Production characteristics of ROS/RNS in water after DC corona discharge exposure

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1. Introduction.
Discharge plasma generated in contact with liquid is used for various applications such as sterilization, stimulation of germination and plant growth, etc.¹,² In these applications, reactive oxygen species (ROS) and reactive nitrogen species (RNS), such as OH, H₂O₂ and NO₂, are regarded to promote chemical reaction, causing biocidal effect, stimulation of plant growth, etc., in water. Precursors of ROS/RNS can be produced in the discharge plasma in gas phase, these dissolve into the water, and then ROS/RNS are produced. To control ROS/RNS concentration, it is important to clarify the mechanism of ROS/RNS production. In this work, we generated a DC corona discharge above water, and then investigated ROS/RNS concentration in deionised water for different ambient gas composition. We also deduced the production processes of the ROS/RNS.

2. Experimental apparatus and conditions
A comb-shaped electrode and a plastic container are placed in an acrylic discharge chamber, which has 140 mm in length, 260 mm in width and 100 mm in height. The comb-shaped electrode consists of 4 clusters, each of which has 26 (13 x 2) combs of 1.6 mm in width and 15 mm in length. The clusters are placed with 4 mm gap between front and back, and with 20 mm between left and right. 100 mL of deionised-water is poured into the plastic container, which has 85 mm in length, 128 mm in width and 10 mm in height, and the distance between the tip of the comb-shaped electrode and the surface of the deionised-water is fixed at 15 mm. An aluminum foil, which is earthed, is put in the water. Mixture of Ar (or N₂) and O₂ is used as a background (BG) gas, and the flow rate of the BG gas is 2.0 L/min. The mixture ratios (%) of the BG gas are Ar/O₂ = 80/20, 60/40 and 40/60, N₂/O₂ = 60/40 and 40/60. A positive DC high voltage is applied to the comb-shaped electrode to generate a corona discharge between the comb-shaped electrode and the water surface. Input power is 6 W and discharge current is 0.38 - 0.41 mA. Samples are taken from the water every 3 min and the samples are analysed by High

Fig. 1. Concentration variations of H₂O₂, NO₂⁻ and NO₃⁻ as functions of input energies.
Performance Liquid Chromatograph (Shimadzu, Prominence, column: IC-NI-424). The aqueous solution of acetic acid (3 mmol/L) and potassium hydroxide (1.9 mmol/L) is used as an elution, and the wavelength of an absorbance detector is fixed at 220 nm in HPLC. Further, an off-gas is analysed by Fourier Transform Infrared spectrophotometer (Shimadzu, FTIRR8900) equipped with a gas cell, which has an optical path length of 10 m.

3. Results and discussion
In HPLC analysis, H$_2$O$_2$, NO$_2^-$ and NO$_3^-$ are detected when N$_2$/O$_2$ is used as a BG gas, and only H$_2$O$_2$ is detected when Ar/O$_2$ is used as a BG gas. Fig. 1 shows concentration variations of H$_2$O$_2$, NO$_2^-$ and NO$_3^-$ as functions of input energies, which are calculated by (input power) x (discharge time). It is found that H$_2$O$_2$ and NO$_3^-$ concentrations increase monotonously with input energy, but that NO$_2^-$ concentration tends to be constant or decrease after monotonously increase at the beginning. It is also found that higher concentration of H$_2$O$_2$, NO$_2^-$ and NO$_3^-$ is obtained at higher content of Ar/N$_2$ in BG gas.

Fig. 2 shows production processes of H$_2$O$_2$, NO$_2^-$ and NO$_3^-$. H$_2$O$_2$ can be produced by reactions (6) and (7), and OH and O$_3$ are generated by reactions (1)-(3) and reaction (5), respectively. In FT-IR analysis, O$_3$ is detected in the off-gas in all gas composition. The concentration of O$_3$ is approximately equal regardless of the gas composition, so that the contribution of O$_3$ to H$_2$O$_2$ production is found to be very low. When the mixture ratio of Ar or N$_2$ increases, the discharge spreads the water surface; therefore, the production of OH by reactions (1)-(3) is promoted. It is probable that these OH contribute to the increase of H$_2$O$_2$ in the sampled water.

In N$_2$/O$_2$ mixture gas, NO, NO$_2$, NO$_3$ and N$_2$O$_3$ may be generated by reactions (10)-(19). HNO$_2$ and HNO$_3$ can be generated by these species in reactions (20)-(22), and then NO$_2^-$ and NO$_3^-$ are produced by dissolving HNO$_2$ and HNO$_3$ in water. OH is consumed for HNO$_2$ and HNO$_3$ production in reactions (20) and (21). Therefore, concentration of H$_2$O$_2$ in N$_2$/O$_2$ atmosphere is lower than that of Ar/O$_2$ atmosphere.

4. Conclusions
The DC corona discharge is generated above water, and ROS/RNS concentration in the water is measured, and then the production processes of the ROS/RNS in the water is deduced. It is found that the concentration of H$_2$O$_2$ increases with the increase of Ar or N$_2$ mixture ratio due to the spread of the discharge. In N$_2$/O$_2$ atmosphere, OH is consumed for HNO$_2$ and HNO$_3$ production so that H$_2$O$_2$ concentration is lower than that of Ar/O$_2$ atmosphere.

References