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GASEOUS AND AQUEOUS REACTIVE OXYGEN AND NITROGEN SPECIES OF AIR PLASMAS WITH WATER

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The need of control and tunability of the chemical composition and biomedical effects of plasma activated water/media (PAW/PAM) is emerging for applications in biomedicine and agriculture. We compare two non-thermal air plasma sources: streamer corona and transient spark, interacting with water in open and closed reactors and enhance the plasma-liquid interaction by water electrospray through these discharges. We demonstrate that the plasma gaseous products strongly depend on the discharge regime, its deposited power and gas flow conditions. The gaseous products then determine the chemical properties of the PAW and the dominant aqueous reactive oxygen and nitrogen species (RONS). Transient spark produces higher concentrations of gaseous and aqueous RONS and induces stronger antibacterial effects than streamer corona.

1. Introduction

Non-thermal plasmas generated by electrical discharges in atmospheric pressure air are sources of various reactive species. When generated in contact with water, they enable the transfer of reactive oxygen and nitrogen species (RONS) formed in the gas-phase plasma into the water or aqueous solutions and so generate the *plasma activated water* (PAW). PAW is typically a strong antibacterial agent and besides multiple uses in medicine for disinfection it has the potential for food processing or agriculture applications. [1-6]

We prepare PAW by a DC-driven streamer corona (SC) and transient spark (TS) discharges operated in air with water electrospray. The production of active species (e.g. O_3, NO, NO_2 and OH) in the gas and consequently the PAW properties can be controlled by the discharge regime and gas-flow and liquid-flow parameters. In low power air corona discharge, water electrospray increased O_3 production, which enhanced the biocidal effects. In the higher power TS, dominant gaseous products are NO_x that lead to significant NO_2^- and NO_3^- in the PAW and practically no O_3. The bactericidal action is then mainly due to the synergy of H_2O_2, NO_2^- and acidic milieu (via ONOOH formation) and typically decays in time within several hours post plasma activation, depending on temperature and pH [4.7]. The controlled and selective generation of RONS using air plasmas with water will facilitate targeted applications of cold plasmas and PAW to various fields including disinfection and antimicrobial applications, food processing, agriculture, and even cancer therapies, where the roles of different key reactive species on cancer cell biochemistry is particularly delicate [6,8].

2. Experiment

DC-driven streamer corona and transient spark discharges in positive polarity were generated in point-to-plane configuration in ambient air at atmospheric pressure. Positive streamer corona and transient spark discharge regimes used here has been described in more details in [9-10]. Figure 1 shows a schematic of the set-up used for water electrospray through SC or TS discharge.

We used a high voltage (HV) hollow needle anode opposite to the metallic (stainless steel) grounded mesh cathode. The inter-electrode spacing between the needle and the mesh was kept at 10 mm. A positive high voltage was applied from the power supply *Technix SR20-R-1200* through the ballast resistor *R* (20 MΩ for SC or 10 MΩ for TS). The discharge voltage was measured by the HV probe *Tektronix P6015A* and the discharge current was measured as a voltage drop across 50 or 1.2 Ω resistors for SC and TS, respectively. The electrical parameters were processed and recorded during the experiments by a 200 MHz oscilloscope *Tektronix TDS 2024C*. Typical current and voltage waveforms and other discharge characteristics of SC and TS discharge with water electrospray or water cathode, were documented in detail in our previous publications [3,4,9,10]. Both TS and SC can be operated in the same versatile setup with the same HV power supply, which represents an advantage for practical applications. Both discharges were combined with water electrospray that enabled the

water flow with various flow rates in the range 0.01-1 mL/min by the syringe pump *New Era Pump Systems NE-300* directly through the high-voltage needle electrode into the active discharge region, where it was sprayed to micrometric droplets. The interaction of plasma with water droplets allows for very efficient mass transfer of plasma-generated active species into water [3-4].
Besides operating in the open ambient air reactor, we operated the same plasma discharges in a closed reactor (50 mL volume) with a defined low air flow rate (0.5 L/min). This air flow rate determines the gas mixing and accumulation of species produced by the plasma.
Gaseous NO and NO_2 concentrations were measured online by electrochemical gas sensors *Membrapor NO2/S-1000* and *NO/SF-1000* (resolution 5 ppm, 0-1000 ppm). Fourier transform infrared (FTIR) absorption spectrophotometer *Shimadzu IRAffinity-1S* was used for the detection of gaseous nitrogen oxides NO, NO_2 and N_2O; nitric and nitrous acids HNO_3, HNO_2, and ozone O_3 with the resolution 1 cm^{-1} inside a 10 cm long gas cell. Ozone concentrations were measured by UV absorption using 253.8 nm mercury lamp and the compact fiber optic spectrometer *OceanOptics SD2000*, employing the Lambert-Beer law with the absorption cross section 1.14×10^{-21} m^2 [11] in a 12.5 cm gas cell.
The detection of aqueous RONS in the PAW is challenging due to the chemical instability of the detected RONS and possible cross-reactivities of the used analytical methods. We tested and adapted colorimetric methods for special PAW conditions, such as colorimetric detection of H_2O_2 by $TiOSO_4$ reagent, NO_2^- and NO_3^- by Griess reagents, and O_3 by indigo blue dye [12]. Here we focus on the detection of RONS formation induced by air plasma gas-liquid chemistry in PAW, namely to H_2O_2, NO_2^- and NO_3^-, and dissolved O_3 produced in PAW by the two discharges.

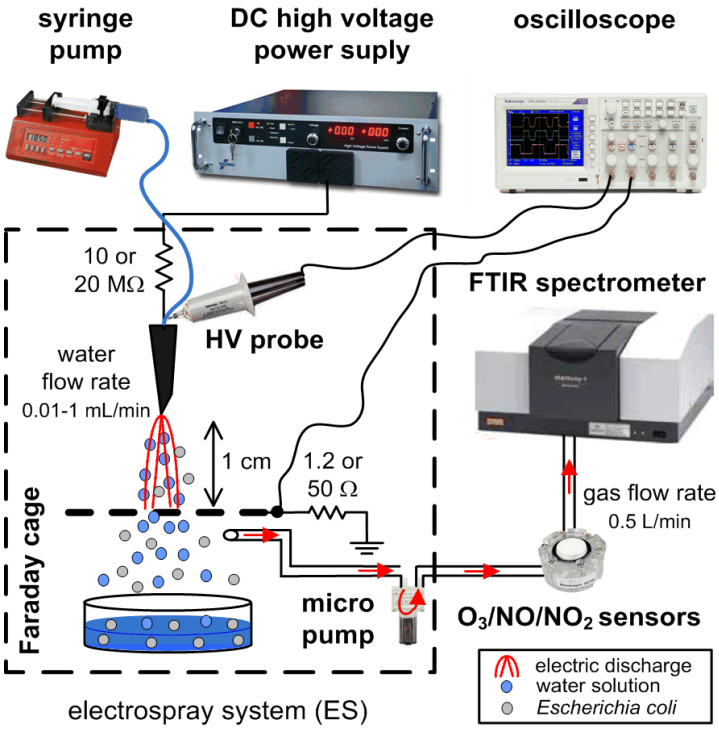


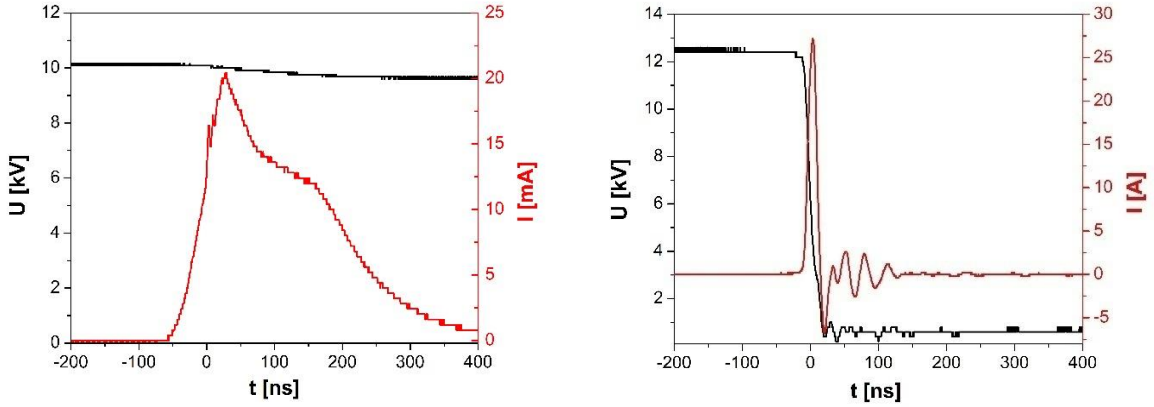
Fig. 1. Schematic of the set-up used for water activation by electrospray through streamer corona or transient spark discharges and gas diagnostics.

3. Results and discussion

Both discharges used in this study are driven by DC high voltage but are self-pulsing. Their typical characteristics are:

***Streamer corona (SC)*:** the mean power 0.2-0.4 W, the pulse repetition frequency ~10 kHz, operated with water electrospray (ES) flow rates 0.01-0.5 mL/min. The typical voltage and current pulse waveforms of SC-ES are depicted in Fig. 2a.

***Transient spark (TS)*:** the mean power 1.5-2.3 W, the typical pulse repetition frequency ~1 kHz, the typical pulse duration ~25 ns. TS was operated with water electrospray flow rates 0.5-1 mL/min. The typical voltage and current pulse waveforms of TS-ES are depicted in Fig. 2b.



a) b)

Fig. 2. The typical voltage and current pulse waveforms of SC (a) and TS (b) with water electrospray.

In air SC, both O_3 and NO_x are produced [13]. Similar to air surface DBDs, low power discharge leads dominantly to O_3 production, while higher power discharges increase the gas temperature which promotes NO_x production and the thermal depletion of O_3 combined with the chemical decay of O_3 by fast reaction with NO. In addition to O_3 and NO_x gaseous products, water vapors in air significantly influence the plasma induced gas-phase chemistry, especially thanks to highly reactive hydroxyl (•OH) radicals. We detected lower concentrations of the gas phase NO, NO_2 and O_3 in humid air compared to the dry air. When the discharges are operated with water electrospray, there is a strong water evaporation and humidification of the air, which enhanced the •OH formation. Moreover, the transport of NO, NO_2, O_3, and other species such as HNO_2 into the bulk water, i.e. their solvation driven by the Henry's law equilibria, also decrease NO, NO_2 and O_3 concentrations in the gas phase.

The water electrospray improves the gas-liquid transport of the gaseous NO_x into the liquid resulting in NO_x dissolution in the water. NO formation in SC-ES was considerably lower compared to TS-ES due to the much lower power. NO_2 formation in general increased with the discharge power in all systems and SC generated considerably lower NO_2 due to the lower discharge power.

Comparison of the NO, NO_2 and gaseous O_3 concentrations produced by TS and SC, without and with ES, in open and closed systems together is shown in fig. 3. Apparently, the closed reactor resulted in considerably higher (~1 order of magnitude) concentrations of all measured species for both TS and SC. The closed reactor with a slow air flow rate enables accumulation of species, whereas immediate dilution of species with the surrounding ambient air occurs in the open reactor.

It is clear that SC in all systems generated lower NO and NO_2 (due to its lower power) but higher O_3 concentrations than TS. SC corresponds well to the low power ozone mode and TS to the high power NO_x mode of the surface air DBD described by [14]. O_3 was completely absent in our NO_x-dominated TS without water and in TS or TS-ES in the closed reactor.

SC in the closed reactor produced negligible NO concentrations, lower than in the open reactor. At the same time, there was considerably more O_3 produced by SC in the closed reactor. The reaction of NO oxidation by O_3 probably depleted most of the generated NO that was oxidized to NO_2, while the excess O_3 remained in the gas. Detailed gas-phase air plasma chemistry is described in [9].

Both air discharges, SC and TS, with water electrospray treatment in both open and closed reactors were tested and by this way prepared the plasma activated water (PAW). We focused on the detection of long-lived aqueous RONS produced in PAW, namely H_2O_2, NO_2^- and NO_3^-, and dissolved O_3. Clearly, the aqueous RONS concentrations are related to the plasma formed gaseous RONS.

Aqueous $H_2O_2(aq)$ is produced by extremely fast dissolution of gaseous $H_2O_2(g)$ formed in the gas. The Henry's law solubility coefficient of H_2O_2 ($k_H \approx 9x10^2$ mol.m^{-3}.Pa^{-1}) is about 7 orders of magnitude larger than that of NO or NO_2 or O_3 [46], thus all $H_2O_2(g)$ readily transfers into $H_2O_2(aq)$ through the gas-liquid interface. Nitrites NO_2^- and nitrates NO_3^- are generated in the PAW from the dissolved gas-

eous NO and NO_2 [10,24,62]. The solubility coefficients of NO or NO_2 are much smaller than that of H_2O_2 [15], thus NO(g) and NO_2(g) would not readily transfer into water to form NO_2^-(aq) and NO_3^-(aq). Enhancement of NO_x dissolution by increasing the surface area of the plasma-liquid interface by spraying water into fine droplets in the ES system is helpful. Since protons H^+ are released in the PAW by the above reactions, acidic pH is typical for PAW prepared by air plasmas.
The reaction between H_2O_2 and NO_2^- occurs under acidic PAW conditions and leads to the formation of peroxynitrites (peroxynitrous acid) [4,7,12]:

$$NO_2^- + H_2O_2 + H^+ \rightarrow O=NOOH + H_2O \quad (1)$$

ONOOH then decomposes at acidic pH to •OH and •NO_2 radicals [7,12]:

$$O=NOOH \leftrightarrow {}^{\cdot}OH + NO_2^{\cdot} \quad (2)$$

Fig. 4 shows the measured concentrations of H_2O_2, NO_2^-, NO_3^- in PAW and corresponding pH for TS and SC with water ES in the open and closed reactor. The low power SC generates less H_2O_2 and much less NO_2^-+ NO_3^-. The higher power TS generates both H_2O_2 and NO_2^- + NO_3^-, with the ratio of H_2O_2/NO_2^- approximately 2 in the open system. On the other hand, after TS water activation in the closed system, much less H_2O_2 and much more NO_2^- and particularly high NO_3^- were detected, which resulted in very acidic pH (2.4). In such case, the antibacterial effects might have been enhanced.
NO_2^- was higher in TS than SC, and mostly increased with energy density per water volume. Closed TS resulted in very high NO_2^- and NO_3^-. SC in the closed reactor also generated high NO_3^- (yet lower than TS-ES closed) at pH 3.1, while very low NO_2^-. This might be possibly due to the NO_2^- depletion with ozone.

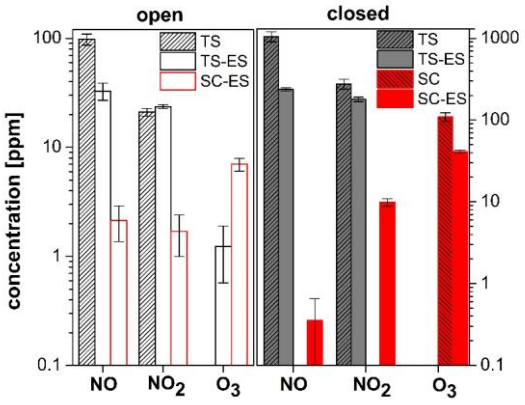


Fig. 3. Gaseous NO, NO_2 and O_3 concentrations generated by TS and SC discharges, without and with water ES, in the open and closed (50 mL, 0.5 L/min air flow) reactors. Logarithmic scale. Statistical mean values with standard error of the mean.

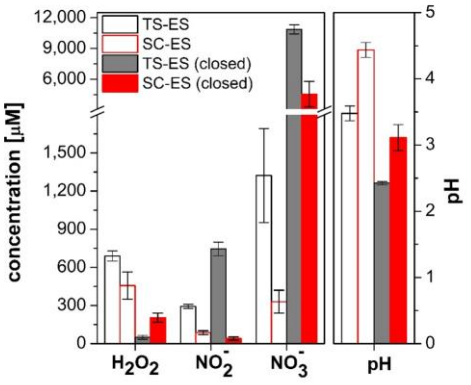


Fig. 4. Concentrations of aqueous H_2O_2, NO_2^-, NO_3^- in PAW and corresponding pH for TS and SC with water ES, in the open and closed reactor. Statistical mean values with standard error of the mean.

H_2O_2 is dominantly formed from •OH radicals in the gas and solvates extremely. We should note that in the ES, there is a good gas-liquid mixing that might enhance the aqueous peroxynitrite chemistry (Equations 1 and 2), which would then faster deplete the produced H_2O_2(aq). The measured H_2O_2(aq) concentrations after treatment may be then lower with respect to the H_2O_2(aq) really produced during the plasma-water interaction. NO_3^- were higher for TS than SC, which can be certainly related with considerably higher gaseous NO and NO_2 production in the TS (Fig. 5).
O_3(aq) concentrations in PAW increased as a function of energy density in the open reactor with SC-ES. Dissolved ozone concentrations O_3(aq) in PAW were detected with at least some degree of reliability in SC. There was almost negligible gaseous O_3 detected in TS, and consequently undetectable O_3 dissolved in PAW either.

4. Conclusions

The potential use of plasma activated water and liquids is constantly growing in various biomedical and agriculture applications. The PAW chemical properties and effects strongly depend on the plasma sources and discharge regimes used and their interaction with water. We compared two non-thermal atmospheric plasma sources operating in air and interacting with water: a lower power streamer corona (SC, 0.4 W) and a higher power transient spark (TS, 2 W). We analyzed their gaseous and aqueous RONS in the air and the PAW. Water was activated in the electrospray system (ES) with fine aerosol droplets sprayed through the plasma zone. We also compared the open air and closed small volume reactor at different air flow rates to understand the effects of reactor volume and air flow rate on the gaseous and aqueous chemistry.

Both SC and TS represent inexpensive and easy to operate nonequilibrium air plasma sources that can be run in the same versatile setup. Switching between them can be easily managed by changing the resistor in the circuit. Each of these discharge regimes generates air plasma of different properties that results in different gaseous products: dominated by O_3 in lower power SC and NO_x in higher power TS. The gaseous products, their production rates and solvation determine the aqueous RONS in the activated water, which then control the antibacterial effects of such PAW. Gas flow conditions in the reactor strongly influence gaseous and aqueous RONS production. We applied water electrospray through the discharges as the efficient method of the transfer of the plasma gaseous species into the PAW. Other ways of water interaction with air plasmas can lead to different transfer mechanisms of some species (especially those with low solubility), which may influence the aqueous chemistry and antibacterial effects and will be a subject of our future study.

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