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Mechanisms of multielectron reactions at the plasma/water interface: Interfacial catalysis, RONS, nitrogen fixation, and plasma activated water

Alexander G. Volkov[a,*], Asya Bookal[a], Jewel S. Hairston[a], Jade Roberts[a], Gamaliel Taengwa[a], Darayas Patel[b]

[a] *Department of Chemistry, Oakwood University, 7000 Adventist Blvd., Huntsville AL 35896, United States*
[b] *Department of Mathematics and Computer Science, Oakwood University, 7000 Adventist Blvd., Huntsville AL 35896, United States*

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ABSTRACT

There are three major multi-electron reactions in nature: nitrogen fixation by bacteria, water oxidation in photosynthesis, and oxygen reduction during respiration. Here we found that a cold atmospheric pressure He-plasma jet (CAPPJ) can oxidize N_2 to HNO_3 and HNO_2 at low temperature and atmospheric pressure at the plasma-air/water interface. Redox reactions induced by cold plasma occur not only at the plasma/air and plasma/water interfaces, but also in the volume of the aqueous phase. Analysis of the images which displayed the presence of pH indicators in the aqueous phase showed that redox reactions and acid formation occur at the plasma-air/water interface and the products of electrochemical reactions slowly diffuse into the bulk of the aqueous solution. Acidification of an aqueous solution during the CAPPJ treatment correlates with an increase in HNO_x concentration in the aqueous phase. HNO_2 is unstable and can be oxidized to HNO_3 by plasma-generated H_2O_2 or ozone. The mechanisms of the interfacial multielectron reactions at the plasma-air/water interface are discussed and evaluated. Plasma-activated water can be used in medicine, food industry, and agriculture for disinfection, sterilization, and decontamination. Plasma-induced production of HNO_x at the plasma/water interface at room temperature and atmospheric pressure can be used in the industry for nitrogen fixation and production of nitrogen compounds, replacing the expensive old technology processes.

1. Introduction

Nitrogen is one of the most abundant elements on Earth, and the total amount of nitrogen in the atmosphere alone is estimated at $3.87 \cdot 10^{15}$ tons [1]. Despite this, the binding of atmospheric nitrogen is extremely difficult - the strong triple bond between the atoms in the N_2 molecule makes this molecule extremely inert. The fixation of molecular nitrogen and the oxidation of water in nature occur at normal air pressure and temperatures. Only certain prokaryotes can fixate atmospheric nitrogen. These include the cyanobacteria of soils, fresh and salt waters, other types of free-living soil bacteria, and nitrogen-fixing bacteria that live as symbionts in the root nodules of legumes [2]. The most important source of nitrogen is the air. However, relatively few species can convert atmospheric nitrogen into forms that are useful for living organisms. In the biosphere, the metabolic processes of different species function interdependently to conserve and reuse biologically available nitrogen in a vast nitrogen cycle. Plants and some microorganisms can convert nitrate to amino acids and other reduced nitrogen-carbon compounds.

Industrial conversion of atmospheric N_2 is a very important process for the production of nitrogen-containing compounds and fertilizers. The Haber-Bosch process [3,4] accounts for 10^8 tons per year [1] of N_2 conversion to NH_3. The Birkeland-Eyde process [5,6] is relatively inefficient for industrial applications in terms of energy consumption for nitrogen fixation and uses 30 GJ of electrical energy per ton of HNO_3 [7].

New methods of nitrogen fixation, such as plasma activated water, are based on the treatment of water by cold atmospheric pressure radiofrequency plasma at low temperatures and normal atmospheric pressure [8-11]. Plasma denotes a quasi-neutral mixture of electrons, ions, and neutral species formed during gas ionization by

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Abbreviations: CAPPJ, cold atmospheric pressure radio frequency He-plasma jet; PAW, plasma-activated water; RONS, reactive oxygen and nitrogen species; RNS, reactive nitrogen species; ROS, reactive oxygen species.

[*] Corresponding author.

E-mail address: agvolkov@yahoo.com (A.G. Volkov).

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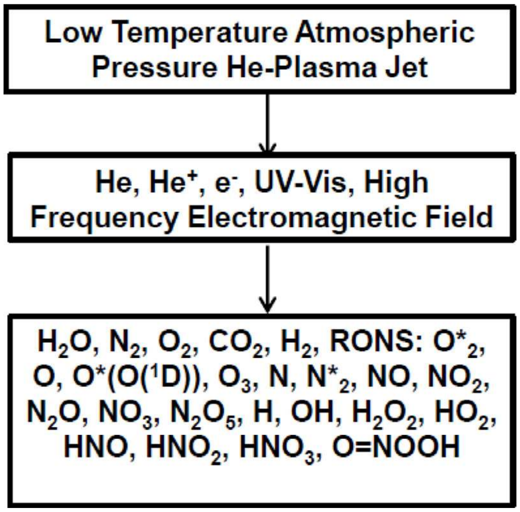

Fig. 1. Schematic diagram of chemical processes at the air/water interface induced by a plasma jet. All reactive oxygen and nitrogen species in this diagram were detected and analysed in the literature [7-20].

fast free electrons. Due to the large difference of electron and atom mass, the electron mean energy (temperature) may exceed gas temperature by two orders of magnitude when electricity passes through a gas [12-17]. Cold atmospheric pressure plasma provides a non-equilibrium catalytic environment for a variety of chemical reactions at ambient gas temperatures. In the present paper, the term "plasma" refers to the fourth state of matter, i.e. a partially ionized quasi-neutral mixture of electrons, ions, and neutral species. CAPPJ's electron temperatures correspond to the threshold energies of the excited states in neutral atoms and molecules, ensuring that the power transfer from electrons to these atoms and molecules effectively produces activated species (radicals, excited states, photons). Energization of ions in CAPPJ sheaths and boundaries can lead to the activation of interfacial redox processes [18,19].

Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) created by plasma in water are mainly responsible for their beneficial effects in chemistry, biology, medicine, material science, agriculture, and food treatment. A CAPPJ in atmospheric air can initiate chemical reactions and produce different radicals, charged and neutral compounds, ions, and UV–Vis light at room temperature (Fig. 1). Plasma-activated water (PAW) can be used for disinfection, sterilization, and decontamination in dentistry, dermatology, and gynecology.

CAPPJs produce various atomic or molecular species when interacting with molecular gasses such as air. For example, a CAPPJ in air can produce reactive oxygen and nitrogen species (RONS) including biologically active compounds N_2O, NO_x, H_2O_2, NO_3^-, NO_2^-, and O_3. These CAPPJ products lead to the activation of surface modifying processes and redox reactions [16,17,21].

Some RONS can be very toxic to biological tissue and can selectively kill bacteria, fungi, and viruses. When exposed to water, cold plasma can initiate interfacial catalytic reactions at the plasma/water interface that can decrease the pH of the solution due to oxidation of nitrogen or water. Nitrogen fixation for the production of fertilizers and nitrogen-containing compounds is a large multi-billion dollar industry. Plasma treatment of water offers opportunities for new products made from renewable and abundant natural resources with substantially improved energy efficiency, reduced capital, lower operating costs, and reduced environmental impact compared to current approaches. Cold plasma activation of water may provide an alternative method for nitrogen fixation compared to the current Haber-Bosch and Birkelaud-Eyde processes, which currently requires a large amount of energy and very expensive technology at a very high temperature and pressure. These processes produce fertilizers and nitrogen-containing compounds with well-known environmental and ecological problems.

There are three major multi-electron reactions in Nature: nitrogen fixation by bacteria, photo-oxidation of water in photosynthesis, and oxygen reduction during respiration [22-25].

Due to its extremely non-equilibrium nature, cold plasma could promote multi-electron heterogeneous chemical reactions at the plasma-gas/water interface that are not possible under ordinary conditions in homogeneous phases. Soft interfacial structures are known for their selective catalytic properties [24-27]. For example, the multi-electron reaction of oxygen reduction in mitochondria, water oxidation in the reaction centers of the photosystem II, and nitrogen fixation by bacteria take place in natural heterogeneous membrane structures. For the five-electron homogeneous reaction of nitrogen oxidation to HNO_3, the energy of activations can be twenty-five times higher than that of one-electron reactions, which dramatically decreases the rate constant. Furthermore, soft interfaces have selective properties and can catalyze or inhibit interfacial charge transfer reactions due to electrostatic effects [24-27]. Thus, the kinetic parameters of interfacial charge transfer depend on the charge being transferred, the charges of reactants, their location in relation to the interface, and the dielectric properties of the media forming the fluid/fluid interface. In the presence of plasma, the interfacial structure and distribution of ions and molecules inside the liquid phase can be different.

In this paper, we report molecular mechanisms of multi-electron heterogeneous reactions at the plasma-air/water interface and nitrogen fixation at room temperature and atmospheric pressure induced by cold He-plasma jet.

2. Materials and methods

Ozone test strips were purchased from *Macherey-Nagel Company* (Duren, Germany). These strips were used for orienting the determination of ozone concentration in air under the plasma jet. H_2O_2, nitrate, and nitrite test strips were purchased from *Bartovation LLC* (Bartovation.com, New York, USA). These strips were used for orienting the determination of H_2O_2, NO_2^-, and NO_3^- concentration in water. pH indicators Methyl Red (0.05% Reagent grade, (*Loudwolf*, USA), Universal Indicator solution (Fisher Scientific, USA), General Hydroponics HGC722145 pH Test Indicator (*General Hydroponics*, Santa Rosa, CA USA), and Bromocresol Purple Indicator solution (0.04% w/w, *Ricca Chemical Company*, Arlington, TX, USA) were purchased from Amazon.com. Bottled ultra-high purity helium was purchased from Sexton Welding Supply (Huntsville, AL, USA). The nitrogen source in these experiments was atmospheric N_2, which entered the plasma and slightly dissolved in water according to its partition coefficient between air and water.

The CAPPJ experimental setup was described earlier [14-17]. The helium was ionized by strong electric fields between electrodes and formed a plasma jet approximately 4 cm long measured from the exit of the outer tube (Fig. 2). The fact that both electrodes are electrically isolated from the plasma prevents arcing to the sample. Treatment by the jet was either via direct contact as shown in Fig. 2, or indirect with a gap. The plasma was powered with a high voltage pulsed DC system consisting of a Matsusada AU-10P60 10 kV DC (*Matsusada Precision Inc.*, Japan) power supply, an IXYS PVX-4110 pulse generator (*Directed Energy, Inc.*, Fort Collins Colorado), and a Rigol DG1ZA203504066 arbitrary waveform generator (*Rigol Technologies USA Inc.*, Beaverton, OR, USA). The system was operated with an 8 kV pulse amplitude, 6 kHz pulse frequency, 1 µs pulse width, and a ~70 ns pulse rise and fall time.

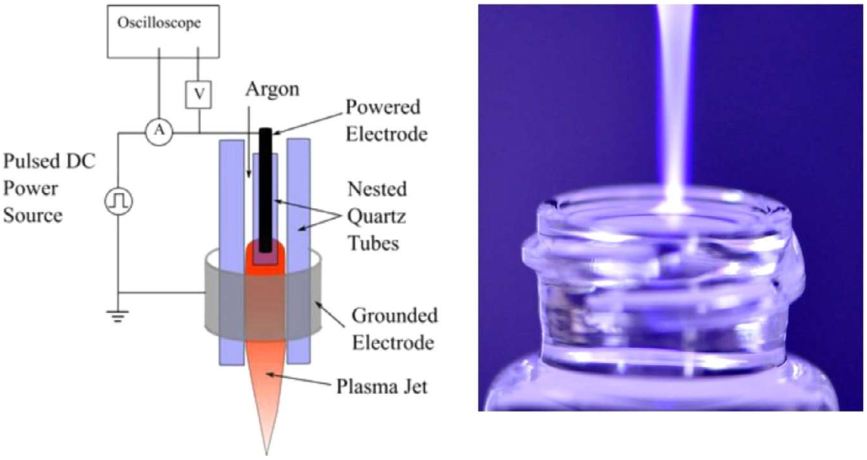

Fig. 2. Schematic diagram of CAPPJ treatment of water surface. (Left) Cold He-plasma jet and (Right) photo of the air/water interface in a contact with the He-plasma jet. 20 ml clear borosilicate glass vials with dimensions of 27 mm x 58 mm were used in all experiments with CAPPJ treatments. The diameter of the water surface was 15 mm. The temperature was 20 °C.

Ion-selective electrodes (*Hanna Instruments, Smithfield, RI, USA*) were used for pH and NO_x^- measurements using a pH200 microprocessor pH/C meter (*Hanna Instruments Smithfield, RI, USA*).

The digital laser temperature gun, Etekcity lasergrip 800 (*Etekcity, Anaheim, CA, USA*), was used for the measurement of temperature in the plasma jet, water, and air.

Absorption spectra were recorded using 1 cm quartz cuvettes with the Shimadzu UV–Vis spectrophotometer ISR-2600 Plus (*Shimadzu*, Japan).

Software SigmaPlot 12 (*Systat Software, Inc.*) was used for the statistical analysis of experimental data. All experimental results were reproduced at least 16 times.

A photo camera Nikon D3x with AF-S Micro Nikkor 105 mm 1:2.8 G ED VR lens (Nikon, USA) was used for the photography.

3. Results

3.1. Generation of reactive oxygen and nitrogen species

Although the plasma jet looks continuous to the naked eye, it actually consists of fast ionization waves (plasma bullets) propagating along the noble gas channel with speeds of about a few hundred m/s. Electrons inside the fast ionization wave have energies of a few eV and are capable of producing ionization and non-equilibrium chemical reactions at room temperature [28,29]. The reactive species in the noble-gas-air mixture are generated by these electrons in the areas where mixing of the noble gas with air takes place. Radicals and charged species (electrons and ions) recombine quickly beyond the plume (the glow plasma region) but some of them and the neutral species with longer life-times can propagate beyond the plasma plume and interact with water at the air/water interface.

CAPPJ produces RONS, but most of them have a very short life span. The exceptions are O_3, H_2O_2, NO_x, HNO_2, and HNO_3, which are more stable and can be easily detected. The production of ozone by the cold atmospheric pressure radiofrequency He-plasma jet (CAPPJ) was detected using ozone test strips (Fig. 3). The solubility of ozone in the aqueous phase depends on pH and temperature. The solubility of ozone in water at a pH of 2.0 to 6.0 is about 50 mg/L, and the partition coefficient between water and air is about 0.32 at a temperature of 20 °C [30-31]. The formation of H_2O_2, HNO_2, and HNO_3 after stirring or shaking the aqueous phase is shown in Fig. 4.

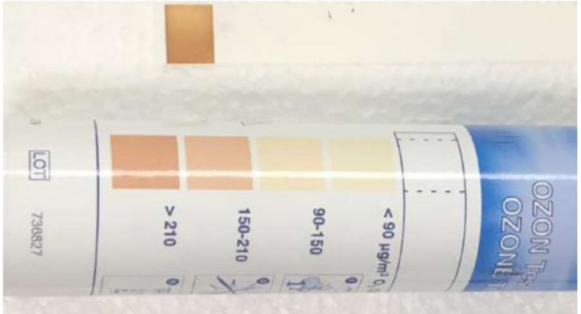

Fig. 3. Test for ozone concentration after 10 min exposition to CAPPJ. The ozone test strips (Macherey-Nagel Company, Duren, Germany), when placed under the cold He-plasma jet at a distance of 1 cm for 10 min, show production of ozone by the He-plasma jet in a concentration of 210 µg/m^3 or more. Temperature was 20 °C.

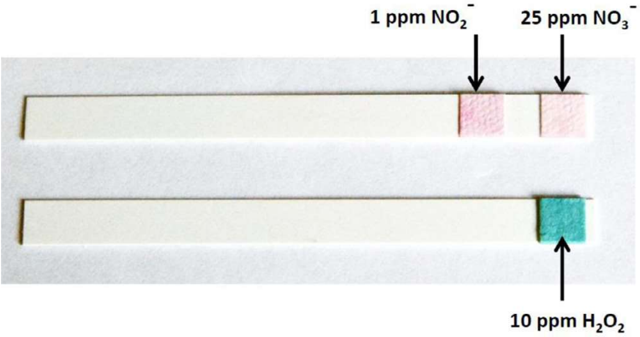

Fig. 4. Test for NO_3^- (≈ 0.4 mM), NO_2^- (≈ 0.02 mM), and H_2O_2 (≈ 0.29 mM) concentration after 130 min exposition to CAPPJ and stirring of the aqueous phase. Test strips (Bartovation.com) were placed in the aqueous solution for 30 s. Test strips show the same concentration of HNO_3 in plasma treated water a couple of weeks after experiments. The volume of an aqueous phase was 20 mL. The diameter of the water surface was 15 mm. The interfacial ratio k is equal to 0.088 cm^{-1}. The temperature was 20 °C.

3.2. Acidification of the aqueous phase starts at the plasma/water interface

A pH indicator, also known as an acid–base indicator, is a substance that can determine the approximate pH of a solution by changing color within a specific pH range. Proton distribution was

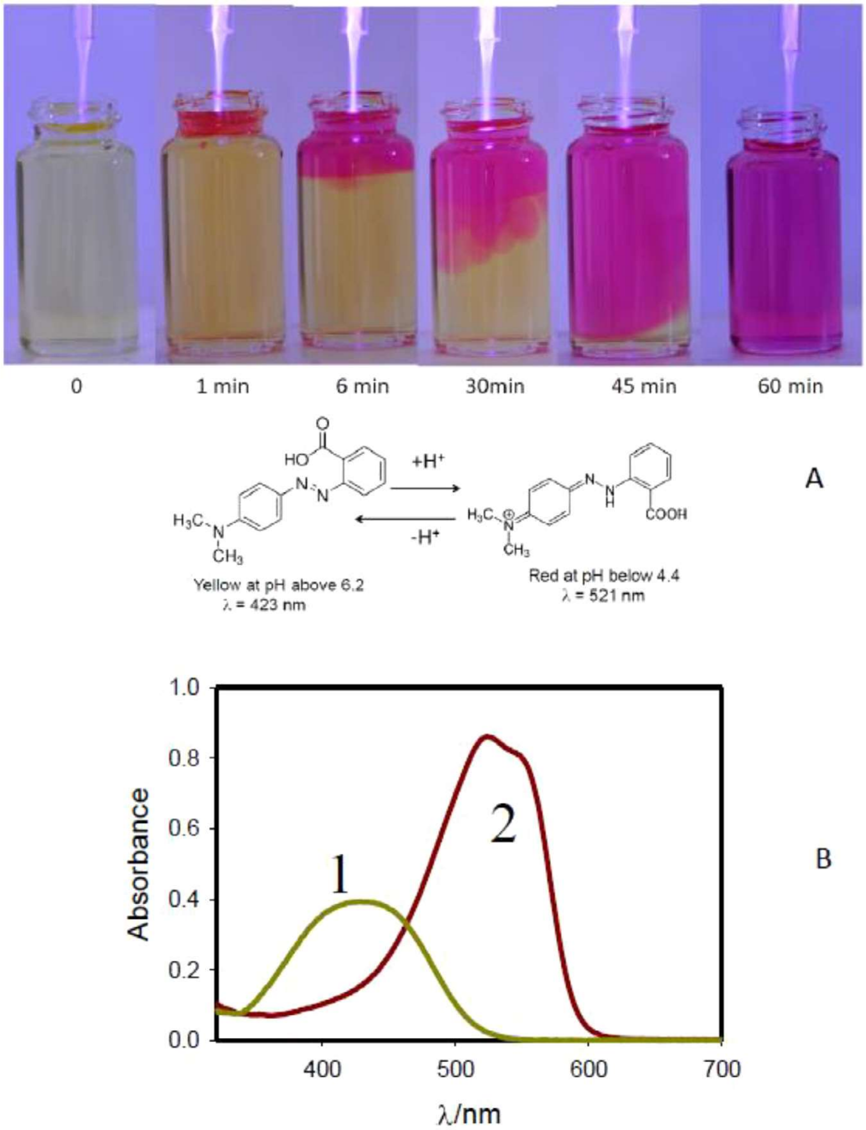

Fig. 5. (A) Visualization of the proton distribution during treatment of water with CAPPJ. 30 µL of 0.05% Methyl Red ($C_{15}H_{15}N_3O_2$) solution was added to 20 mL H_2O before treatment with plasma jet. The diameter of the water surface was 15 mm. (B) Absorption spectra of the aqueous phase before treatment with plasma (1) and after 1 hr treatment with He-plasma jet (2). The interfacial ratio k is equal to 0.088 cm^{-1}. The temperature was 20 °C.

investigated with four types of pH indicators. Methyl red produced the most distinct images of acidification of the plasma/water interface treated by plasma (Figs.5, 6). All experiments with pH indicators show that the proton concentration at the plasma/water interface was higher than in the rest of the bulk solution (Fig. 5). The lowering of the solution's pH can be an important indicator for the fixation of nitrogen or water oxidation (Figs. 5).

The spatial distribution of protons can be measured using solutions of pH indicators [32], which allow us to visualize the kinetics of acidification of the aqueous phase when interacting with the plasma at the interfacial border (Figs. 5). The acidification of the aqueous phase begins at the plasma/water interface and then diffuses downwards in the form of a red-colored cloud (Fig. 5). Similar visualization of fast acidification of the plasma/water interface and diffusion of protons to an aqueous phase were obtained with different pH indicators such as Universal Indicator solution, General Hydroponics pH Indicator, and Bromocresol Purple. Since the reaction of the cold plasma with air and water occurs at the interfacial area, the yield of the reaction products depends on the interfacial ratio 'k' of the surface area "S" and the volume "V" of the aqueous phase $k = S/V$. An increase in the parameter k leads to a faster acidification of the solution and an increase in the concentration of products such as NO_x^- and H_2O_2.

Due to the electrical nature of the plasma discharge and the electrical noise, the pH cannot be accurately read using a pH glass electrode while the plasma is energized. Thus, pH measurements can be obtained at certain time intervals when the plasma is turned off (Fig. 7A). The concentration of protons linearly increased as time exposure of water to the plasma jet increased (Fig. 7B). The rate of increase in the proton concentration can be described by the equation: $d[H^+]/dt = 3.059\times10^{-6}$(M/min), when the volume of the aqueous phase was 20 mL and the diameter of the water surface was 15 mm.

The kinetics of fixed NO_x^- nitrogen compounds production from the air in the aqueous phase can be continuously monitored by ion-selective electrodes. This process can be controlled by the electric double layers at the plasma/water interface, which have already been theoretically and experimentally investigated [26].

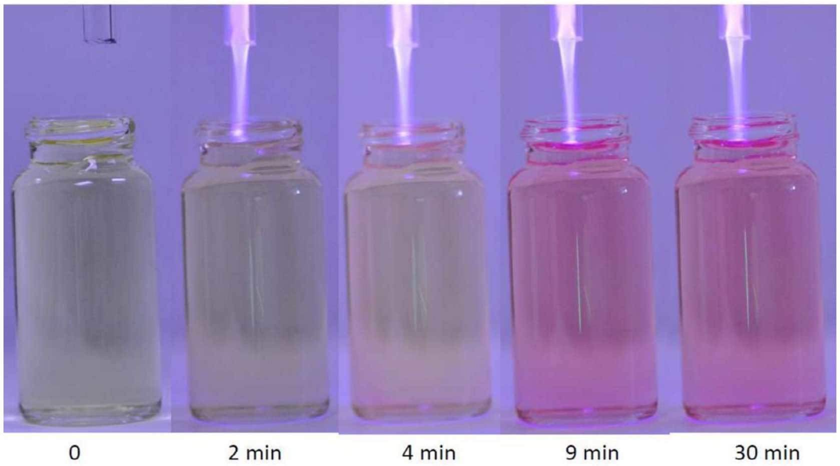

Fig. 6. Acidification of water CAPPJ. 50 µL of pH General Hydroponics HGC722145 pH Test Indicator Wide Spectrum solution was added to 20 ml H_2O before treatment with plasma jet. The diameter of the water surface was 15 mm. The interfacial ratio k is equal to 0.088 cm^{-1}. The temperature was 20 °C.

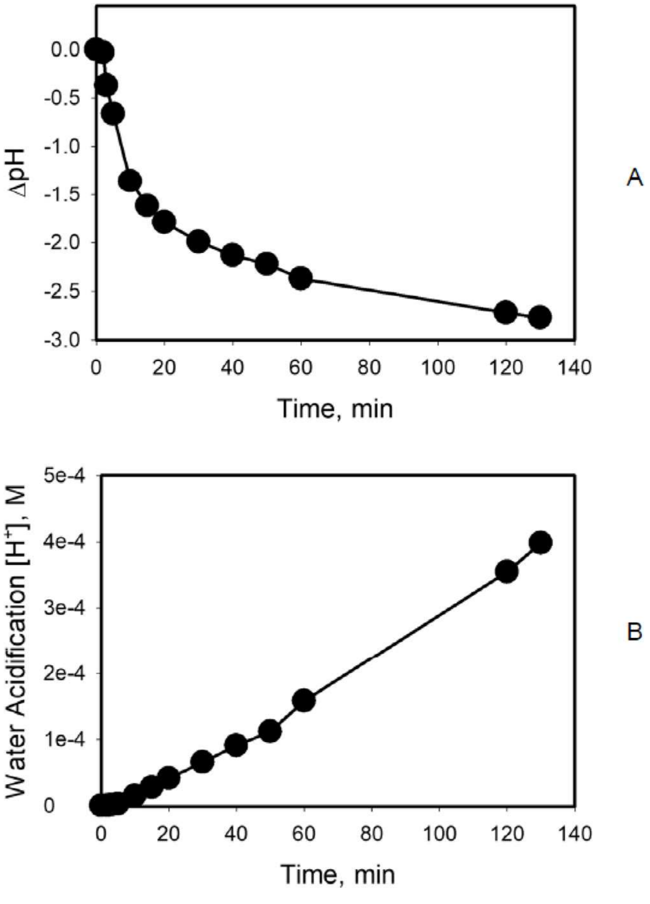

Fig. 7. Time dependence of water acidification during contact of cold atmospheric pressure plasma and air at the water surface with stirring of the aqueous phase. The volume of an aqueous phase was 20 mL. The diameter of the water surface was 15 mm. The interfacial ratio k is equal to 0.088 cm^{-1}. The temperature was 20 °C.

4. Discussion

4.1. Nitrogen fixation in nature, industry, and with cold plasma

Plants and some microorganisms can convert nitrate to amino acids and other reduced nitrogen-carbon compounds (Fig. 8). The reduction of nitrates by plants and bacteria to NH_4^+ is vital for maintaining the nitrogen cycle in nature.

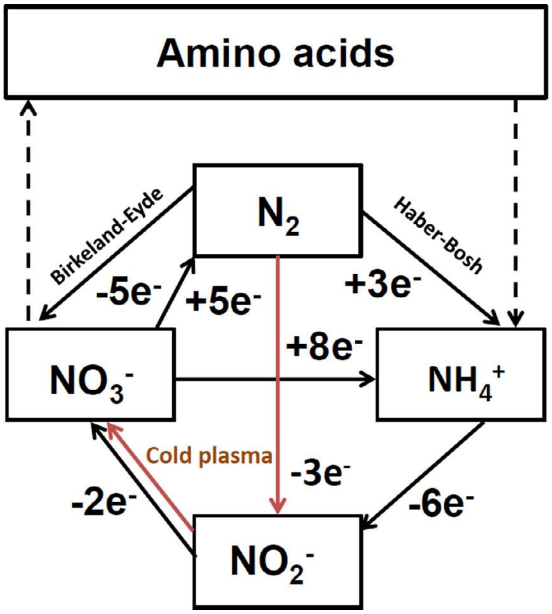

Fig. 8. Schematic diagram of atmospheric nitrogen fixation in nature, in industrial Birkeland-Eyde and Haber-Bosch processes, and in biomimetic process at plasma-air/water interface (red lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The industrial Haber-Bosch process of atmospheric nitrogen fixation N_2 (Fig. 8) requires extremely high temperatures and pressures:

$$\begin{aligned}&400^o - 500^oC,\ 20\,MPa\\&N_2 + 3H_2 \rightarrow 2NH_3\end{aligned} \tag{1}$$

Hydrogen in the Haber-Bosch process is produced by a multi-stage conversion of natural gas or coal, which leads to the formation of greenhouse gasses. The ammonia from the Haber process is then converted into HNO_3 in the Ostwald process:

$$\begin{aligned}&4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O\\&2NO + O_2 \rightarrow 2NO_2\\&3NO_2 + H_2O \rightarrow 2HNO_3 + NO\end{aligned} \tag{2}$$

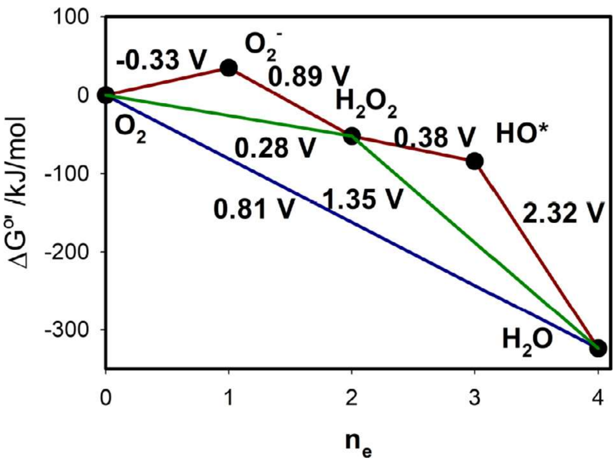

Fig. 9. Energy diagram for possible routes of oxygen reduction. ΔG°' is the standard Gibbs energy at pH 7.0 and n_e is the number of electrons transferred during redox reactions. Redox potentials were taken [18,33,34]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

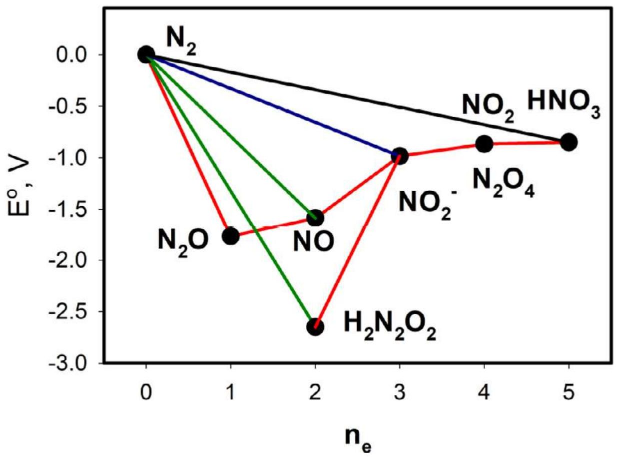

Fig. 10. Energy diagram for possible routes of nitrogen oxidation. E° is the standard redox potential and n_e is number of electrons transferred during redox reactions. Redox potentials were taken by Dean and Lange [33]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The Birkeland-Eyde process [5,6] of atmospheric nitrogen fixation uses electrical discharge at 3000 °C:

$$\begin{aligned} &N_2+O_2 \rightarrow 2NO \\ &2NO+O_2 \rightarrow 2NO_2 \\ &3NO_2+H_2O \rightarrow 2HNO_3+NO \end{aligned} \tag{3}$$

The oxidation of nitrogen by cold radio-frequency atmospheric pressure plasma at the plasma-air/water interface is an efficient multi-electron process on the surface of plasma activated water (Fig. 8, red lines).

4.2. Thermodynamics of multi-electron redox reactions induced by low temperature atmospheric pressure plasma

Thermodynamics of oxygen reduction, water oxidation, and redox reactions of hydrogen peroxide are shown in Fig. 9. The fact that the first electron addition to O_2 is an endothermic process accounts for the relative chemical inertness of oxygen in nature and permits the existence of life on Earth (Fig. 9). Possible multi-electron mechanisms of oxygen reduction and water oxidation are shown in Fig. 9 as a blue line (a synchronous 4-electron mechanism), green lines (synchronous 2-electron mechanisms), and red lines which show one-electron multistep redox reactions. A synchronous 4-electron mechanism is unlikely due to its extremely high energy of activation.

The thermodynamics of nitrogen redox reactions are shown in Fig. 10. Oxidation of nitrogen to nitric acid is a 5-electron process. Let's look at redox reactions of nitrogen and its oxides shown in Fig. 10. Oxidation of molecular nitrogen is an endothermic process and requires a significant amount of energy. Possible multi-electron mechanisms of nitrogen oxidation are shown in Fig. 10 as a black line (a synchronous 5-electron mechanism), green lines (synchronous 2-electron mechanisms), a blue line (synchronous 3-electron mechanism), and red lines which show one-electron multistep redox reactions.

Nitric acid is subject to thermal or light decomposition and thus was often stored in brown glass bottles:

$$4HNO_3 \rightarrow 2H_2O + 4NO_2+O_2 \tag{4}$$

$$3NO_2+H_2O \rightarrow 2HNO_3+NO \tag{5}$$

$$2NO_2+H_2O_2 \rightarrow 2HNO_3 \tag{6}$$

$$4NO_2(g)+O_2(g)+2H_2O(l) \rightarrow 4HNO_3(aq) \tag{7}$$

Due to the correlation between H^+ and NO_x^- production, the decreasing of pH in an aqueous phase can be caused by redox reactions (5)-(7).

Nitrous acid, HNO_2, is a weak and monobasic acid known only in solution, in the gas phase, and in the form of nitrite ($NO^-{}_2$) salts. In water, it can change quickly into nitric oxide and nitric acid:

$$3HNO_2 \rightarrow HNO_3+2NO+H_2O \tag{8}$$

Nitrous acid decomposes into nitric oxide and nitric acid. It can also react as either an oxidizing or reducing agent. Gaseous nitrous acid, which is rarely encountered, decomposes into nitrogen dioxide, nitric oxide, and water:

$$2HNO_2 \rightarrow NO_2+NO+H_2O \tag{9}$$

Nitrogen dioxide can disproportionate into nitric acid and nitrous acid in aqueous solution:

$$2NO_2+H_2O \rightarrow HNO_3+HNO_2 \tag{10}$$

A cold atmospheric pressure plasma jet produces RONS (Fig. 1) including ozone (Fig. 3) and nitric oxides. Ozone is one of the most powerful oxidizing agents and also oxidizes nitric oxide to nitrogen dioxide:

$$NO+O_3 \ \rightarrow NO_2 \ +O_2 \tag{11}$$

The NO_2 can be further oxidized:

$$NO_2 \ +O_3 \ \rightarrow NO_3 \ +O_2 \tag{12}$$

Peroxynitrite can be produced in aqueous solution as result of redox reactions

$$H_2O_2+NO_2{}^- \rightarrow ONOO^-+H_2O \tag{13}$$

or

$$*O_2{}^- + *NO \rightarrow ONOO^- \tag{14}$$

Peroxynitrous acid ONOOH has pK = 6.8 is unstable in aqueous solutions and can isomerize to nitric acid HNO_3 at low pH.

4.3. Interfacial acidification

A CAPPJ can induce different heterogeneous and homogenous reactions between oxygen, ozone, nitrogen, and water, which include production of HNO_x at the plasma-air/water interface as well as within the plasma-activated water. Among these reactions the most important are

$$N_2 + O_2 \rightarrow NO_x \tag{15}$$

$$4NO + 2H_2O + O_2 \rightarrow 4HNO_2 \rightarrow 4NO_2^- + 4H^+ \tag{16}$$

$$2HNO_2 + O_2 \rightarrow 2HNO_3 \rightarrow 2NO_3^- + 2H^+ \tag{17}$$

$$2NO + O_2 \rightarrow 2NO_2^- \tag{18}$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3 \rightarrow 4NO_3^- + 4H^+ \tag{19}$$

The plasma-induced acidification of water and the production of HNO_x and NO_x at room temperature is a newly demonstrated phenomenon, but the yield is currently too low for industrial use [1,28,29]. However, the process is advantageous as it does not require high temperatures and pressures, which denotes its future potential as a strong competitor for current industrial nitrification. This subtask will experimentally determine the rate of acidification of the electrolyte solution under a range of operating conditions. The results will determine the operating conditions to produce the optimal solution for the fixation of nitrogen.

Another possible process of acidification of an aqueous phase can be the oxidation of water. This process is sometimes called plasma electrolysis in literature [29]:

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \tag{20}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \tag{21}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{22}$$

Redox reactions (16), 17) and (19) – (22) can produce acidification of the aqueous phase.

4.4. Kinetics of multi-electron redox reactions

Cold plasma is a quasi-neutral mixture of electrons, ions, atoms, molecules, radicals, and UV–Vis photons in a highly non-equilibrium state. Plasma electrons, due to their small mass, are easily accelerated by external electric fields up to energies sufficient for ionization of neutral species and chemical reactions. In low-temperature plasmas, the heavy species such as ions and neutral molecules remain near room temperature while the electron temperature can reach values of thousands of degrees.

Cold plasma and the plasma-air/water interface can act as catalysts, promoting chemical reactions not possible under ordinary conditions in a homogeneous aqueous phase. These multi-electron chemical reactions become possible due to a highly non-equilibrium plasma state. Exploration of these unique catalytic properties of low-temperature plasmas leads to the understanding of heterogeneous chemical reactions at the plasma-air/water interface and the production of plasma-activated water (PAW).

Plasma behaves as a unique catalyst for chemical reactions, reducing the activation energy required to convert atmospheric nitrogen to forms useful for agriculture. Plasma-induced chemical reactions at the plasma/water interface between oxygen, nitrogen, electrons in plasma, hydrated electrons in water, He^+ cations, and water [12,35-41] include the production of HNO_3 and unstable intermediates such as HNO_2. The schematic diagram of the most probable mechanism of N_2 oxidation to HNO_3 at the plasma/water interface is shown in Fig. 11.

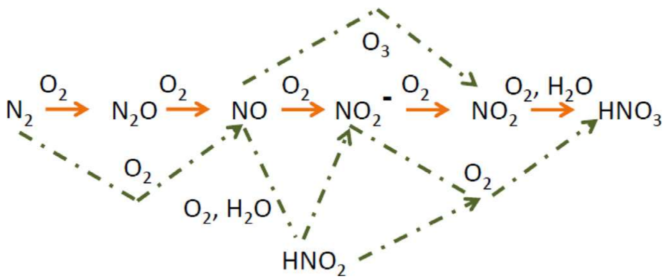

Fig. 11. Schematic diagram of molecular nitrogen oxidation to HNO_3 mechanisms at the plasma/water interface.

Soft interfaces have selective catalytic properties and can accelerate or inhibit interfacial charge transfer reactions due to electrostatic interfacial effects [22-25]. Thus, the kinetic parameters of interfacial charge transfer depend on the charge being transferred, the charges of reactants, their location in relation to the interface, as well as the dielectric properties of the media forming the fluid/liquid interface. The activation energy of electron transfer depends on the charges of the reactants and dielectric permittivity of each conducting phase [22-25].

A direct endothermic synchronous 5-electron reaction $N_2 \rightarrow HNO_3$ and synchronous 3-electron reaction $N_2 \rightarrow HNO_2$ (Fig. 11) are impossible due to very high energy activation and kinetic limitations [18,25]. An approximate calculation of the solvent reorganization energy during charge transfer in a homogeneous polar media such as an aqueous solution of electrolytes was first performed by Marcus [42]. Assuming that the distance h_{12} between the reactant centers of the reactant is much larger than their radii a and b, and that the reactants can be described as nonpolarizable spheres with charges rigidly and uniformly distributed over the surfaces, the expression for the reorganization energy is:

$$E_s = \frac{e_0^2 n^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2a} + \frac{1}{2b} - \frac{1}{h_{12}}\right) \tag{21}$$

where E_s is the energy of reorganization, n is the number of electrons, a and b are the radii of a donor and an acceptor of electrons, and h_{12} is the distance of a charge transfer. For homogeneous reactions in water, energies of reorganization and activations are proportional to n^2. For the 5-electron homogeneous reaction of nitrogen oxidation, the energy of activation is 25 times higher than for 1-electron reactions, which dramatically decreases the rate constant according to the Arrhenius equation. Multistep one-electron reactions of N_2 oxidation by plasma to HNO_3 (Fig. 11, red arrows) and synchronous 2-electron reactions (Fig. 11. green arrows) are possible thermodynamically and kinetically. The term *synchronous multi-electron* reaction does not mean that all n electrons started synchronously, since this is impossible according to quantum mechanics. Instead, each electron is transferred from donor to acceptors individually, but the time required for "intermediate" formation is much less than the time required for the reorganization of the medium so that "intermediates" as individual chemical compounds do not exist.

Conclusion

Molecular nitrogen can be oxidized to nitrogen compounds at room temperature with cold atmospheric pressure radiofrequency plasma. Redox reactions induced by cold plasma occur at the plasma/water and plasma/air interfaces, but also in the volume of the aqueous phase.

Analysis of the images (Figs. 5, 6) which displayed the presence of pH indicators Bromocresol Purple, Methyl Red, Universal Indicator, and pH Test Indicator showed that redox reactions of acidification of the aqueous phase occur at the plasma-air/water interface and the products of multielectron electrochemical reactions slowly diffuse into the bulk of the aqueous solution. It follows from Fig. 5 that in the absence of stirring of the aqueous phase, acid is formed at the plasma/water interface.

An increase in the surface area to volume of the aqueous phase ratio can increase the yield of interfacial HNO_3 synthesis. It will be interesting to check if molybdenum and iron-containing compounds can accelerate nitrogen fixation as in the nitrogenase complex of nitrogen-fixing bacteria. In addition to gaseous nitrogen oxidation by cold plasma in air, we also explored nitrification in aqueous solutions and found the molecular mechanisms responsible for these multielectron processes. Acidification of an aqueous solution during CAPPJ treatment correlates with an increase in HNO_x concentration in the aqueous phase. A co-product HNO_2 is unstable and can be oxidized to HNO_3 by hydrogen peroxide or ozone [43]. A slightly acidic aqueous solution can stabilize a hydrogen peroxide concentration for a prolonged period of time. Plasma-induced production of HNO_3 at the plasma/water interface at low temperature and atmospheric pressure can be used in the industry for nitrogen fixation, production of nitrogen compounds, fertilizers, and to replace the expensive Birkelaud-Eyde, Haber-Bosch, and Ostwald processes if the yield of nitric acid will be increased in the presence of additional catalysts.

Plasma activated water can be used in medicine for disinfection, sterilization, and decontamination due to a combination of antibacterial and antiviral properties of H_2O_2, nitrogen species NO_x, and acidic pH. PAW can also be used in the food industry for disinfection without the side effects of UV radiation and toxic radicals.

Ethics declaration

The authors declare no competing interests.

Declaration of Competing Interest

The authors declare no competing interests.

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Contributions

A. G. V. conceived the idea, analyzed the data, and participated in manuscript writing. All authors provided the data and edited the manuscript.

Data availability

The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

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