

Mass spectrometric observations of the ionic species in a double dielectric barrier discharge operating in nitrogen

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Abstract:

Negative and positive ions generated in an atmospheric-pressure DBD with double dielectric were identified and their relative intensities characterised with variation of water vapour concentration in the discharge, gas residence time and inter-electrode spacing. The most abundant negative ions were O^- , OH^- , CN^- , CNO^- , NO_2^- , $NO_2^-(H_2O)$ and NO_3^- while the positive ions were dominated by N^+ , CH_2^+ , N_2^+ , CO^+ , HCO^+ , N_2H^+ , O_2^+ , $H^+(H_2O)_n$, CNO^+ and CN_2O^+ . Increasing the water concentration in the discharge led to an increase in the intensity of $H^+(H_2O)_n$, NO_2^- and its hydrated clusters, while the intensity of all carbon containing species decreased. Increasing the residence time of the species in the plasma region decreased the concentration of O^- , OH^- and NO_2^- , while the concentration of NO_3^- increased. Changing the inter-electrodes spacing did not have any effect on the formation of ionic species in the discharge.

Introduction

Dielectric barrier discharges (DBDs) are widely used in materials processing due to their capacity to treat surfaces of areas from several square millimetres and up to many square meters.^[1-3] The material and geometry of the electrodes and the dielectric are easily adaptable for numerous

applications. Properties of DBDs and their applications were explained in our previous work.^[4] The discharge properties of DBD's have been studied previously using a variety of diagnostic methods such as optical emission spectroscopy, Fourier transform infra-red spectroscopy (FTIR), infra-red laser absorption spectroscopy and electrical diagnostics.^[2, 5] In our previous work^[4] we reported the first mass spectrometry study of ionic species generated in a single barrier DBD operating in helium and water vapour mixtures. However, the use of nitrogen gas instead of expensive noble gases such as helium is more attractive for several practical applications such as surface cleaning and polymer modification. There are several mass spectrometric studies of atmospheric-pressure plasmas generated in nitrogen and air. All these studies use plasma jets^[6] or point-to-plane corona discharges.^[7-10] Mass spectrometry studies for atmospheric-pressure DBDs are missing and this study addresses this significant deficiency. Here we report the first use of molecular beam mass spectrometry to probe the ionic species produced in a nitrogen DBD generated at atmospheric-pressure. The effect of several operating parameters such as water vapour concentration, gas residence time and inter-electrodes spacing on the generation of ionic species was also investigated. Two dielectric barriers were present, one on the driven electrode and the other on the mass spectrometer extraction orifice plate which acted as the ground electrode allowing for in-situ measurements of the species arriving at the boundary. The use of two dielectrics prevents the glow-to-arc transition with the discharge displaying a filamentary nature. The discharge was operated in a controlled environment where water vapour was added to the gas at fixed concentrations. To determine the effect that changing the operating parameters had on the ionic species, the water vapour present within the discharge was varied from 0.15 to 0.4 % (by volume) by increasing the nitrogen flow into a bubbler containing water at room temperature. The gas residence time was changed from 2.5 to 9.4 ms and the inter-electrode spacing was varied from 0.25 to 1.75 mm. Initial plasma treatment of polypropylene films positioned over the ground electrode with different treatment time were also made.

Experimental set-up

A circular parallel plate reactor consisting of two metal electrodes with two dielectric discs of alumina (99.6 % alumina and dielectric constant 9.9) covering the driven and grounded electrodes was used to generate the atmospheric pressure discharge. **Figure 1** shows a schematic of the experimental arrangement. The alumina discs were 1 and 0.5 mm thick respectively. The disk over the ground plate was 0.5 mm thick to allow for accurate laser cutting of the tapered hole as described below. Similar to our previous work,^[4] the mass spectrometer was incorporated into the reactor as the ground electrode. The major difference in this study was the addition of a dielectric disc over the ground plane. A 25 μm hole was positioned at the disc centre and aligned with the 200 μm orifice of the extraction cone of the mass spectrometer. The centre hole in the alumina was laser cut and tapered from 50 μm to 25 μm . This small aperture allowed a continuous sheath to form across the orifice and prevented plasma penetration into the instrument itself, which reduced the chances of internal ion production and unwanted ion acceleration. The effective sheath thickness for similar plasma sources is in the range of 100 μm .^[11] A 6 μm layer of copper sputtered onto the top dielectric was used as the driven electrode with a diameter of 2 cm. The reactor was encased in a gas filled chamber of nitrogen; this allowed us to control the environmental conditions surrounding the electrodes. The two dielectric configuration prevented the glow-to-arc transition occurring in the discharge. The main carrier gas used in this case was nitrogen (oxygen free). Part of the total nitrogen flow was diverted to a water filled bubbler at room temperature to obtain the required concentration of water entering the plasma reactor.^[4, 12] The nitrogen flow into the bubbler was fully submerged in the water to ensure a good saturation of the nitrogen with water vapour. The discharge was powered using a high voltage (12 kV), sinusoidal 10 kHz power source consisting of a digital function generator, driving a commercial audio amplifier. A purpose built voltage step-up transformer was connected to the output to

generate the required high voltages. A 1000:1 Tektronix voltage probe and Pearson current monitor were used to characterize the discharge power. The average power delivered to the plasma reactor was calculated from the integral of the product of the time-dependent voltage and current over one pulse duration, normalized by the repetition frequency, f (10 kHz) namely,

$$P = f \int_0^T V(t) \times I(t) dt . \quad (1)$$

Here T is the pulse duration, $V(t)$ is the applied voltage and $I(t)$ is the input current.^[4, 13, 14] This simple calculation gives an upper limit of the consumed power at any applied voltage.

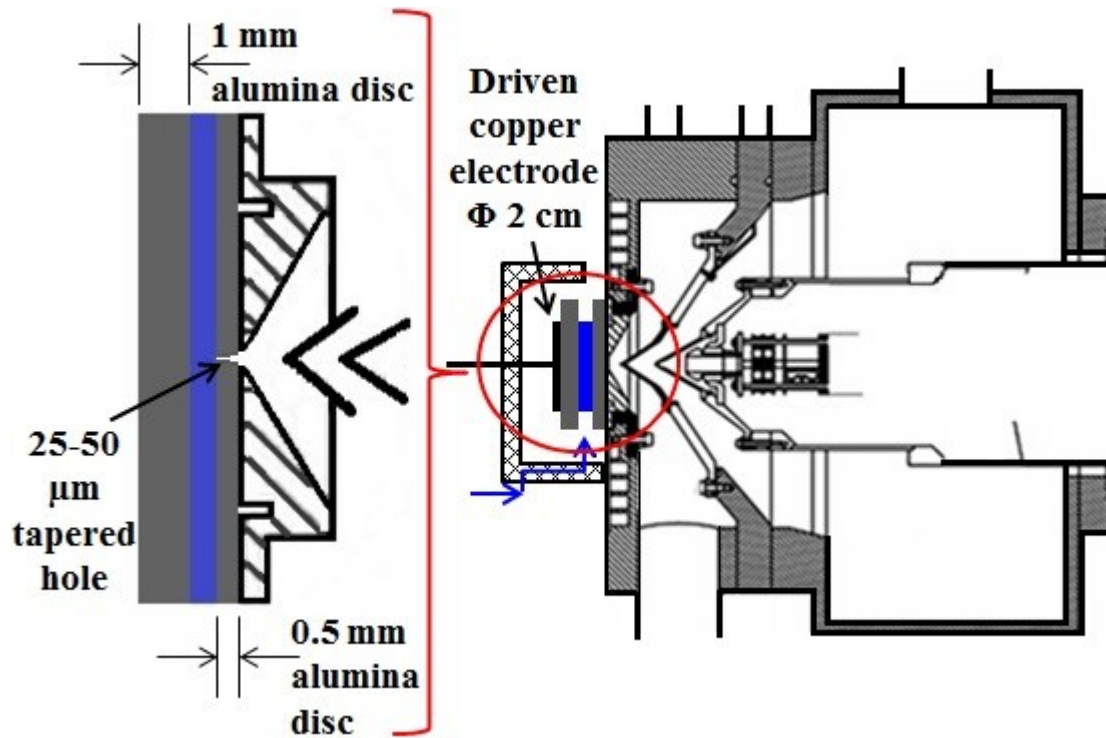


Figure 1. Experimental set up showing the DBD-MS arrangement.

The mass spectrometer employed here was a quadrupole-based molecular beam mass spectrometer, HPR-60, manufactured by HIDEN Analytical Ltd. The internal configuration of the mass spectrometer was described in our previous work.^[4] The HPR-60 has two operational modes, residual gas analyser (RGA) mode, used to detect neutral species; and secondary ion mass spectroscopy (SIMS) mode, used to detect positive and negative ions. For this study, a mass range

from 0 to 200 amu with a resolution of 0.2 amu was chosen. However, no ions were detected above 100 amu, and thus mass spectra are only shown up to 100 amu. Auto-tuning for the mass spectrometer analyser components was carried out in nitrogen. This was performed for neutrals, negative and positive ions before commencing the experiments. The Auto-tuning program chooses the most abundant ion in the discharge and tunes the analyser to get the best signal intensity.

Results and discussion

In the following sub-sections we will present in-situ mass spectrometry measurements of negative and positive ions generated in a DBD with a double dielectric operating in nitrogen. The influence of water concentration, residence time and inter-electrode spacing on the intensity of ionic species in the discharge is also examined. Results are presented as a function of relative yield (Y (%)), which was calculated by dividing the count intensity of a specific ion (i) on the total count intensity of all the detected ions (Y (%) = $Y_i \times 100 / \sum_i Y_i$). To reduce error in the relative yield, three separate scans of each spectrum were obtained and averaged.

In-situ measurements of neutrals, negative and positive ion in a nitrogen discharge

Mass spectrometry measurements using RGA and SIMS modes were carried out to characterize the feedstock composition and the ionic species in the discharge gas mixture. **Figure 2** shows neutral species in the gas feed before initiating the plasma. As expected, nitrogen was the predominant species. Trace amounts of water, oxygen and carbon dioxide with relative yields of 0.8, 0.1 and 0.1 respectively were also detected indicating either the presence of a small leak from the surrounding atmosphere into the environment system, or possible impurities in the nitrogen gas cylinder. Negative and positive ions generated in the discharge were also measured and presented in **figures 3 and 4**. Here the inter-electrode spacing was 0.5 mm and the applied

power was 9.8 W. The total gas flow rate to the reactor is 1 slm, corresponding to a residence time of 9.4 ms. The main negative ions detected were O^- , OH^- , $H^-(H_2O)_n$, CN^- , $OH^-(H_2O)_n$, CNO^- , NO_2^- , NO_3^- and $NO_3^-(H_2O)$. The most abundant positive ions measured were N^+ , CH_2^+ , H_2O^+ , N_2^+ , CO^+ , HCO^+ , N_2H^+ , O_2^+ , CNO^+ and CN_2O^+ .

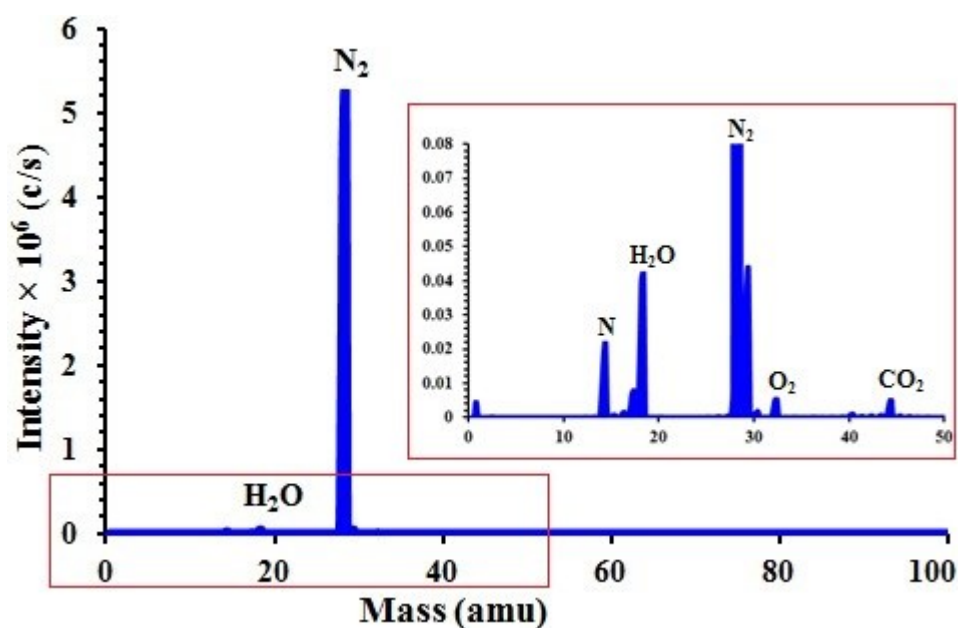


Figure 2. Mass spectrum for neutrals present in nitrogen. A total flow rate of 1 slm, inter-electrode separation of 0.5 mm and electron energy on the ionisation unit of 70 eV were used.

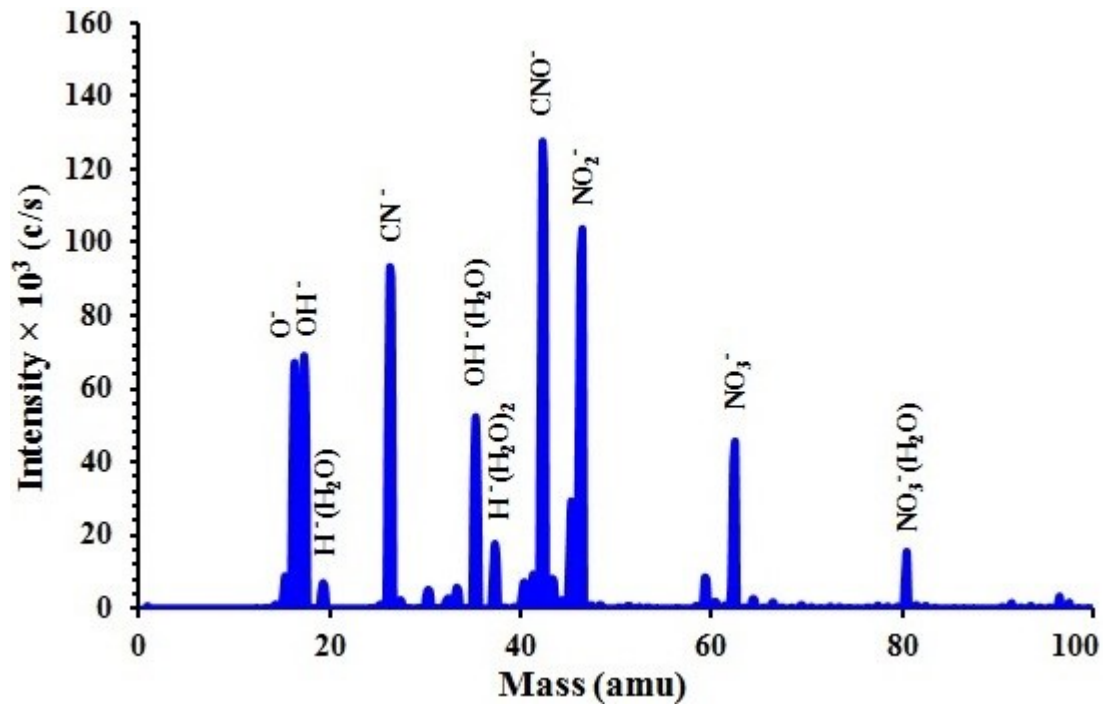


Figure 3. Negative ion mass spectra for nitrogen plasma. A total flow rate of 1 slm, applied power 9.8 W, electrode separation 0.5 mm, residence time 9.4 ms and frequency of 10 kHz were used. No additional water vapour was added to the nitrogen flow.

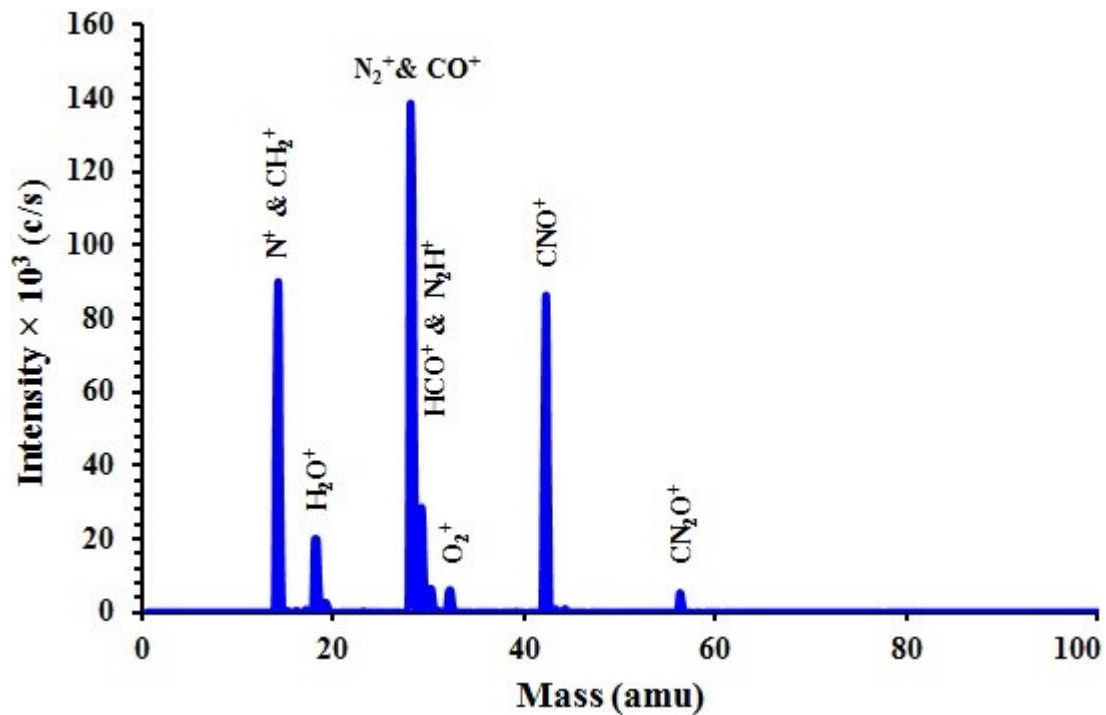


Figure 4. Positive ion mass spectra for nitrogen plasma. A total flow rate of 1 slm, applied power 9.8 W, electrode separation 0.5 mm, residence time 9.4 ms and frequency of 10 kHz were used. No additional water vapour was added to the nitrogen flow.

Influence of water concentration on negative and positive ion composition

The concentration of water vapour present within the discharge was varied from 0 to 0.4 % (by volume) by increasing the nitrogen flow into the bubbler. **Figure 5** shows negative and positive mass spectra of ions produced in the discharge, at an applied power of 9.8 W, inter-electrode spacing of 0.5 mm and 0.3 % of water vapour. The total gas flow rate to the reactor is 1 slm, corresponding to a residence time of 9.4 ms. **Figures 6 and 7** present the relative yield (Y (%)) of the most dominant negative and positive ions as a function of water concentration. Increasing the water concentration in the discharge led to an increase in the intensity of NO_2^- , $H^+(H_2O)_n$, HCO^+ , N_2H^+ and NO^+ while the intensity of most carbon containing species such as CN^- , CNO^- , CO^+ and CNO^+ decreased. NO_2^- hydrated clusters appeared with water vapour concentration of 0.225 % and their concentration increased with increasing water vapour. No large size water clusters were produced in this study. This is in stark contrast to our previous study involving helium and water vapour, where increasing the concentration of water vapour in the discharge resulted in the formation of large size water clusters such as: $O^-(H_2O)_n$, $OH^-(H_2O)_n$, $NO_2^-(H_2O)_n$ and $H^+(H_2O)_n$ with n up to 8, 9, 5 and 9, respectively.^[4] The discharge power in the case of nitrogen and water vapour was 33 times greater than that previously used for the helium and water vapour. While the reduced electric field strength (E/N) was approximately 7 times larger. This higher discharge energy seems to prevent the formation of large water clusters.

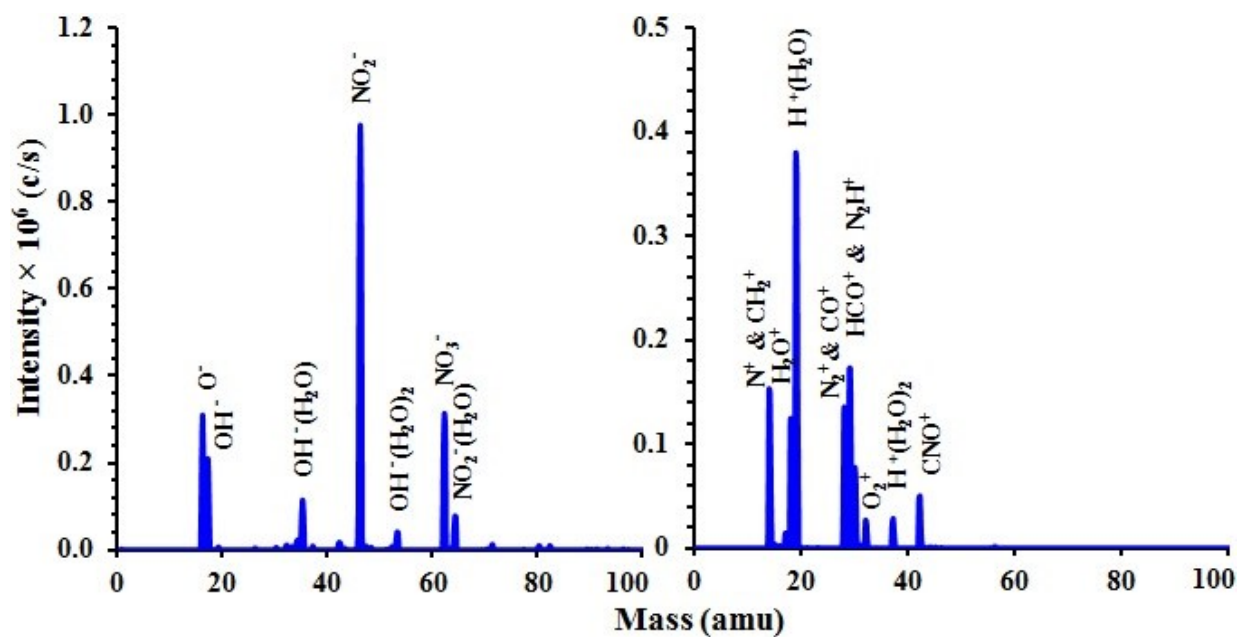


Figure 5. Negative and positive ion mass spectra for nitrogen and 0.3 % water vapour. A total flow rate of 1 slm, applied power 9.8 W, electrode separation 0.5 mm, residence time 9.4 ms and frequency of 10 kHz were used.

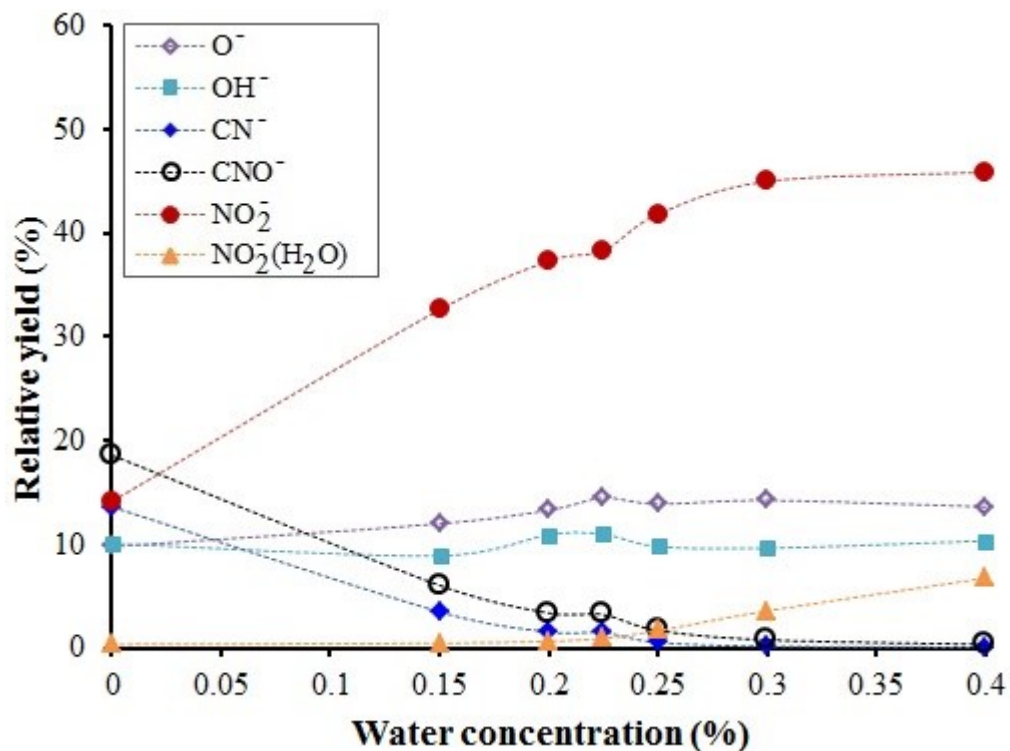


Figure 6. The relative yield of negative ions as a function of water concentration in nitrogen. Total flow rate of 1 slm, applied power 9.8 W, electrodes separation 0.5 mm, residence time 9.4 ms, reduced electric field strength, $E/N \sim 400$ Td and frequency of 10 kHz were used.

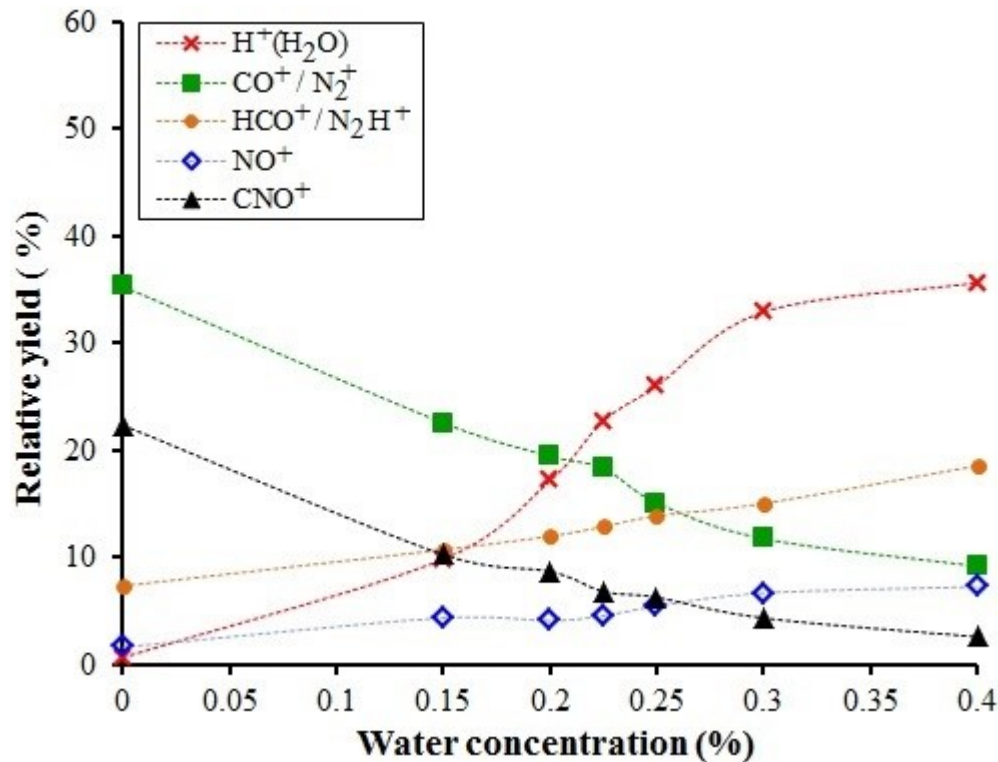


Figure 7. The relative yield of positive ions as a function of water concentration in nitrogen. Total flow rate of 1 slm, applied power 9.8 W, electrodes separation 0.5 mm, residence time 9.4 ms, reduced electric field strength, $E/N \sim 400$ Td and frequency of 10 kHz were used.

Influence of plasma residence time

The effect of gas residence time on the formation of negative and positive ions was investigated. The residence time was controlled by changing the total gas flow rate entering the reactor. Varying the total gas flow rate from 1 to 3.75 slm gives residence times between 9.4 and 2.5 ms. Water concentration, inter-electrode spacing and applied power were fixed to 0.3 %, 0.5 mm and 9.8 W, respectively. **Figures 8 and 9** show the effect of residence time on the intensity of negative and positive ions produced in the discharge. Results show that increasing the residence

time leads to a decrease in the relative yield of O^- , OH^- and NO_2^- , while the concentration of NO_3^- increased. No significant change in the relative yield was observed for other negative ions in the discharge. Figure 9 shows that increasing the residence time did not have any effect on the relative yield of positive ions. Our investigation showed no effect of the inter-electrode spacing on the formation of negative and positive ions in the discharge.

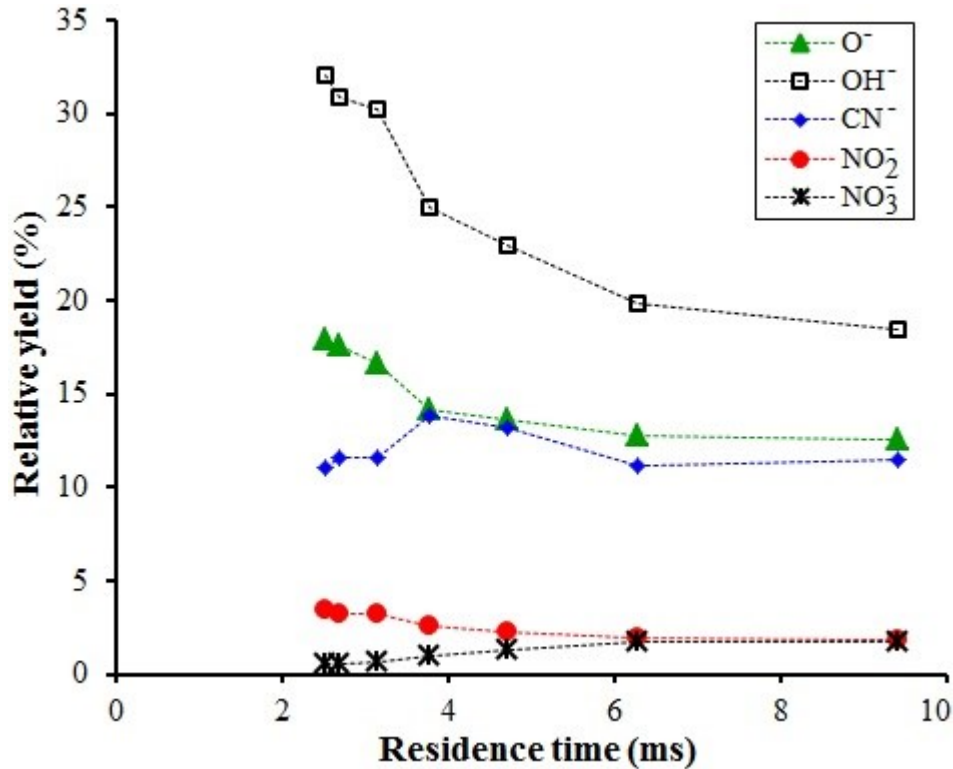


Figure 8. The relative yield of negative ions as a function of gas residence time in the plasma. Applied power 9.8 W, electrodes separation 0.5 mm, reduced electric field strength, $E/N \sim 400$ Td and frequency of 10 kHz were used.

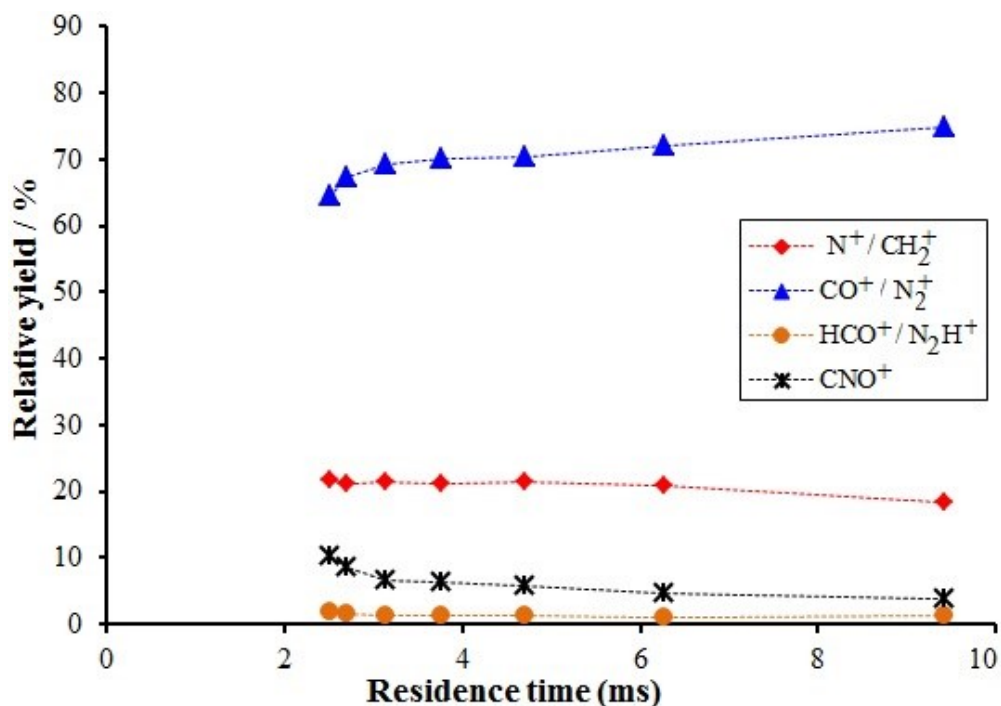


Figure 9. The relative yield of positive ions as a function of gas residence time in the plasma. Applied power 9.8 W, electrodes separation 0.5 mm, reduced electric field strength, $E/N \sim 400$ Td and frequency of 10 kHz were used.

Conclusions

Here we report on the first use of molecular beam mass spectrometry to examine positive and negative ionic species generated in nitrogen, double dielectric DBD, operating at atmospheric-pressure. This was achieved by modifying the first extraction cone of the spectrometer to incorporate a dielectric disc of alumina, through which the species were sampled, via a $25\mu\text{m}$ hole. The influence of water concentration, residence time and inter-electrode spacing on the intensity of ionic species in nitrogen was investigated. The dominant negative ions were O^- , OH^- , $H^-(H_2O)_n$, CN^- , $OH^-(H_2O)_n$, CNO^- , NO_2^- , $NO_2^-(H_2O)$, NO_3^- and $NO_3^-(H_2O)$, while the main positive ions were N^+ , CH_2^+ , H_2O^+ , N_2^+ , CO^+ , HCO^+ , N_2H^+ , O_2^+ , $H^+(H_2O)_n$, CNO^+ and CN_2O^+ . Results revealed that increasing the

concentration of water vapour in the discharge resulted in increasing the intensity of NO_2^- , $H^+(H_2O)_n$, HCO^+ , N_2H^+ and NO^+ , while CN^- , CNO^- , CO^+ and CNO^+ concentration decreased. When the gas residence time in the discharge region was increased, the concentration of O^- , OH^- and NO_2^- decreased and NO_3^- concentration increased. No significant changes of the concentration of ionic species produced in the discharge were noticed with changes in the inter-electrode spacing.

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Keywords: Double dielectric barrier discharge (DBD), mass spectrometry, non-thermal plasma.

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Table of contents:

The first use of molecular beam mass spectrometry to detect the ionic species arriving at the grounded side of an atmospheric-pressure double dielectric barrier discharge (DBD) driven at mid-frequency (10 kHz) in nitrogen is presented. The method involves sampling ions directly through the dielectric plate via a 25 μ m hole between the discharge and the extraction orifice of the instrument.

