Infrared absorption spectroscopy investigation of molecular species generated by surface dielectric barrier discharge micro-plasma in humid air

A. Dascalu[1], A. Besleaga[1], S. Teodoroff-Onesim[1] , V. Pohoata[1], K. Shimizu[2] and L. Sirghi[1,*]

[1]*Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Blvd. Carol I nr. 11, Iasi 700506, Romania*
[2]*Organization for Innovation and Social Collaboration, Shizuoka University, 3-5-1, Naka-ku, Johoku, Hamamatsu, Shizuoka 432-8561, Japan*

[*]*E-mail: lsirghi@uaic.ro*

Abstract: Molecular species generated in a closed volume of air (0.5 L) at atmospheric pressure by surface dielectric barrier (SDBD) mico-plasma were monitored by Fourier Transform Infrared (FTIR) absorption spectroscopy during discharge and post discharge times. The measurements showed that the presence of water vapour in the discharge medium impede on SDBD plasma generation of radical oxygen and nitrogen species. The SDBD generated species contribute to desorption of water from the inner wall of the discharge chamber and enhance evaporation of liquid water, which cause an increase of air humidity and a corresponding decrease of the generation rate of reactive species. During post discharge time, concentration of O_3, NO_2 and CO_2 molecular species decreases exponentially with slow decay rates (characteristic decay time of tenths of minutes). Presence of liquid water in the discharge chamber hampered the plasma generation of reactive oxygen and nitrogen species and enhances the decay rate of these species during the post discharge time.

Keywords: Surface Dielectric Barrier Discharge, atmospheric-pressure plasma, , Infra Red Absorption Spectroscopy, reactive species in air plasma, plasma water treatment.

1. Introduction

Atmospheric pressure plasmas in air are intensely studied for their applications in technological processes as surface treatments, bio decontamination, water treatment, and biomedical devices [1]. Particularly, surface dielectric barrier discharge (SDBD) plasma is a handy and low-cost plasma source, which is scalable for either small devices used in laboratory research or medical applications to large industrial applications [2]. In our group, we have studied the capability of SDBD micro-plasma generated on dielectric surface of small devices to treat water for either removal of organic chemical pollutants [3] or for activate water [4]. In these experiments, SDBD plasma generates primary reactive oxygen and nitrogen species in gas phase, which in contact with water produce secondary reactive species as hydrogen peroxide H_2O_2, nitrites NO_2^-, nitrates NO_3^- and peroxynitrites/peroxynitrous acid ONOO-/ONOOH [5]. These secondary reactive species oxidize and mineralize the organic molecules in contaminated water. Generated in clean water, they confer upon it special properties useful for applications in medicine and agriculture [6]. However, we found that during the working time, the SDBD plasma enhances evaporation of water and, thus, raise the humidity of air in the treatment chamber with bad consequences on the efficiency of the treatment. To investigate this effect, in the present work we use FTIR absorption spectroscopy measurements to fallow the time evolution of molecular species in gaseous phase during discharge and post-discharge times. The FTIR measurements were performed in a small treatment chamber that encloses a volume of 0.5 litre of air in absence and, then, in presence of water to be treated. The measurements were performed during 20 minutes of discharge time and 60 minutes of post discharge time. Time evolution of concentrations of molecular species in gas phase as O_3, NO_2, CO_2 and H_2O were thus investigated. Results show the strong effect that the presence of water in the treatment chamber has on plasma generation of reactive oxygen and nitrogen species.

2. Experiment

The SDBD microplasma was generated by a small device (area of 2.1×3.9 cm^2) consisting in two silver electrodes (around 20 μm in thickness) deposited on the two faces of a thin glass slide (250 μm in thickness). The hot electrode was structured as 7 equidistant and parallel stripes (1 mm in width and 38 mm in length) with gap width of 2 mm. The SDBD was powered by high voltage amplifier that applied a sinusoidal voltage wave (frequency about 13 kHz) with peak-to-peak value around 4000V. The voltage and intensity of discharge current signals were acquired by a digital oscilloscope. Time series of voltage and discharge current intensity values indicated a multi filamentary SDBD. The SDBD device was placed in a stainless steel vessel with the volume of 0.5 litres with two IR windows (Fig. 1). The vessel was places in the pathway of the IR beam of a FTIR apparatus (Bomem MB-104). Prior to FTIR measurements, the ambient air was purged through the discharge chamber for 10 minutes. The air humidity was measured by a high precision hygrometer. Experiments were performed in air at RH of 60% and in air in presence of a small amount (20 mL) of liquid water in a Petri dish (40 mm in diameter) placed on the bottom of the discharge chamber at 13 cm distance of SDBD device (Fig. 1). The FTIR spectra acquired after 20 minutes of SDBD working in air (RH =60%) and in air in presence of water in the Petri dish are presented in Figure 2. The spectra show presence of O_3, OH, H_2O_2, NO_2, NO_3, CO_3 and H_2O molecular species in the discharge chamber. The assignment of IR absorption bands to these species is presented in Table 1. The spectra taken in discharge medium in presence of liquid water showed, apart of gaseous species, a broad absorption band at 3400 cm^{-1} that corresponds to liquid water condensed on the surface of FTIR windows. The FTIR spectrum taken in absence of liquid water (in air at RH = 60%) showed much less liquid water condensed on the FTIR windows. To determine qualitatively the time variation of various molecular species in the chamber, the area of absorption bands corresponding to these species were determined after the extraction of base line from spectra. The FTIR spectrum taken before the SDBD was started was taken as reference.

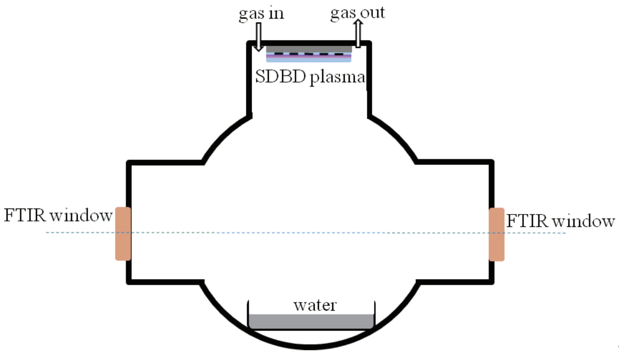

Fig. 1 Sketch of the experimental setup used in FTIR measurements in discharge and post discharge environment (ambient air with relative humidity of 60%). The distance between SDBD plasma and IR wave path is about 10 cm and the IR optical absorption path length is 20 cm. The volume of the stainless steel chamber is 0.5 litres.

3. Results

Figure 3 presents time variations of absorption band area at 1030 cm^{-1} and 1055 cm^{-1} , which correspond to O_3 [7, 8]. It is noticed that presence of the liquid water in the discharge chamber impeded on the generation of O_3, the concentration of ozone in the discharge chamber after 20 minutes of SDBD operation being two times smaller when liquid water was present. The maxima of O_3 concentration in the discharge chamber, which are achieved after 20 minutes of SDBD operation, are estimated to 250 ppm and 140 ppm in air (RH = 60%) in absence and, respectively, in presence of liquid water. Moreover, the decay rate of ozone concentration during post discharge time was higher in presence of liquid water.

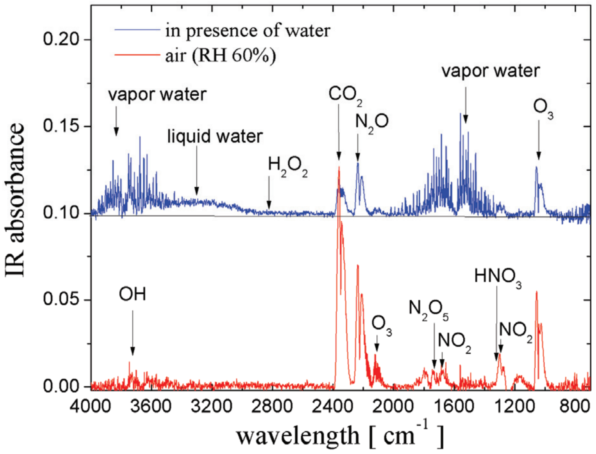

Fig. 2 Infrared (IR) absorbance of discharge medium after 20 minutes of SDBD in air (RH = 60%) and in air in presence of water to be treated. The baselines of spectra were shifted apart with 0.1 units. Assignment of the IR absorption peaks is presented in Table 1.

Table 1. FTIR absorption band assignment.

Wavelength number [cm^{-1}]	Assignment	Reference
1055, 1030	O_3	[7, 8]
2326, 2366	CO_2	[7]
1600, 1627	NO_2	[7]
1313, 1341	HNO_3	[7]
1247, 1720	N_2O_5	[7]
3689	OH radical	[9]
3400	Liquid water (condensed)	[10]
3800	Vapour water	[10]

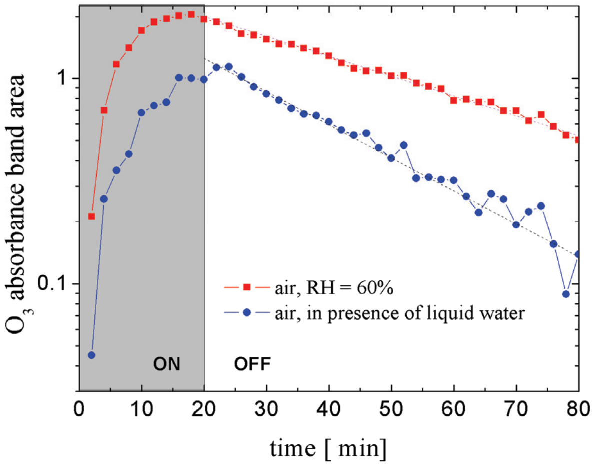

Fig. 3 Time evolution of areas of IR absorption peak corresponding to O_3 molecules (1055 cm^{-1}) in the chamber during 20 minutes of SDBD operation (ON) and 60 minutes of post discharge (OFF) time.

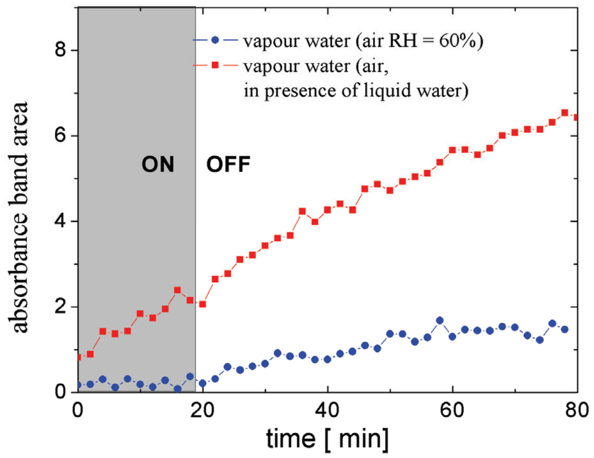

Fig. 4 Time evolution of areas of IR absorption band corresponding to OH stretching vibrations in vapour water in the chamber during 20 minutes of SDBD operation (ON) and 60 minutes of post discharge (OFF) time.

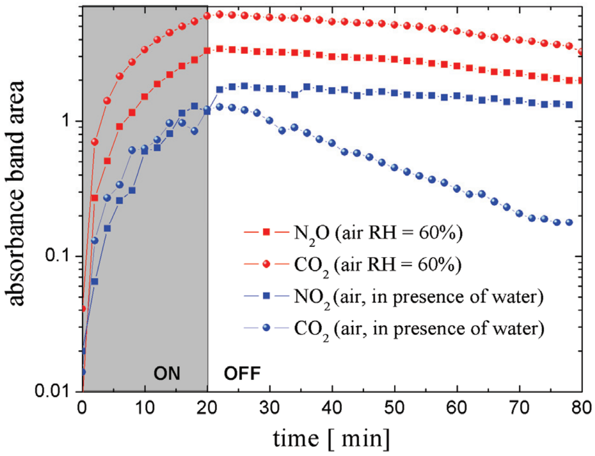

Fig. 5 Time evolution of areas of IR absorption bands corresponding to presence of N_2O and CO_2 molecular species in the chamber during 20 minutes of SDBD operation (ON) and 60 minutes of post discharge (OFF) time.

These indicate that ozone production is hampered by water evaporation and ozone is consumed at surface of liquid water in reactions leading to formation of secondary reactive species in plasma activated water. To prove that the SDBD plasma enhances evaporation of water, the time evolution of the area of absorption band at 3800 cm^{-1} corresponding to OH stretching vibrations in vapour water was determined (Fig. 4) during discharge and post discharge times. This analysis showed that concentration of water vapour increase linearly in time, but the concentration of water vapour when the liquid water was present in the discharge chamber is five times larger. The increase of water concentration in absence of liquid water in the discharge chamber is due to plasma-enhanced desorption of water from the inner walls of the discharge chamber. This desorption continues during post discharge time due to long living reactive species (including ozone) generated by plasma. Presence of large amount of water vapour in air impede on plasma generation of other molecular species too. Figure 5 shows the time evolutions of areas of IR absorption bands corresponding to presence of N_2O and CO_2 molecular species in the chamber during 20 minutes of SDBD operation and 60 minutes of post discharge time. These time evolutions showed that the concentration of these species after 20 minutes of SDBD operation are at least 5 times lower when the liquid water is present in the discharge chamber. During the post discharge time the concentration of these species decay slowly, probably due to their adsorption to the inner walls of the discharge chamber. Particularly, the decay of CO_2 concentration during post discharge time in presence of water is much faster than in the absence of water in the discharge chamber. This is an indicator that the CO_2 in the gaseous phase dissolve quickly in liquid water. This is not the case with NO_2, of which concentration show equally slow decay in post discharge chamber medium in absence or in presence of liquid water.

4. Conclusion

Molecular species generated SDBD plasma in the atmospheric-pressure air enclosed by a small discharge chamber was monitored by FTIR absorption spectroscopy measurements. The SDBD plasma was generated at the surface of the glass dielectric of a small surface DBD device by applying a sinusoidal high voltage with frequency around 13 kHz. Time series of voltage and discharge current intensity values indicated a multi filamentary SDBD. The FTIR measurements were performed during 20 minutes of discharge time and 60 minutes of post discharge time in absence and, then, in presence of a small amount of liquid water to be treated. Time evolution of concentrations of molecular species in gas phase as O_3, NO_2, CO_2 and H_2O were thus investigated. The results show that the presence of water in the treatment chamber has strong effect on plasma generation of reactive oxygen and nitrogen species. During the discharge time the SDBD plasma enhances evaporation of liquid water and water desorption from the inner wall of the discharge chamber and this causes an increase of the concentration of water vapour in the discharge chamber. Presence of water vapour in the SDBD medium impedes the plasma generation of primary oxygen and nitrogen reactive species with a corresponding decrease of treatment efficiency.

5. References

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Ivo Milton Raimundo Jr3, Arnaldo Alves Cardoso1 & Boris Mizaikoff2

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