ISPC 24

24TH INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY
NAPLES (ITALY) JUNE 9-14, 2019

Final Program

Naples

ISPC 24

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INVITED SPEAKERS

Igor Adamovich
The Ohio State University, Columbus (U.S.A.)
Topic 1: Fundamentals, diagnostics and modelling in plasma chemistry
Electric field measurements in atmospheric pressure plasmas used for plasma-assisted combustion and plasma flow control applications

Julia Bandow
Ruhr-Universität Bochum, Bochum (Germany)
Topic 7: Plasma medicine and plasma agriculture
Plasma meets biotechnology – coupling plasma and enzymatic reactions

Cristina Canal
Universitat Politècnica de Catalunya, Barcelona (Spain)
Topic 7: Plasma medicine and plasma agriculture
Potential of hydrogels and liquids in plasma therapy of osteosarcoma

Maria Adriana Creatore
Technische Universiteit Eindhoven, Eindhoven (The Netherlands)
Topic 4: Plasma deposition of functional coatings and treatment of inorganic and organic materials
Plasma-assisted atomic layer deposition of highly conductive HfNx layers

Uros Cvelbar
Jožef Stefan Institute, Ljubljana (Slovenia)
Topic 3: Plasma processing of nanomaterials and nanostructures: synthesis, modification and nanofabrication
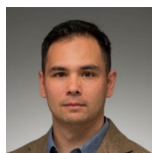*On the quest for deterministic approach to plasma synthesis and conversion of nanowires*

Richard Engeln
Technische Universiteit Eindhoven, Eindhoven (The Netherlands)
Topic 1: Fundamentals, diagnostics and modelling in plasma chemistry
Vibrational kinetics of CO2 in non-thermal plasma

David Go
University of Notre Dame, South Bend (U.S.A.)
Topic 6: Plasma-assisted conversion, combustion, propulsion and aerodynamics
Rethinking the design of catalysts for plasma-catalysis systems

Vasco Guerra
Universidade de Lisboa, Lisboa (Portugal)
Topic 1: Fundamentals, diagnostics and modelling in plasma chemistry
CO_2 plasmas: from solar fuels to oxygen production on Mars

Yuzuru Ikehara
Chiba University, Chiba (Japan)
Topic 7: Plasma medicine and plasma agriculture
Low temperature plasma treatment is a new tissue processing technology: plasma induced blood coagulation limits the excessive host immunological responses

Mark J. Kushner
University of Michigan, Ann Arbor (U.S.A.)
Topic 10: Plasmas for environmental applications and resource recovery
Chemical Conversion in Atmospheric Pressure Plasmas Sustained in Packed Bed Reactors

Zdenko Machala
Comenius University, Bratislava (Slovakia)
Topic 9: Plasma in and in contact with liquids
Plasma activated water chemical and antibacterial effects correlate with gaseous and aqueous RONS, plasma source, and air and water flow conditions

Diego Mantovani
Laval University, Québec (Canada)
Topic 8: Plasma treatment of biomaterials
Direct functionalization of metals by low-pressure plasma improves the clinical performances of coronary stents: From surface modification to in vitro and in vivo validation

Ester Marotta
Università degli Studi di Padova, Padova (Italy)
Topic 10: Plasmas for environmental applications and resource recovery
New mechanistic insight in plasma based water treatments

Plasma activated water chemical and antibacterial effects correlate with gaseous and aqueous RONS, plasma source, air and water flow conditions

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Abstract: Control and tunability of the chemical composition and biomedical effects of plasma activated water/media for emerging applications in biomedicine and agriculture is possible by controlling the discharge regime, deposited power, plasma-liquid interface area, and gas flow conditions. We compare gaseous and aqueous RONS of two cold air plasma sources: streamer corona and transient spark, interacting with water in open and closed reactors with water electrospray through these discharges or in water batch treatment.

Keywords: Cold air plasma, plasma activated water, reactive oxygen and nitrogen species

1. Introduction

Non-thermal plasmas generated by electrical discharges in atmospheric pressure air are sources of various *reactive oxygen and nitrogen species (RONS)*. When generated in contact with water, they enable the transfer of 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/without 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, O_3 production probably results in enhanced antibacterial effects. In the higher power TS; the dominant gaseous products are NO_x that lead to significant NO_2^- and NO_3^- in the PAW and practically no O_3. The antibacterial 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. Experimental set-up and methods

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 or batch treatment with SC or TS discharge.

We used a high voltage (HV) hollow needle anode opposite to the metallic (stainless steel) grounded mesh or bulk water surface cathode. The inter-electrode spacing between the needle and the mesh (water surface) 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 run either with water electrospray (ES) 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; or the discharge hit directly the water surface with a submerged grounded cathode in the batch system (BS).

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 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.
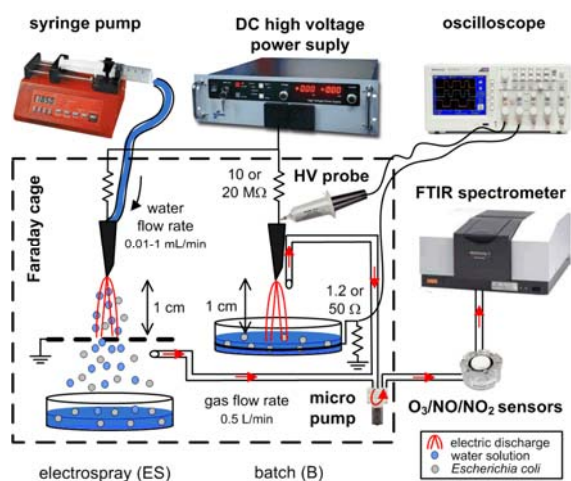

Fig. 1. Schematic diagram of the set-up used for water activation by electrospray or batch treatment through air streamer corona or transient spark discharges and gaseous diagnostics.

Bacterial suspensions of planktonic *Escherichia coli ATCC25922* with initial concentration $\sim 10^7$ CFU/mL were prepared. We treated bacterial suspension directly by TS/SC with water ES or in BS. The bacterial inactivation was evaluated by classic thermostatic cultivation on Petri dishes with LB agar.

3. Results and discussion

Air discharges

Both discharges used in this study are DC driven, but 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 and typical voltage ~ 10 kV and current pulses ~ 20-30 mA of 100-200 ns duration.

Transient spark (TS): the mean power 1.5-2.3 W, the typical pulse repetition frequency ~ 1 kHz, the typical current pulse amplitude 25 A and duration ~ 25 ns without water. The current pulses were similar for TS operated with water electrospray flow rates 0.5-1 mL/min. In the

batch treatment, the current pulses were of lower amplitude ~ 2.2 A but longer ~ 200 ns due to the additional resistance in the circuit imposed by the liquid.
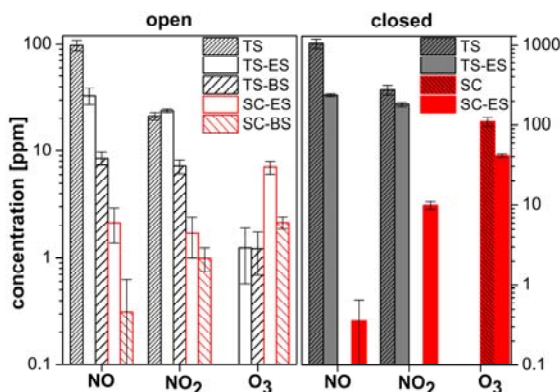
Gaseous RONS in air

Fig. 2. Gaseous NO, NO$_2$ and O$_3$ concentrations generated by TS and SC discharges, without and with water ES and in water BS, 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.

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 air discharges with water 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. In the batch system, especially with SC discharge, the ionic wind enhanced the RONS transfer into the liquid, despite its significantly lower surface to volume ratio (if compared with ES). NO formation in SC-ES was considerably lower compared to TS-ES due to the much lower delivered 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 and in BS, in open and closed systems together is shown in Fig. 2. 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 enabled 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 the 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 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].
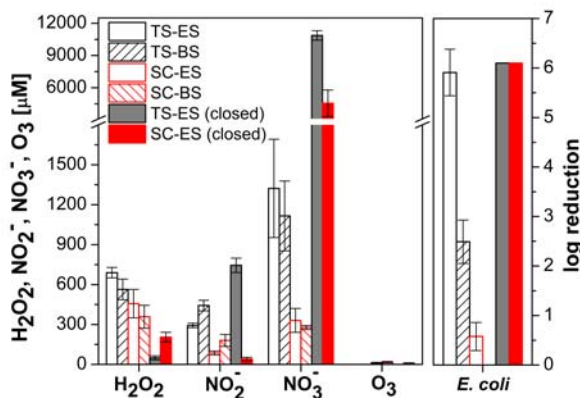
Aqueous RONS in PAW

Fig. 3. Concentrations of aqueous H_2O_2, NO_2^-, NO_3^- in PAW and corresponding pH for TS and SC with water ES and in BS, in the open and closed reactor. Statistical mean values with standard error of the mean.

Both air discharges, SC and TS, with water electrospray or in batch 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, shown in Fig. 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 ($k_H \approx 9 \times 10^2$ $mol.m^{-3}.Pa^{-1}$) 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 gaseous 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~3.3 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]:

$$NO_2^- + H_2O_2 + H^+ \rightarrow O=NOOH + H_2O \qquad (1)$$
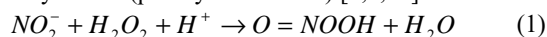
ONOOH then decomposes at acidic pH to $^\bullet OH$ and $^\bullet NO_2$ radicals [7,12]:

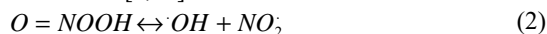$$O=NOOH \leftrightarrow {^\bullet OH} + NO_2^\bullet \qquad (2)$$

Fig. 3 shows the measured concentrations of H_2O_2, NO_2^-, NO_3^- in PAW and corresponding antibacterial effect for TS and SC with water ES or in BS 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.

H_2O_2 is dominantly formed from $^\bullet OH$ 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 (Eq. 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. Higher NO_3^- were reached in TS than SC, which can be certainly related with considerably higher gaseous NO and NO_2 production in TS (Fig. 2).

$O_3(aq)$ 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 in SC. There was almost negligible gaseous O_3 detected in TS, and consequently undetectable O_3 dissolved in PAW either.

4. Summary

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, discharge regimes 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 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 or in water batch system (BS) where ionic wind plays a role. 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 and solvation rates determine the aqueous RONS in the activated water, which then control the antibacterial effects of such PAW. Gas flow conditions in the reactor, as well as the type of interaction with water (electrospray vs. batch) strongly influence gaseous and aqueous RONS production. The water electrospray through the discharges is more efficient to transfer 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 are being subjected to our future studies.

5. Acknowledgement

6. References

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