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Ambient mass spectrometric diagnosis of an atmospheric-pressure helium plasma jet
質量分析法を用いた大気圧Heプラズマジェットの気相診断

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Ambient molecular beam mass spectrometry (MBMS) has been used to investigate the gas-phase reactive species in atmospheric-pressure helium plasma jets with the aim to understand better physical and chemical phenomena. Numerous neutrals and charged species are generated through the interactions, collision and attachment, between helium plasma jet and ambient air. It is believed that the generated reactive species, reactive oxygen species (ROS) and reactive nitrogen species (RNS), in plasma linked to liquid-phase ROS/RNS having biomedical effects such as bacteria inactivation and cancer cell destruction.

1. Introduction

Mass spectrometry (MS) is a versatile diagnostic method for characterization of reactive plasmas [1]. For an example, a work in the early 1960s has used in the field of traditional gas discharge plasma to detect ionic species [2]. MS enables to detect a wide range of plasma generated species including neutrals and ions. It also can be used to study the kinetic energy of the species.

Operating pressure range of MS is typically very low of ultrahigh vacuum between10^{-5}–10^{-7} Torr. With an ambient sampling system, however, the operating pressure range is expended to high pressure range. Thus, MS enables to detect plasma generated species in atmospheric-pressure [3,4]. On the other hand, it is open discussed that a pressure gradient towards the sampling orifice caused by the gas molecules to flow through the orifice into the low pressure region. This is the reason increase of the velocity of the molecules.

2. Atmospheric-pressure plasma jet

We used a low frequency driven atmospheric-pressure helium plasma jet (LFAPPJ) based on a cylindrical dielectric barrier discharge (DBD) scheme as shown in Fig. 1. [5] The plasma jet consisted of a glass tube having 15 cm long and an inner diameter of 4 mm. Helium gas of 1 slm was fed into the glass tube via a digital mass flow controller (KOFLOC8500) and a pulsed-dc high voltage of 5 kV at a low-frequency of 5 kHz was applied on a metallic external single electrode. Under the electrical and gas conditions above, the main helium plasma was ignited and a visible jet around a few cm was emerged into the ambient air. The plasma source was placed in front of the electrically grounded sampling orifice with a fixed distance of 5 mm.

3. Ambient MBMS [6]

As mention above, the collisional sampling can negatively influence the plasma and results increase of the flow velocity reaching supersonic

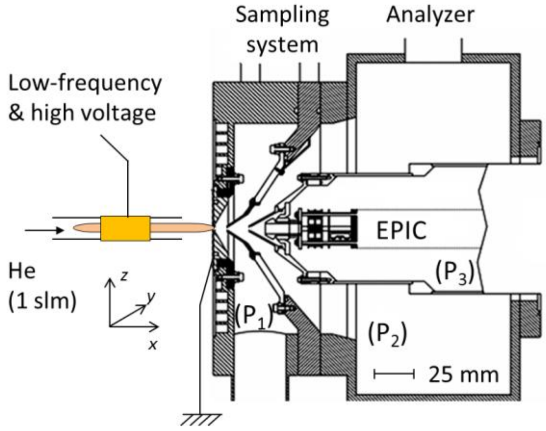

Fig. 1 Ambient MBMS (HRP-60 and EPIC) with APPJ

values, exceed the speed of sound. In case of plasma jet, however, the propagation speed of charged species in plasma bullet are much faster, ~10 km/s. It is no more serious problem in the measurement of charges in plasma jet.

Molecular beam mass spectrometer (MBMS, Hiden Analytical Ltd) system was used for detecting positively and negatively charged species in atmospheric pressure helium plasma jets. MBMS consists of HPR-60 sampling system and energy pulse ion counting (EPIC) analyzer as show in Fig. 1. The instrument was sampled via the three differentially pumped inlet cones, forming a molecular beam. Here we used 200 μm inner diameter sampling orifice for the 1st cone, 400 μm for the 2nd one and 1 mm for the 3rd.

For the measurement of neutral gas, internal electron beam ionized the gas molecules and the ions travelling into a quadrupole mass (QMS) filter working in residual gas analyzer (RGA) mode, while ions generated by the external plasma are measured in the secondary ion mass spectroscopy (SIMS) mode without internal ionizer.

4. Charged species in plasma jet

Fig. 2 shows the time-averaged mass spectra of positive and negative ions created through jet–air interactions. Ref. 6 revealed that He^+ ions are created inside the main discharge via electron-neutral ionization process ($e^- + He \rightarrow 2e^- + He^+$) and major secondary ions of *m/z* 28 N_2^+ and 32 O_2^+ from ambient air via collisional ionization process ($He^+ + M \rightarrow He + M^+$), where M denotes molecules in air. While, numerous negative ions are created by the dissociative electron attachment ($e^- + AB \rightarrow A^- + B$) and further attachment process ($A^- + M \rightarrow A^-M$). 34 negative ions species are detected and many of these are clusters. Therefore, the negative ions are more massive than the positive ions.

Time-resolved MS work also revealed that the positive ions are mainly generated during the positive discharge, while the negatives are done during the negative discharge.

3. Correlation between gas- and liquid-phase ROS/RNS

Atmospheric-pressure plasmas are known to contain a rich mixture of reactive oxygen and nitrogen species (ROS/RNS). Some of these species include the hydroxyl radical (OH•), nitric oxide radical (NO•), superoxide anion radical (O_2^-•), hydroperoxyl radical (HOO•), nitric dioxide radical (N_2O•), hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), ozone (O_3), nitrate (NO_3^- or $ONOO^-$) and

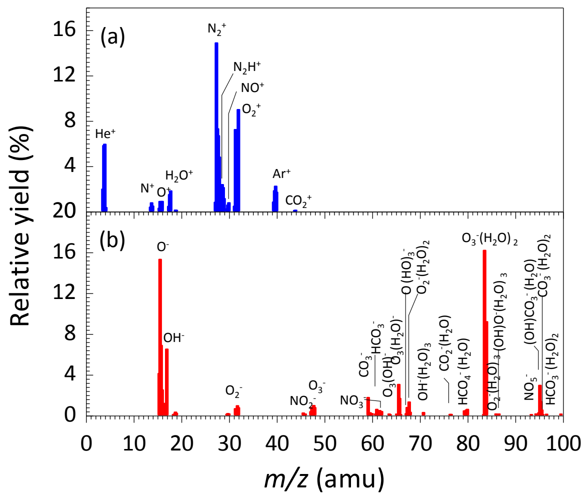

Fig. 2 Mass spectra of positive ions (a) and negative ions (b) generated in plasma jet.

nitrite (NO_2^-). These ROS/RNS in gas-phase and in liquid solution have been linked to biomedical effects such as bacteria inactivation and cancer cell destruction.

Overview of previous MBMS works, it was noticed that many of ROS/RNS are existed in gas-phase plasma jet. An inspection of mass spectrum in Fig. 2(b), *m/z* 46 NO_2^-, 62 NO_3^-, and negative ion core water cluster ions have been measured. In plasma treated liquid, however, relatively small number of ROS/RNS was reported by Ikawa *et al* [7]. There are short-lived species OH•, O_2^-•, and HOO• and also long-lived species such as NO_2^- and NO_3^-. It is believed that the hydration process (water cluster formation) is an important key process to understand how the ROS/RNS exist in liquid solution.

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