Diagnostics and biomedical applications of radiofrequency plasmas

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Abstract. In this paper we present spatial profiles of ion and atomic oxygen concentrations in a large scale cylindrical 13.56 MHz capacitively coupled plasma low pressure reactor suitable for indirect biomedical applications (like treatment of textile to increase antibacterial properties) and direct (treatment of seeds of rare and protected species). Such reactor can easily be used for the sterilization of medical instruments by removing bacteria, spores, prions and fungi as well. We also discuss electrical properties of the system based on the signals obtained by the derivative probes and show the light emission profiles close to the sample platform. In the case of seeds treatment, the desired effect is to plasma etch the outer shell of the seed which will lead to the easier nutrition and therefore increase of the germination. In the case of textile treatment the functionalization is done by bounding atomic oxygen to the surface. It appears that antibacterial properties of the textile are increased by incorporating nanoparticles to the fibres which can successfully be done after the plasma treatment. From these two examples it is obvious that the balance of ion and atomic oxygen concentrations as well as proper choice of ion energy and power delivered to the plasma direct the nature of the plasma treatment.

1. Introduction
Non-thermal plasmas are widely used in many industrial processes due to high and controllable chemical reactivity at low gas temperatures [1, 2]. This enables treatment of sensitive materials like cells, polymers, textile and seeds [3, 4, 5, 6, 7, 8]. It is much easier to achieve non-equilibrium conditions at low pressure compared to atmospheric pressure (due to lower ionization growth) and uniformity over the large volumes [9]. Of course, this comes at the cost of using a pumping system and not being able to apply plasma directly to patients.

The specifics of material that we wanted to treat with plasma led us to develop a large scale, low-cost reactor of simple design. Sensitive materials like textile and seeds were treated in air plasma [10, 11]. After the treatment of textile, the surface became hydrophilic leading to increased wettability and therefore easier dying of the samples. Plasma treatment also makes it possible to incorporate nanoparticles like that of silver or TiO₂ which increases antibacterial properties of the textile [3, 4]. Plasma treated textile can be used in hospitals, surgery, military, food production facilities to lower the chance of bacterial infections. In the case of seeds, plasma improves the nutrition of the seeds by etching the outer shell. In nature it is done mechanically, usually by the birds and it also can be done chemically. Nevertheless, plasma shows good results in increasing the seeds germination which is especially important for the rare and protected species. Similar effects can be achieved with the atmospheric pressure plasma [12] but the advantage of a low pressure plasma reactor is the uniform
covering of large treatment area. Damaging or even destruction of the seeds is inevitable if the plasma is too aggressive so the proper optimization of the discharge parameters is necessary.

In this paper we will discuss plasma properties of the asymmetric cylindrical reactor and discuss characteristic features introduced by using such geometry. Ion and atomic oxygen concentrations were radially measured using Langmuir and catalytic probes. Development of plasma light emission was recorded using ICCD camera. Derivative probes that we have used to measure the power delivered to the plasma can be used for all sources in the MHz range regardless of the operating pressure (low or atmospheric). Finally, plasma influence to the germination of Gentiana asclepiadea L. seeds will be shown.

2. Experimental setup

The discharge is developed in a cylindrical vessel made of stainless steel, 2.5 m long and 1.17 m in diameter. The powered electrode made of aluminium (1.5 m long) is placed axially in the chamber. The reactor is powered at 13.56 MHz using a Dressler Cesar 1310 together with Variomatch matching network. The chamber wall is grounded. Low pressure is maintained using a mechanical pump.

The samples are placed beneath the powered electrode on a platform which can be moved closer or away from the electrode. Derivative probes are placed as close as possible to the powered electrode as shown at Figure 1. The signals form the probes are collected using an oscilloscope and a PC and then processed [13, 14].

![Experimental setup diagram](image)

Figure 1. Experimental setup.

Radial profiles of ion and atomic oxygen concentrations are recorded using Langmuir probe (Hiden ESPION) and a nickel catalytic probe [15, 16, 17] respectively. ICCD camera (Andor iStar DH720-18U-03) placed end on to the sample platform was used to record the light emission in the vicinity at the location where sample are to be placed.
3. Plasma diagnostics

3.1. Electrical properties

Signals from the derivative probes were recorded for the range of pressures from 100 to 800 mTorr and the results are presented at Figure 2. The working gas was air.

![Figure 2. Current a) and voltage b) signals obtained by derivative probes in air at 100, 200, 400, 600 and 800 mTorr. RF generator power was 200 W.](image)

We can see that the shape of both current and voltage are influenced by the working pressure. With the increase of the pressure, the amplitudes of current signals are decreasing and starting to be sine-like. At low pressures the voltage signals are less distorted compared to the current signals. Their shape is changing from the triangle-like to the sine-like when increasing the pressure.

The changes of current and voltage with pressure lead to the change in the power calculated as the integral of their product as shown at Figure 3. We can see that the power transmitted to the plasma is actually higher than 75% in all cases. At 600 mTorr this percent is even higher meaning that the power transfer efficiency is slightly higher compared to 100 mTorr.

![Figure 3. Average power delivered to the plasma at 100 and 600 mTorr.](image)

Measuring of the power delivered to the plasma represents a good parameter for characterizing the treatment procedures and insures its reproducibility. Derivative probes are capable of measuring small powers (less than 1 W) achieving good accuracy of 0.1 W.
3.2. Light emission profiles

Light emission profiles were recorded using ICCD camera placed end-on to the sample platform underneath the powered electrode (see the top picture at Figure 4.). The generator power was increased from 20 to 400 W. The maximum intensity is moving towards the platform, more intensive light emission starts to develop across the surface of the platform where samples are to be placed.

![Light emission profile](image)

**Figure 4.** Light emission profile recorded end-on to the sample platform. The gas was air at 100 mTorr.

For smaller powers, after the plasma ignition, light emission intensity is maximal around the powered electrode. With the power increase emission intensity is also increasing around the powered electrode, but at the same time another region of increased intensity can be observed between the powered electrode and sample platform (Fig. 4. - 100W). With further increase in power, the maximum of emission moves towards the sample platform and for powers higher than 200 W the emission is centered on the platform. The light emission is uniform across the large area of the platform for high powers.

3.3. Ion and atomic oxygen concentrations

As mentioned before in the text, the nature of the treatment is strongly dependent on the choice of plasma parameters where concentrations of ions and reactive atomic oxygen represent one of the key players for many of the biomedical applications. Radial profiles were investigated using Langmuir and catalytic probes for the discharge in air by placing the probes on several distances from the powered electrode.

Figure 5. shows the results of ion concentrations which are of the order of $10^{15} \text{ m}^{-3}$ to $10^{16} \text{ m}^{-3}$. The measurements are made close to the grounded chamber wall (50.5 cm from the powered electrode), at 20.5 cm from the powered electrode and in-between at 35.5 cm. With the increase of rms voltage (by increasing the power given by the generator) the concentrations increase but the changes are much less pronounced compared to the changes introduced by moving the probes closer to the electrode.
This leads to the conclusion that a specific value of ion concentration can be achieved either by increasing the power or by moving closer to the electrode. The results also show that it is more practical to obtain higher concentrations by adjusting the distance of the treated sample than to increase the power.

The last conclusions can also be made for the atomic oxygen concentrations. These concentrations are of the order of $10^{19}$ m$^{-3}$ which is less than in the ICP reactors by 1 to 2 orders of magnitude [18, 19].
We can see that the concentrations are decreasing when moving towards the stainless steel wall which also recombines atomic oxygen and contributes to its loss term. At higher pressure the concentrations are higher as expected.

3.4. Biomedical application
Here we present the effects of the plasma to the germination of the *Gentiana asclepiadea* L. (see Figure 7.). The seeds were treated in air plasma at 200 mTorr for the generator power of 100 W. Depending on the treatment time the germination can be increased but if the treatment is too long, the seeds are damaged and the germination is decreased (20 min exposure).

![Figure 7](image)

**Figure 7.** Effects of the plasma to the germination of the *Gentiana asclepiadea* L. seeds.

4. Conclusions
We have shown the properties of the low pressure cold plasma capable of indirect (textile treatment) and direct (seeds treatment) biomedical applications. Antibacterial properties of textile and increased germination of seeds are accomplished due to the functionalization of fiber surface by oxygen atoms and then incorporating the nanoparticles and plasma etching of the seed outer shell, respectively [3, 4, 6]. The advantages of cylindrical geometry of the reactor are shown by presenting the ion and atomic oxygen concentrations at different distances from the powered electrode making it possible to adjust their ratio to the certain amount and achieve different effects. The ion energy is also strongly dependent on the position where the sample is placed.

The uniformity of plasma light emission at the location where samples are to be placed is demonstrated for higher powers. The power delivered to the plasma is measured with good accuracy providing proper treatment characterization and reproducibility. The low pressure cold plasma is not an alternative to atmospheric plasma sources when it comes to biomedical applications but is the preferred tool for all materials that may be treated under low pressure including organic materials and even some biological samples such as seeds. Full understanding of the processes and phenomena occurring in such plasmas as well as optimization of new applications may be achieved by using swarm based data [20, 21], plasma models [21,22] and possibly known scaling [23] to connect to other types of discharges.
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References
[1] Makabe T and Petrović Z Lj 2006 Plasma Electronics (Taylor and Francis:New York);
Lieberman M A and Lichtenberg A J 2005 Principles of Plasma Discharge and Materials Processing, (Wiley:Hoboken)
[2] Roth J R 1995 Industrial Plasma Engineering (Institute of Physics: Bristol, UK); Kelly-Wintenberg K, Hodge A, Montie T C, Deleanu L, Sherman D, Roth J R, Tsai P and WadsworthL. 1999 J. Vac. Sci. Technol. A 17 p 1539
[3] Ilic V, Saponjic Z, Vodnik V, Lazovic S, Dimitrijevic S, Jovancic P, Nedeljkovic J M and Radetic M 2010 Ind Eng Chem Res 49 p 7287
[4] Mihailovic D, Saponjic Z, Radioicic M, Lazovic S, Baily C J, Jovancic P, Nedeljkovic J and Radetic M 2011 Cellulose 18 p 811
[5] Lazovic S, Puć N, Miletić M, Pavlica D, Jovanović M, Bugarski D, Mojsilovic S, Maletić D, Malović G, Milenković P and Petrović Z 2010 New Journal of Physics 12 p 083037
[6] Zivkovic S, Puć N, Giba Z, Grubisić D and Petrović Z L 2004 Seed Sci Technol 32 p 693
[7] Junkar I, Vesel A, Cvelbar U, Mozetić M, and Strnad S 2009 Vacuum, 84(1) p 83
[8] Vesel A, Junkar I, Cvelbar U, Kovač J, and Mozetić M 2008 Surf. Interface Anal., 40(11) p 1444
[9] Petrović Z Lj, Puć N, Lazovic S, Maletić D, Spasić K and Malović G 2012 J. of Phys.: Conf. Ser. 356 p 012001
[10] Radetić M 2012 Journal of Materials Science DOI 10.1007/s10853-012-6677-7
[11] Gorensek M, Gorjanc M, Bukosek V, Kovac J, Petrovic Z and Puac N 2010 Textile Research Journal 80 p 1633
[12] Puć N 2008 Journal of Physics: Conference Series 133 p 012007
[13] Puć N, Petrović Z Lj, Malović G, Đorđević A, Živković S, Giba Z and Grubišić D 2006 J. Phys. D: Appl. Phys. 39 p 3514
[14] Puć N, Petrović Z Lj, Živković S, Giba Z, Grubišić D and Đorđević A 2005 Plasma Processes and Polymers ed. R d’Agostino, P Favia, C Oehr, M R Wertheimer (Wiley-VCH:Berlin) p 193
[15] Drešnik A, Vesel A and Mozetić M 2005 Inform. Midem 35 p 85.
[16] Mozetic M, Vesel A, Cvelbar U and Ricard A 2006 Plasma Chem. and Plasma Proc. 26 (2) p 103
[17] Vrlinic T, Mile C, Debarnot D and Poncin-Epaillard F 2009 Vacuum 83 p 792
[18] Primić, Zaplotnik R, Vesel A and Mozetic M 2011 AIP Advances 1 p 022129
[19] Zaplotnik R, Vesel A and Mozetic M 2011 EPL (Europhysics Letters) 95 p 55001
[20] Dujko S, Ebert U, White R D and Petrović Z Lj 2011 Japanese Journal of Applied Physics 50 p 08J01
[21] Petrović Z Lj, Dujko S, Marić D, Malović G, Nikitović Ž, Šašić O, Jovanović J, Stojanović V and Radmilović-Radenović M 2009 J. Phys. D: Appl. Phys. 42 p 194002
[22] Savić M, Radmilović-Radenović M, Šuvakov M, Marjanović S, Marić D and Petrović Z Lj 2011 IEEE Trans. Plasma Sci. 39 (11) p 2556
[23] Petrović Z Lj, Škoro N, Marić D, Mahony C M O, Maguire P D, Radmilović-Radenović M and Malović G 2008 J. Phys. D: Appl. Phys. 41 p 194002