Threshold ionization mass spectrometry for the measurement of nitric oxide (NO) generated by an atmospheric-pressure radical source

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Abstract: Nitric oxide (NO) is an important molecule in biomedical applications. It is known that the NO enables to improve signal transmission between nerves, maintaining blood pressure, suppressing infection, and renewal tissue. In this study, we used a new atmospheric pressure plasma based NO radical generator and we investigated optimized condition to generate NO using a threshold ionization mass spectrometry.

Keywords: atmospheric-pressure plasma, nitric oxide radical (NO), threshold ionization mass spectrometry (TIMS)

1. Introduction

Non-thermal atmospheric pressure plasmas (herein referred to as plasma) used in biology and medicine typically provide a rich of reactive oxygen and nitrogen species (RONS). These RONS are neutral or ions that open discussed e.g. hydroxyl radical (OH•), nitric oxide (NO), singlet oxygen (¹O₂), ozone (O₃), superoxide anion radical (O₂−), hydroperoxyl radical (HOO•), nitric dioxide radical (N₂O•), hydrogen peroxide (H₂O₂), nitrate (NO₃⁻) and nitrite (NO₂⁻). [1][2][3][4] For the detection of the plasma generated RONS in ambient air, optical emission spectroscopy (OES), absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR), and mass spectrometry are often used.

Here, we focus on the investigation of the absolute density of NO which is a well-known molecule in biomedical application. For examples, it is known that the NO enables to improve signal transmission between nerves, maintaining blood pressure, suppressing infection, and renewal tissue. [5][6]

For the production of NO, Birkeland-Eyde process (N₂ + O₂ → 2NO) and Ostwald (4NH₃ + 5O₂ → 4NO + 6H₂O) process are well-known traditional processes to synthesize NO. These traditional NO productions always accompany with high temperatures e.g. 2000-3000 K for the Birkeland-Eyde process and about 1100 K for the Ostwald process, respectively. [5] On the other hand, electrical gas discharge plasma can generate NO near room temperature.

In this study, we generated NO molecules using a radical generator which was modified a high density atmospheric-pressure plasma source. [7] To obtain the quantitative study of NO and other neutral species, we used a threshold ionization mass spectrometry (TIMS). [2]

2. Experimental procedure

A commercially available radical generator (Tough Plasma, Fuji Machine MFG Co., Ltd.) was used in this study. NO is generated based on a high density atmospheric-pressure discharge plasma operated with a mixed gas of N₂-O₂ (1 slm for the both gases) in Ar (4 slm). The use of a large amount of Ar provides a high electron density on the order of 10¹⁶ cm⁻³ [7]. In addition, it is expected that the use of Ar as a buffer gas that decreases the three-body collision between the oxygen and nitrogen species to be RONS (O₂, O₃ and NO₂), resulting in an increase of NO production in the atmosphere. The structure of nozzle exit (a slit) with a bended flow channel at downstream intercepts high energy photons and the electrically grounded potential on the flow channel terminates charged species, respectively, as shown in Fig. 1.

Quadrupole-based HPR-60-EQP300 system (Hiden Analytical Ltd.) was applied to measure NO density in an atmospheric pressure. NO molecules were generated by the radical generator operated a simple gas mixture of N₂-O₂ in Ar. The generated neutral reactive species from the radical generator were measured by the mass spectrometer which was operated in the residual gas analysis (RGA) mode with an internal electron-impact ionization source.

Fig. 1 Schematic of experimental set-up of threshold ionization mass spectrometry for the measurement of neutral species generated by atmospheric pressure radical generator.
This allows production of positive ions from neutral gas and excited species by the radical generator. For the measurement of neutral species, electron-energy of NO was scanned with a resolution of 0.1 eV. The results with and without plasma were compared and the difference was considered to be the neutrals generated by plasma.

3. Results and discussion

Fig. 2 shows the electron scan results of NO (m/z 30) with and without plasma, and the difference of the both scan results. The difference reflects the NO generated by the plasma and the intensity shows the NO density. We obtained the maximum NO intensity with the gas mixture condition of about 35% N₂.

For the absolute densities of NO and other possible species e.g. NO₂ and O, we should know the correlation between the mass intensity and the known gas density (2.415 × 10¹⁹ cm⁻³) at a standard atmosphere. We optimized the internal ionization condition of the mass spectrometer based on the known gas mixture ratio of N₂ and O₂. For example, the gas density of 35% N₂ is to be 8.58 × 10¹⁹ cm⁻³.

For the estimation of the absolute density of NO, we used the correlation between the measured value of the mass intensity and the electron impact ionization (EII) cross-section of a species with known gas density. [8] The NO density (n_NO) is given by an equation below, [2]

\[ n_{NO} = n_{N_2} \frac{I_{NO}}{\sigma_{NO}} \frac{\sigma_{N_2}}{I_{N_2}} \]

where, \( n \) is a density mentioned above, \( I \) is intensity of mass spectrometry, and \( \sigma \) is an averaged EII cross-section in the electron-energy range between 15.6–18 eV. The lower energy of 15.6 eV was taken by the highest ionization threshold of N₂ (N₂ + e → N₂⁺ + 2e) and the higher energy of 18 eV was done by the lowest dissociative ionization threshold of water (H₂O + e → OH⁺ + H + 2e). EII cross-section of N₂ is averaged value (\( \sigma_{N_2} = 5.144 \times 10^{-18} \text{ cm}^² \)) between the energy range.

As a result, n_NO was estimated 2.963 × 10¹⁷ cm⁻³ with an error range of 12%. This density is four times larger than our previous study (n_NO = 7.66 × 10¹⁶ cm⁻³) using a UV absorption spectroscopy. With the same plasma condition, NO₂ (m/z 46) density was estimated to be 1.747 × 10¹⁶ cm⁻³ when EII cross section of NO (n_NO= 3.691 × 10¹⁶ cm⁻³) in Fig. 3. In case of O₃ (m/z 48), it was unable to estimate due to the small signal which is lower than the detection limit of 10¹⁵ cm⁻³.

4. Conclusions

Using a threshold ionization mass spectrometry, we investigated the absolute density of neutral species generated by atmospheric pressure plasma radical generator. We obtained the highest density of NO (n_NO = 2.963 × 10¹⁷ cm⁻³) at a N₂(N₂-O₂) mixture ratio of 35% with a lower density of NO₂ (n_NO₂= 1.747 × 10¹⁶ cm⁻³) and O₃ (below detection limit). Further results will be discuss on-site.

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5. References