong academic literature on thermal-catalytic ammonia synthesis and the absence of byproducts.

However, plasma-based nitrogen fixation requires process consideration beyond the plasma reactor, such as feedstock purification and product separation. In this presentation, the techno-economic feasibility of plasma-catalytic ammonia synthesis is presented [3]. This is based on the current state-of-the-art for plasma-catalytic ammonia synthesis, as well as a hypothetical best-case scenario. Plasma-catalytic ammonia synthesis is then compared to other non-conventional technologies for ammonia synthesis, including electrochemical ammonia synthesis, and low temperature catalytic ammonia synthesis [4, 5]. From this evaluation, it can be concluded that plasma-catalytic ammonia synthesis is not a feasible alternative for large-scale ammonia synthesis, in part due to the exothermic nature of the ammonia formation from its elements, hydrogen and nitrogen.

A brief outlook is provided regarding the role of renewable ammonia in the hydrogen economy. In recent years, renewable ammonia production has gained traction, due to increasing CO₂ emission costs and decreasing renewable energy cost from solar and wind. Ammonia may become the renewable commodity that is shipped around the globe, as hydrogen feedstock for the hydrogen grid in Europe, as fuel for stationary power in gas turbines, and as maritime fuel in engines or solid oxide fuel cells [6, 7].

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Nitrogen fixation in a pulsed microwave discharge: combining experiment and modelling

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Nitrogen fixation (NF) is a process of converting molecular nitrogen into valuable chemicals, such as NH₃ or NO_x, whose are used as a feedstock for the production of fertilizers [1]. Industrial NF is associated with high energy consumption and dramatic environmental impact. In quest for alternative NF technologies, plasma-assisted NF is a highly promising cost-effective approach when considering the utilization of intermittent green energy sources. Numerous efforts have been spent aiming at maximization of the product yield and minimization of the corresponding energy cost in the fixation process. Among the plasma technologies that are being considered, the low-pressure pulsed microwave (MW) discharges [2], already renown for optimum CO₂ gas reforming [3], are found to suit well also for plasma-assisted NF, since both processes rely on similar plasma-kinetic mechanisms, such as molecular vibrational excitation. MW discharges, however, remain still barely explored in the field of NF.

Addressing this point, here we report the recent results on NO formation in a low-pressure MW discharge, in order to get better understanding of the plasma-chemical mechanisms responsible for efficient NF. The study has been conducted in a surfaguide-type MW 2.45 GHz discharge working in the 0.5-12 Torr pressure range in N₂:O₂ gas mixtures. Evaluation of the NO density is realized by using Fourier Transform Infrared (FTIR) calibrated spectroscopy. For this purpose the corresponding ro-vibrational absorption bands of the corresponding molecular species were monitored at different discharge conditions. In particular, the vibrational excitation of molecular nitrogen is found correlating with the obtained production yield of NO, using optical emission spectroscopy. Particular attention is devoted to estimate the evolutions of the NO yield and energy cost at different discharge conditions. Minimum energy cost of about 8 MJ mol⁻¹ corresponding to the yield of about 7% are found for NO formation.

The experiments are supported by plasma modelling, confirming the decisive role of N₂ and O₂ vibrational excitation in molecular dissociation and so in the NO formation. The Zero-Dimensional Plasma Kinetics solver (ZDPlasKin) [4] has been used to calculate the species number densities by taking into account the production and loss terms of the chemical reactions.

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Plasma-based NO_x formation: potential avenue for sustainable N₂ fixation

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Plasma-based NO_x formation is gaining increasing interest as a flexible, electricity-driven alternative for the Haber-Bosch process. The plasma-based process requires air as its only resource, which eliminates the energy-intensive and polluting H₂ production step needed for the classical Haber-Bosch process, giving it an edge over the classical process when it is optimized towards its limit.

Plasma-based NO_x formation has already been tested in different kinds of plasma reactors. Recently, very notable performances have been achieved by three different atmospheric pressure plasma reactor types: (I) a rotating gliding arc (RGA) reactor, (II) a microwave (MW) reactor and (III) a pulsed plasma jet. The performance of the RGA reactor was studied for two arc modes: a rotating and steady mode. When the arc is in steady mode, record-value NO_x concentrations up to 5.5% are achieved with an energy consumption of 2.5 MJ mol⁻¹ [1], i.e. to the best of our knowledge, among the best values so far achieved by atmospheric pressure plasma reactors. A very similar performance, i.e., NO_x concentrations of 3.8% with an energy consumption as low as 2.0 MJ mol⁻¹, is achieved by our MW plasma reactor [2], yielding efficient “electrode-free” plasma-based NO_x production, while avoiding metal contamination due to the absence of metal electrodes, leading also to longer reactor lifetime. The lowest energy cost is achieved in our pulsed plasma jet reactor [3], which takes advantage of power pulsing to decrease the energy cost of the plasma-based process down to 0.5 MJ mol⁻¹. To the best of our knowledge, such a low energy cost - close to the theoretical minimum energy cost of 0.2 MJ mol⁻¹ - has never been reported yet in atmospheric pressure plasmas. For all three plasma reactors, computational investigations provide more insight in the underlying chemistry and mechanisms.

One of the current limitations of the plasma-based NO_x process is the recombination of the formed NO back into N₂ and O₂ molecules immediately after the plasma reactor. Therefore, we developed a novel so-called “effusion nozzle”, to improve the performance of our RGA plasma reactor for NO_x production, but the same principle can also be applied to other plasma types. Experiments demonstrate an enhancement in NO_x concentration by about 8%, and a reduction in energy cost by 22.5%. In absolute terms, we obtain NO_x concentrations up to 5.9%, at an energy cost down to 2.1 MJ mol⁻¹. In addition, we developed five complementary models to describe the gas flow and plasma behavior, including arc dynamics and plasma chemistry, aiming to reveal why the effusion nozzle yields better performance.

Our simulations reveal that the effusion nozzle acts as very efficient heat sink, causing a fast drop in gas temperature when the gas molecules leave the plasma, hence limiting the recombination of NO back into N₂ and O₂, which explains the improved performance [4].

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Plasma-catalytic NH₃ production in DBD plasma: Chemical kinetics modeling

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Applications in fertilizer production and energy storage cause increasing interest in plasma-catalytic ammonia (NH₃) synthesis, as plasma technology is able to be deployed locally and on a small scale. It can also be driven by green energy sources and it is compatible with the associated intermittency [1]. Especially dielectric barrier discharge (DBD) plasmas have received widespread attention for plasma-catalytic NH₃ synthesis due to their operational simplicity and existing industrial adoption (i.e., for ozone generation).

Gaining a fundamental understanding of plasma catalysis is a difficult task due to the various combined and often synergistic effects owing to the complex interaction between the plasma and the catalyst. This is true also for plasma-catalytic NH₃ synthesis from N₂/H₂ feed gases, which is an important case study, as generally only a few products (NH_x species) are formed. In order to elucidate the complexity of plasma catalysis, both experimental and modelling studies are required.

We developed a global plasma kinetics reactor model for (packed bed) DBDs [2, 3], which allows us to study the effect of the plasma conditions on the NH₃ synthesis. We found that depending on the plasma conditions, vibrational excitation has the potential to play a major role [3]. Furthermore, the developed model allows us to consider explicitly the strong microdischarges and the weaker afterglows in between those microdischarges, in a reaction analysis for plasma-catalytic NH₃ synthesis. Plasma radicals created in the microdischarges were found to recombine to NH₃ in the afterglows through various Eley-Rideal and Langmuir-Hinshelwood elementary reaction steps [4]. In parallel, the development of a more detailed microkinetics model, describing the surface reactions on various transition metals, also indicates a significant role of plasma radicals and Eley-Rideal type reactions [5]. Those findings are in good agreement with experimental observations [6].

The ultimate goal is the combination of the above-mentioned plasma kinetics reactor model and the microkinetics surface model, for a more self-consistent description of plasma-catalytic NH₃ synthesis in a DBD. However, this task still poses many challenges, which will be briefly addressed.

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POSTER SESSION

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Over the past few years, ammonia synthesis via direct electrochemical N₂ fixation has gained substantial interest due to its low carbon footprint and small-scale character. In an electrolytic cell with aqueous electrolyte, nitrogen gas is reduced to ammonia on the cathode. The protons are subtracted from water and oxygen gas is evolved at the anode. This single step process would completely eliminate the need for hydrogen gas and could operate under mild conditions. The production rate of the electrolyser could be tuned to meet the intermittent power output of renewables and there is a possibility for delocalisation and remote production.

As of today, the main limitation of the N₂ electrolyser remains the activity of the cathode material. A so-called electrocatalyst should be able to substantially increase the ammonia formation rate and minimize the activation overpotential. Additionally, a high faradaic efficiency and stability is desired. Clever methods have been found to deal with a poor faradaic efficiency but the production rate of the tested materials is still orders of magnitude lower than the minimum required level for industrial application (300mA/cm² and 90% FE according to the US DoE). Moreover, the measured (partial) currents and associated production yields are extremely small; in the range of a few microamps and nano to picomoles per second per cm² respectively. This low activity gives rise to several experimental challenges and pitfalls when it comes to validating potential electrocatalysts for nitrogen reduction.

Our group has been identifying and carefully investigating these pitfalls and came up with a dedicated experimental setup for studying electrocatalysts. Combined with the right, rigorous protocols, we are able to estimate and minimize the contributions of contaminants and impurities in the gas and liquid phase.

NO_x production in a rotating gliding arc plasma: potential avenue for sustainable nitrogen fixation

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The fast-growing world population demands food to survive, and nitrogen-based fertilizers are essential to ensure sufficient food production. Today, fertilizers are mainly produced from non-sustainable fossil fuels via the Haber–Bosch process, leading to serious environmental problems. We propose here a novel rotating gliding arc plasma, operating in air, for direct NO_x production, which can yield high nitrogen content organic fertilizers without pollution associated with ammonia emission. We explored the efficiency of NO_x production in a wide range of feed gas ratios, and for two arc modes: rotating and steady. When the arc is in steady mode, record-value NO_x concentrations up to 5.5% are achieved which are 1.7 times higher than the maximum concentration obtained by the rotating arc mode, and with an energy consumption of 2.5 MJ mol⁻¹ (or ca. 50 kW h kN⁻¹); i.e., the lowest value so far achieved by atmospheric pressure plasma reactors. Computer modelling, using a combination of five different complementary approaches, provides a comprehensive picture of NO_x formation in both arc modes; in particular, the higher NO_x production in the steady arc mode is due to the combined thermal and vibrationally-promoted Zeldovich mechanisms.

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N₂ Fixation with H₂O Vapour by Non-equilibrium Plasma: Towards Sustainable NH₃ Production

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Ammonia is a crucial nutrient used for plant growth and as a building block in the pharmaceutical and chemical industry, produced via nitrogen fixation of the ubiquitous atmospheric N₂. Current industrial ammonia production is extremely energy-demanding and relies heavily on fossil resources. Hence, a lot of work is put into developing non-fossil-based pathways. Among these is the use of nonequilibrium plasma. Plasma technology is investigated for NH₃ production from N₂ and H₂ (where H₂ can be obtained in a sustainable way from water electrochemically), but also directly from N₂ and H₂O with no additional electrolysis step or setup [1,2].

In this work, we investigated water vapour as a H source for nitrogen fixation into NH₃ by nonequilibrium plasma. We used a pulsed plasma setup (Soft jet) operated with a feed gas of N₂, to which various amounts of H₂O vapour were added. The highest selectivity toward NH₃ was observed with low amounts of added H₂O vapour. At the same time, the highest NH₃ production rate was reached at high H₂O vapour contents. We also studied the role of H₂O vapour and of the plasma-exposed liquid H₂O in nitrogen fixation by using isotopically labeled water to discriminate between these two sources of H₂O [3]. We show that added H₂O vapour, and not liquid H₂O, is the main source of H for NH₃ generation (Figure 1).

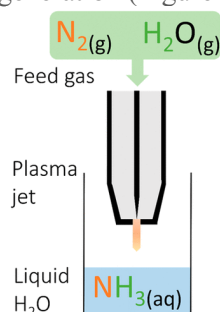


Figure 1. H₂O vapour in the feed gas as the source of H atoms for NH₃ production by plasma.

The studied catalyst- and H₂-free method offers excellent selectivity toward NH₃ (up to 96%), with energy consumption (ca. 95–118 MJ/mol) in the range of many plasma-catalytic H₂-utilising processes [4].

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SECAM Process for Energy-Efficient Ammonia Production from Air and Water using Electrocatalysts with Limited Faradaic Efficiency

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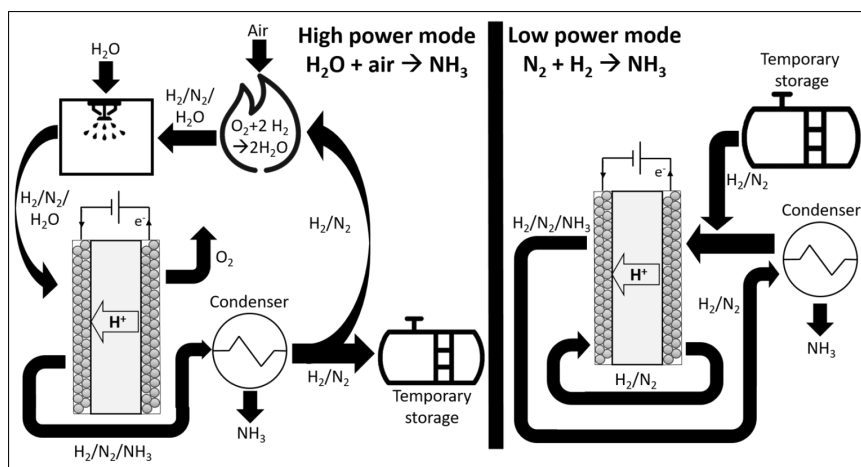
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Ammonia is an industrial large volume chemical. It is used in fertilizers and many chemical products and materials, and it pops up as a candidate green energy vector. Today, the industrial production of ammonia is dominated by the Haber-Bosch process departing from natural gas or other fossil fuel. This process is responsible for about 1-2 % of the global CO₂ emissions. Electrochemical ammonia production from water and nitrogen gas using renewable electricity is a potential solution to reduce the CO₂ footprint of ammonia production. Electrocatalysts with steadily increasing faradaic efficiency are being reported, but there seems to be a tradeoff between ammonia selectivity and catalytic activity. Hydrogen gas is the main byproduct. The SECAM process (Solar ElectroChemical AMmonia synthesis)¹, illustrated in the figure below, shows low ammonia selectivity of electrocatalysts not to be an obstacle to energy-efficient ammonia production.

The SECAM process integrates nitrogen gas production from air, electrocatalytic ammonia synthesis, reaction product separation and hydrogen recycling with an overall energy efficiency similar to the Haber-Bosch process departing from grey hydrogen. The SECAM process also benefits from the intermittent nature of renewable energy sources, by switching between a high power mode (left) and a low power mode (right), depending on energy availability. In the high power mode, the electrochemical cell converts air and water into ammonia, producing a mixture of nitrogen and hydrogen gas as byproduct. In the low power mode, the nitrogen/hydrogen mixture is converted to ammonia at a significantly lower energy cost. This way, all byproducts can be converted to additional ammonia.

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Nitrogen fixation in an electrode-free microwave plasma

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Plasma-based gas conversion has great potential for enabling carbon-free fertilizer production powered by renewable electricity. Sustaining an energy-efficient plasma process without eroding the containment vessel is currently a significant challenge, limiting scaling to higher powers and throughputs. Isolation of the plasma from contact with any solid surfaces is an advantage, which both limits energy loss to the walls and prevents material erosion that could lead to disastrous soil contamination. This work [1] presents highly energy efficient nitrogen fixation from air into NO_x by microwave plasma, with the plasma filament isolated at the center of a quartz tube using a vortex gas flow. NO_x production is found to scale very efficiently when increasing both gas flow rate and absorbed power. The lowest energy cost recorded of ~2 MJ/mol, for a total NO_x production of ~3.8%, is the lowest reported up to now for atmospheric pressure plasmas.

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Nitrogen fixation by needle-water DC microplasma: comparison between an water-anode and water- cathode system

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Nitrogen is an essential element for all forms of life on earth. While nitrogen is the most abundant element in our environment (78% of earth atmosphere), it is the least available to living organisms due to its natural form of N₂ molecules. Breaking the triple bond between two nitrogen atoms requires a significant amount of energy (9.79eV)[1]. Therefore, before being involved in biological reactions or used in industrial processes, nitrogen atoms must be bound to other elements in order to provide accessible compounds such as nitrates (NO₃⁻) or ammonia (NH₃). The nitrogen fixation (NF) is naturally carried out via lightnings and by micro organisms. It is also artificially implemented using the Haber-Bosch/Ostwald processes though ammonia synthesis and conversion to nitric acid. Over the past few years, plasma-based processes have attracted more attention as a “clean” alternative to Haber-Bosch for nitrogen fixation. This is due to the unique properties of non-equilibrium plasmas which could allow a drastic reduction of the energy cost for nitrogen fixation while being compatible with renewable precursors and energy sources.

A needle-water DC microplasma system working at atmospheric pressure in N₂/O₂ gas mixtures is used to study the fundamental mechanisms of nitrates/nitrites synthesis in highly complex and yet little-known plasma-water systems. Plasmas are investigated by means of optical emission spectroscopy while the activated water is analyzed using ionic chromatography and UV-Vis absorbance spectroscopy. A comparison between the water used as cathode or anode is also made.

Experiments highlight that the extended Zeldovich mechanism (reaction between N atoms and OH radicals) is likely the dominant mechanism for NO formation in the gas phase. By using the water as a cathode, it is possible to achieve a nitrite free synthesis, with an increase of the energy efficiency of the whole system. The stronger water evaporation, different plasma properties and broader plasma-water interface lead to a much stronger OH radical density in the plasma and H₂O₂ formation in the water. H₂O₂ formation and OH radical are involved in an enhanced conversion of the different NO_y into HNO₃/NO₃⁻ in both the gas phase and aqueous phase[2].

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Nitrogen fixation in a N₂-O₂ Gliding Arc plasma, an optical emission and IR absorption spectroscopy study

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Nitrogen Fixation (NF) stands for the process allowing for the conversion of N₂ into molecules usable by the chemical industry such as NH₃. Currently NF is mostly performed through the Haber-Bosch (HB) process, consuming 1-2% of the world's total energy output and emitting more than 300 million metric tons of CO₂ [1-2]. Plasma-driven NF, such as in Gliding Arc Plasma discharges (GAP), has gained a lot of interest as an effective and efficient environmentally friendly alternative for gas conversion [3].

This work focuses on studying the production of NO_x in a GAP operating at atmospheric pressure and its relation with the thermal conditions in the plasma.

The GAP is operated in N₂-O₂ gas mixtures using a 15 kOhm resistance between the cathode and a DC power supply while the discharge current ranges between 125 and 275 mA and the total gas flow rate injected between 7 and 20 slm. The densities of the produced species were analyzed by Fourier Transform Infrared (FTIR) spectroscopy through the absorption lines at 1875 cm⁻¹ for NO and at 1616 cm⁻¹ and 2906 cm⁻¹ for NO₂.

Optical Emission Spectroscopy (OES) analysis was used for the determination of rotational and vibrational plasma temperatures on the N₂ second positive system in UV/visible range after fitting the spectra with Specair 3.

Our results reveal a minimum energy cost of 8 MJ/mol that corresponds to the maximum NO_x yield measured of approximately 1.35%. This is obtained in a 50%-50% N₂-O₂ gas mixture which proved to be the optimal gas ratio for NO_x synthesis in a GAP. From an energy cost perspective, the results show lower currents and higher gas flow rates to be the optimal discharge conditions.

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Plasma-catalytic ammonia synthesis: Effect of metal composition and synthesis method on performance of Co-based Al₂O₃-supported catalysts

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Ammonia is an essential chemical not only due to its use in fertilizers and other applications, but also because it could serve as an energy vector for hydrogen.[1] Currently, ammonia is mainly produced via the energy-intensive Haber-Bosch process, which generates 1.87 tons of CO₂ per ton of NH₃ produced. [2-4] Consequently, a lot of research has been conducted towards finding carbon-free, sustainable alternatives. Recently, plasma-catalytic nitrogen fixation has gained a lot of attention as a potential green alternative for the Haber-Bosch process as it combines the advantages of catalysis and plasma.[1]

Herein we investigate the plasma-catalytic synthesis of ammonia (NH₃) in a dielectric barrier discharge (DBD) plasma reactor packed with various Co-based, Al₂O₃-supported catalysts, including Co/Al₂O₃, CoCe/Al₂O₃, CoLa/Al₂O₃, CoMg/Al₂O₃, CoCeLa/Al₂O₃ and CoCeMg/Al₂O₃ (all 20 wt%). This study discusses the effect of operational parameters such as the feed gas ratio and the flow rate, as well as the effect of the metal composition of the catalysts on the NH₃ concentration and the energy consumption. Various characterization techniques, including Raman spectroscopy, X-ray powder diffraction, 1D scanning electron microscopy energy dispersive X-ray analysis and N₂ sorption, were used to determine the structural and physicochemical properties of the different catalysts.

The optimal H₂:N₂ ratio for an empty and an Al₂O₃-packed DBD reactor is 3:1, while the optimal ratio for a catalyst-packed DBD reactor shifts towards 1:1. Further, a higher flow rate resulted in a decrease in NH₃ concentration and energy consumption. Lastly, the best performing catalyst was found to be CoLa/Al₂O₃ with an ammonia concentration in the reaction effluent of 9101 ppm and an energy consumption of 83 MJ/mol, achieved at a total flow rate of 100 mL/min, a 1:1 H₂:N₂ ratio and a plasma power of ca. 50 W.

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Heat distribution visualization in N₂/O₂ dielectric barrier discharge

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Dielectric barrier discharges allow to create non-thermal plasmas at low temperature and at atmospheric pressure. Because of the easiness of use and implementation they have been implemented in reseau of laboratory and industry throughout the years for gas conversion [1], activation of surfaces [2], deposition of polymeric coatings [3], and even crystalline inorganic coatings [4]. Recently DBD's for gas conversion have regained more attraction, through their characteristic of non-thermal plasma they allow to create specific mix of reactive molecules and atoms without heat losses associated with thermal equilibrium plasma. This property has raised new gas conversion application in CO₂ conversion [5], CH₄ dry reforming [6] or Nitrogen fixation [7]. One of the most challenging aspect to understand the reactivity of DBD at atmospheric pressure in N₂/O₂ is the temperature distribution inside the discharge gap and how it influences the reactivity of ozone and nitrogen oxides production. Those discharge exhibit a highly filamentary behavior and this behavior is tightly linked to the driving frequency of the DBD. High speed imaging (10000 fps) of the discharge have showed homogenous filamentary aspect at low frequency (under 12 kHz) and an increasing inhomogeneous filamentary aspect at high frequency (over 17 kHz). Rotational temperature has been calculated by optical emission spectroscopy of the N₂⁺ First negative system line at 391,4 nm and compared to the rotational temperature of the N₂(C-B) Second positive system at 335 nm which are associated respectively to the micro- discharge and to the afterglow of the discharge [8]. As the streamers are one of the energy dissipation phenomena in a filamentary discharge through exothermic reaction and electrical heating [9], their distribution and behavior influence the distribution of the heat inside the DBD. To image the heat distribution over the frequency of the DBD, we used a new approach, based on, the application of the discharge onto a thermal sensitive paper with and without an N₂/O₂ flowrate. This provides thermal images of the heat produce inside the discharge and allows to highlight the relation between the frequency and the heat distribution of the discharge.

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Evaluation of NO_x Formation in a Catalyst Assisted Microwave Plasma

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Nitrogen oxides (NO_x) are valuable chemical feedstock because of their commercial relevance [1]. Most of today's synthetic NO_x is made by oxidizing ammonia, while NO_x formation in N₂ and O₂ atmosphere takes place at high temperatures (>2000°C) [2]. In the literature, continuous developments on sustainable methods for NO_x formation –known as Nitrogen Fixation (NF) have been reported. Technologies based on renewable electricity that can transform base molecules (i.e., H₂O, N₂, and O₂) into chemical-rich molecules are very interesting. Among them, plasma technology, as an inherent “green” technology, is considered to be most practical for reducing the environmental impacts and improving the energy efficiency of the NF process [1]. However, catalyst-assisted plasma for the synthesis of NO_x has not been thoroughly investigated and only a few researches have been reported [3].

In this work, the study deals with NF via catalyst-assisted microwave plasma in the post-discharge zone. The heterogeneous catalysts -MoO₃ with various loading on γ -alumina support were prepared according to “conventional wet impregnation” method and characterized by the XRF, XRD, BET, XPS, and SEM/TEM microscopy. Our FTIR studies show NO_x formation can be significantly influenced by the experimental conditions as well as by the catalysts.

Based on this study, the highest yield of NO_x formation was obtained with Al₂O₃-MoO₃ 10wt% in which, based on the literature, the Molybdenum oxide monolayer coverage reaches its threshold on the existed surface of γ -alumina. Surface study of samples via XPS revealed two oxidation states of Mo on γ -alumina. Comparing Mo 3d_{5/2} peak position and FWHM value of different samples suggest that by increasing MoO₃ loading, these values are approaching the pure reference MoO₃, which is in agreement with our XRD and TEM studies. Results for different calcination temperatures of alumina show the highest NO_x formation for a substrate treated at 800°C and it was unexpected since at this temperature phase transition from gamma to delta takes place and is accompanied by a surface area reduction. Furthermore, considering the stoichiometry of the reaction, the chemical stoichiometric equilibrium of the reaction within the catalytic activity is in coherence with gases flow ratio to gain the highest NO_x formation. The results show that fresh catalysts –even after calcination– are contaminated with water. However, after being exposed to the plasma downstream for a short time, the catalysts loosed the adsorbed water and their performances are stable for prolonged use. Finally, we evaluated the influence of the gas residence time by varying the flow rate and the gases pressure in the reactor. The former has a negligible influence on the NO_x formation compared to the impact of gas pressure which causes gas temperature increment. The evidence shows the NO formation can be channelized regarding the gas temperature by producing N₂O as an intermediate species before NO formation that can explain NO₂ formation within the catalytic activity.

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Effusion nozzle for energy-efficient NO_x production in a rotating gliding arc plasma reactor

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Plasma-based NO_x production is of interest for sustainable N₂ fixation, but more research is needed to improve its performance. One of the current limitations is recombination of NO back into N₂ and O₂ molecules immediately after the plasma reactor. Therefore, we developed a novel so-called “effusion nozzle”, to improve the performance of a rotating gliding arc plasma reactor for NO_x production, but the same principle can also be applied to other plasma types. Experiments in a wide range of applied power, gas flow rates and N₂/O₂ ratios demonstrate an enhancement in NO_x concentration by about 7.7%, and a reduction in energy cost by 22.46%. In absolute terms, we obtain NO_x concentrations up to 5.89%, at an energy cost close to 2.5 MJ/mol, which are the best values reported to date in literature. In addition, we developed five complementary models to describe the gas flow and plasma behavior, including arc dynamics and plasma chemistry, aiming to reveal why the effusion nozzle yields better performance. Our simulations reveal that the effusion nozzle acts as very efficient heat sink, causing a fast drop in gas temperature when the gas molecules leave the plasma, hence limiting the recombination of NO back into N₂ and O₂. This yields an overall higher NO_x concentration than without the effusion nozzle. In addition, this higher NO_x concentration can be obtained at a slightly lower power, because the effusion nozzle allows for the ignition and sustainment of the plasma at somewhat lower power. Hence, this also explains the lower energy cost. Overall, our experimental results and detailed modeling analysis will be useful to improve plasma-based NO_x production in other plasma reactors as well

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Sustainable NO_x Production from Air in Pulsed Plasma: Elucidating the Chemistry behind the Low Energy Consumption

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ABSTRACT In this work, we show that pulsed plasmas can be the key for energy-efficient sustainable fertiliser and base chemical production.

N-based fertilisers are paramount to support our still-growing world population. Over the past century, fertilisers and base chemicals like ammonia (NH₃) have been avidly produced synthetically to make up for the high demand. Currently 50% of the world's population depends on the production of said fixed N₂ in the form of NH₃ through the Haber-Bosch (HB) process.¹ Present-day industrial N₂ fixation is heavily fossil fuel-dependent, therefore, a lot of work is put into the development of fossil-free pathways.² Plasma technology offers a fossil-free and flexible method for N₂ fixation that is compatible with renewable energy sources.

We present here a pulsed power plasma source (Soft Jet) for direct NO_x production from air at atmospheric pressure. The pulsed power allows for a record-low energy consumption (EC) of 0.42 MJ/(mol N). This is the lowest reported EC in plasma-based N₂ fixation at atmospheric pressure thus far. To gain insight into the underlying mechanisms of this record-low EC, we developed a chemical kinetics model, which provides very good agreement with the experiments at the full range of flow rates (0.4 – 2.0 L/min) and can thus be used for reaction analysis. The model pinpoints the specific aspects of pulsed plasma power, that allow for such a low EC.

The pulsed power and the corresponding pulsed gas temperature are at the base for the very low EC: they provide a strong vibrational-translational non-equilibrium and affect the forward and back reactions of the non-thermal Zeldovich mechanism in a delicate way. This insight is important for the development of the next generation of plasma sources for energy-efficient NO_x production.

In order to assess the economic viability of this source, it was benchmarked against a techno-economic analysis by Rauwenhorst et al.³ and a life cycle assessment by Anastasopoulou et al..⁴

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