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POSTER PRESENTATIONS

MASS SPECTROMETRY OF DIELECTRIC BARIER DISCHARGE WITH WATER ELECTRODE

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This paper presents the results of an investigation into the generation of reactive species in two setups of a dielectric barrier discharge (DBD) plasma source, using a water target with different vessels. By analyzing both neutral mass spectra and MID-scan spectra, we explore the concentrations of reactive oxygen and nitrogen species (NO, NO_2 and O_3) under varying plasma conditions and mass spectrometer configurations.

1. Introduction

In the past decade, a lot of interest has been drawn to atmospheric pressure plasmas (APPs) because of their unique properties and wide range of applications in fields such as material processing, agriculture, food industry and biomedicine [1, 2, 3, 4]. Since they do not require costly vacuum systems and operate at atmospheric pressure, APPs have the advantage of being accessible and versatile. Lately, atmospheric pressure plasma in contact with water has attracted significant interest due to its potential to generate reactive species and drive advanced chemical processes for various applications.

The behaviour and chemistry of APPs are greatly affected when they come into contact with water, either as an electrode or as a target. Reactive oxygen, nitrogen and hydrogen species are found in water and are essential for a variety of processes, such as biomedical treatments, sterilization, and water purification. Water forms a dynamic interface where plasma-induced reactions take place, producing reactive species like ozone (O_3), hydrogen peroxide (H_2O_2), hydroxyl radicals (OH), nitrates (NO_3^-), nitrites (NO_2^-) etc. These species play an essential role in enhancing the efficacy of plasma-based processes [5].

Also, higher humidity introduced in feeding gas of APPs has been demonstrated to increase the generation of reactive species, such as OH radicals, which are necessary for surface modification and decontamination [6]. The interaction, however, is complex and depends upon a number of variables, including ambient circumstances, water composition, and plasma characteristics. To optimize plasma processes and customize them for particular applications, it is essential to comprehend these interactions.

Dielectric barrier discharges (DBDs) are widely used for surface activation in atmospheric-pressure plasma applications. However, treating sensitive materials like polymers can be challenging because high-density plasma may cause damage, such as pin-holing. This issue often occurs in volume barrier discharges or coronas, where the plasma moves perpendicular to the treated surface. A practical solution is to generate plasma that travels parallel to the surface. This approach minimizes the risk of damage while maintaining effective treatment. One promising method is the surface dielectric barrier discharge (SDBD), where the plasma spreads along the surface of a dielectric plate. This setup not only protects the material but also improves the efficiency of the process.
In our earlier work [7, 8, 9] we introduced a novel plasma discharge reactor for efficiently activating polymers at the gas/liquid interface. This design uses liquid electrodes to ignite the SDBD directly from the liquid surface. Although the plasma-water interaction is limited to the edge of the dielectric tube, the system is both scalable and flexible, making it suitable for a wide range of applications.

Mass spectrometry is an analytical technique that measures the mass-to-charge ratio of ions to identify and quantify molecules in a sample. Primary advantage of atmospheric pressure mass spectrometry lies in its ability to rapidly and accurately analyse a wide range of chemical species [10]. These instruments are equipped with specialized pumping systems that create a pressure gradient, enabling the effective intake of gases from atmospheric plasmas. For neutral species, the mass spectrometer incorporates an ionization chamber that converts neutrals into ions, enabling their detection and analysis. The mass analyser which filters and detects neutral species or positive and negative ions, generating detailed mass spectra for all components. The technique provides real-time measurements of reactive species, ions, and neutral molecules, which are essential for understanding plasma processes and optimizing plasma-based applications.

When it comes to plasma in contact with water, due to technical challenges, mass spectrometric analysis of the plasma has so far been conducted by introducing water vapour into the working gas [11]. In this paper, we tackled the technical challenge and developed a setup where the mass spectrometer inlet was positioned in close proximity to the plasma-water interface, allowing us to successfully record mass spectra.

In this paper, we will present the results of our investigation into the reactive species generated by the dielectric barrier discharge (DBD) setup, but with two different water vessel configurations. The analysis includes both neutral mass spectra and MID-scan spectra, offering insights into the concentrations of key reactive oxygen and nitrogen species, such as NO, NO_2, CO_2 and O_3, as well as the detailed composition of the plasma obtained under these conditions.

2. Experimental set up

The schematic of the DBD at atmospheric pressure and HIDEN HPR60 mass-energy spectrometer is given in Figure 1. The DBD device is in the triple-phase interface (plasma-liquid-solid) plasma system consisting of a thin glass test tube with a 10 mm diameter and a 0.5 mm wall thickness was used. The liquid inside the test tube served as the high-voltage electrode and was connected to a power supply generating a sinusoidal voltage waveform. The Petri dish bath, which grounded the system, completed the circuit. Tap water with an electrical conductivity of approximately 0.3 mS/cm was used as the liquid electrode. The water was electrically insulated both inside and outside the test tube to ensure stability. The discharge operated in ambient air at atmospheric pressure. The high-voltage sine waveform had an amplitude range of 0 to 20 kV and could be adjusted to frequencies between 23 and 30 kHz. Power was delivered to the liquid electrodes through a high-voltage resonance generator (Lifetech-300W) paired with a function generator (FY3200S-24M).

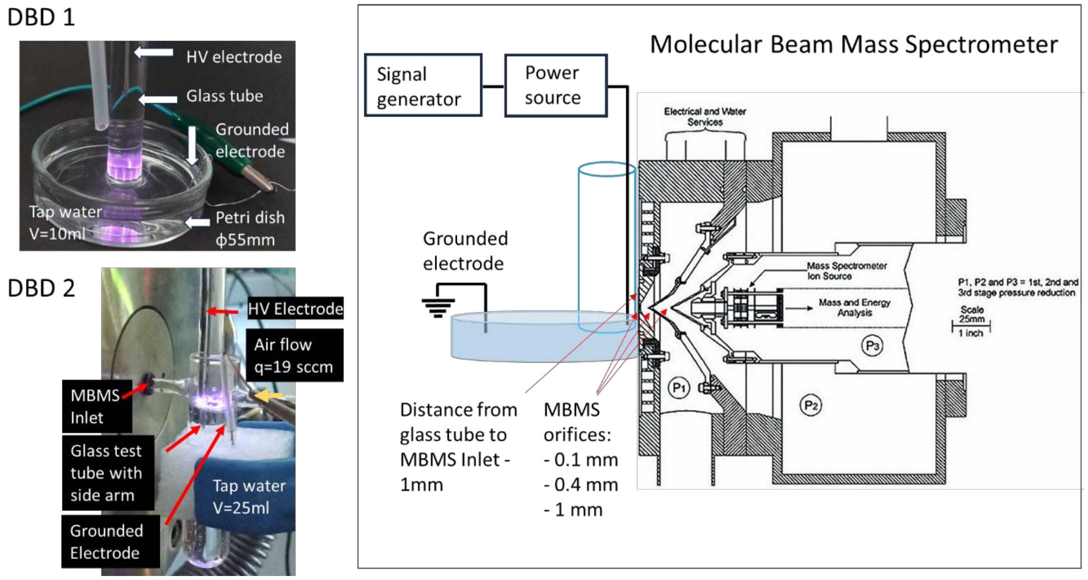

Fig. 1. DBD device in two configurations (DBD1 and DBD2) with a schematic representation of mass spectrometry measurements. In DBD1 setting, the device was immersed in 10ml of tap water placed in a Petri dish (ϕ55mm). In DBD2 setting, the device was placed in a glass test tube filled with 25ml of tap water, equipped with a side arm for gas sampling and a hole for synthetic air intake (q = 19 sccm).

Mass spectrometry measurements were performed by using MBMS (Molecular Beam Mass Spectrometer) HIDEN HPR60. To ensure the formation of a molecular beam, the geometry of the MBMS HPR60 system consists of a centralized combination of the orifice, cone1, and cone2 (P1 vacuum section is formed between the orifice and cone1, P2 vacuum section is formed between cone1 and cone2, and P3 vacuum section is formed after cone2 in the region of the mass analyzer). The orifice had an opening diameter of ⌀0.1 mm, cone1 ⌀0.4 mm, and cone2 ⌀1 mm, accompanied by the following voltages for DBD setups (the orifice was grounded, Vcone1 = 0 Vand Vcone2 =0 V).

During all experiments for DBD setups, the regions within the vacuum section of the mass spectrometer responsible for generating the pressure gradient had the following pressure values: $P_1 = 3.3 \cdot 10^{-1}$ Torr, $P_2 = 7.5 \cdot 10^{-6}$ Torr, and $P_3 = 2.4 \cdot 10^{-7}$ Torr. To identify the species of interest, we first recorded the mass spectra of neutrals (0–100 amu) using the RGA (Residual Gas Analyzer) mode, during which the ionization chamber was active. Within the ionization chamber, the electron emission current from the filament was for DBD1 = 5 µA and for DBD2 =10 µA. In both cases, the electron energy was 70 eV.

After that, we used MID-scan to monitor the temporal changes of selected species for different formation conditions: without plasma, with plasma at specific applied powers for DBD1 (5W and 15W) and DBD2 (15W), with Swagelok open, and with swagelok closed. Swagelok open represents the sum of foreground and background species, while swagelok closed corresponds to background species only.

3. Results and discussion

In this study, we have measured the neutrals mass spectra by using a mass spectrometer for two different configurations of Dielectric Barrier Discharge (DBD) system. In both configurations, titled DBD1 and DBD2, discharge was in contact with water during mass spectrometry measurements. The analysis of neutral species was performed in two different measurement modes of HPR60: RGA mode for neutral mass spectra and MID-scan mode for track in time changes of specific neutral species. These modes provide a comprehensive overview of the ionization processes and chemical compositions present in the plasma generated by each DBD system. The neutral mass spectra revealed the types and relative concentrations of neutral species, the MID-scan measurement provided insight into the temporal evolution of these species.

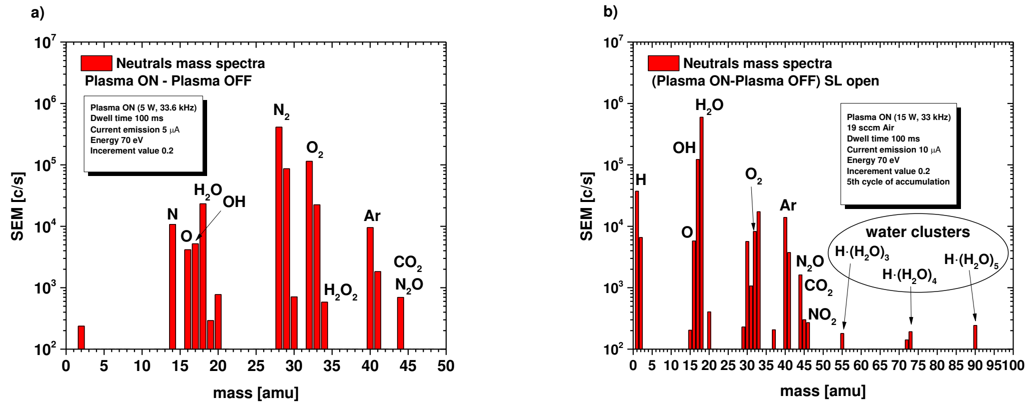

Fig. 2. Neutral mass spectra for a) DBD1 setting and b) DBD2 setting at an operating frequency of 33.6kHz. In the case of the DBD2, an airflow of 19sccm was added. The graphs were obtained by passing the raw results through a MatLab script to integrate the obtained lines for specific mass number.

Figure 2(a) and (b) present Neutral mass spectra for configurations DBD1 and DBD2, respectively. The presented spectra show the difference of Plasma ON mass spectra and Plasma OFF mass spectra. Plasma ON/OFF mass spectra represent the foreground signal i.e. the difference of total signal (swagelok open) and background signal (swagelok closed). The spectra in Figure 2 clearly show that the dominant species in the discharge are nitrogen and oxygen compounds (N, O_2, H_2O_2, N_2O, H, H_2O) which is to be expected because it is a discharge at atmospheric pressure where the target is water. Atomic nitrogen and atomic oxygen are present as a result of plasma reactions, along with the NO radical. The OH radical is also present, resulting from both plasma reactions and water dissociation in the MBMS. In Figure 2(b), water clusters can also be observed at mass numbers 53, 73 and 91, which appear in neutral mass spectra due to water vapor from the bottle containing the discharge. The high humidity in the DBD2 configuration and the plasma conditions promote cluster formation unlike in the case of DBD1 configuration where we did not detect any water clusters of mass above 50 amu.

While the mass spectra results provided an overall view of the main species present in the discharge chamber, nitrogen oxides and ozone can impact the industrial environment even at much lower concentrations (below the detection limit of the mass spectra used). Therefore, more sensitive measurements were conducted specifically for the important species NO, NO_2, N_2O, and O_3, as represented here. It was recorded for different conditions, Plasma ON and OFF with background only (BG), as well as Plasma ON and OFF with foreground and background (FG+BG). Unlike the case of BG, where only the inner part of the MS is considered in the measurement, in the case of FG+BG, the mass spectrometer is open so outside ambient air is also evaluated.

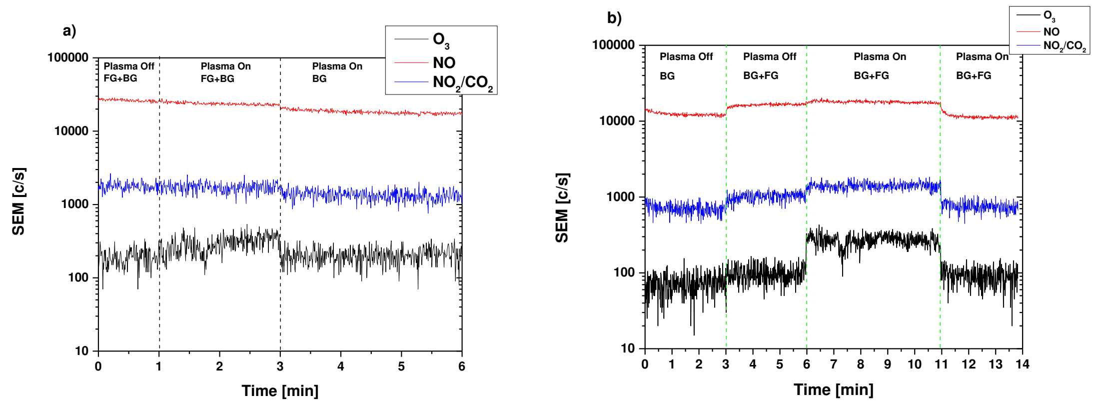

Fig. 3. The mid-scan provides constant tracking of selected species, with different stages of the experiment marked by labels: plasma on and off, foreground (FG) and background (BG); (a) DBD1 Setup, ionization filament current set to 5 µA at 70 eV, and (b) DBD2 Setup, ionization filament current set to 50 µA at 70 eV.

The MID-scan for DBD1 setup (Figure 3(a) starts with Plasma OFF and swagelock open (1^{st} minute), both the foreground (outside the spectrometer) and background are measured. The discharge is ignited in minute 1 and swagelok is open. Here we can see that NO continues to decrease slightly, NO_2 remains constant, and O_3 increases, indicating plasma-driven production of O_3. After the 3^{rd} minute, with the plasma still on but swagelock closed, all species (NO, NO_2, and O_3) decrease as expected (only background inside device is measured).

The Figure 3(b) shows MID-scan spectra for DBD2 configuration. In the first three minutes, with the plasma off and the swagelock closed, only the background signal is measured. After opening of the swagelok (3-6 minutes), the increase in NO and NO_2 suggests the influence of ambient air, while O_3 remains unchanged. Between 6 and 11 minutes, with the plasma on and the swagelok open, NO and NO_2 rise slightly, but O_3 increases significantly, indicating plasma-driven O_3 production. Finally, from 11^{th} minute, with the plasma on and the swagelok closed, all species decrease due to limited external interaction (only background is measured).

4. Conclusion

Mass spectrometry analysis of two setups of a DBD source with a water electrode, generated at atmospheric pressure was performed. Despite the difference in the water vessel used in each setup, in both setups similar trends in the behavior of reactive species were shown, indicating strong influence of plasma on water target. In both cases, plasma activation leads to the generation of reactive oxygen and nitrogen species, such as NO, NO_2, CO_2, and O_3, with notable increases in O_3 concentration when the plasma is on. Differences in the water vessel may affect the plasma's efficiency in producing reactive species, but both setups demonstrate that the plasma's interaction with the water is crucial for modulating the levels of reactive species. These findings highlight the importance of the plasma-water system in applications such as water treatment and agriculture, where reactive species generated in plasma-activated water could have significant biological and chemical effects.

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