Influence of oxygen on generation of reactive chemicals from nitrogen plasma jet

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A nonthermal plasma jet is operated at atmospheric pressure inside a vacuum chamber filled with nitrogen gas. Various chemical compounds are fabricated from nitrogen and water molecules in plasma jet with varying oxygen content. Detailed theoretical investigation of these chemical compounds is carried out in terms of different oxygen ratio $\xi$. Experimental measurements are also carried out for comparison with theoretical results. Hydroxyl molecules are mostly generated at surface of water, and some of them can penetrate into water. The density of hydroxyl molecules has its maximum without oxygen, and decreases to zero as $\xi$ increases to 0.25. The density of the ammonia of NH$_3$ also deceases as $\xi$ increases to 0.25. On the other hand, theory and experiment show that the density of the NO$_3$ increases drastically as $\xi$ increases to 0.25. The hydrogen peroxide density in plasma activated water decreases, reaches its minimum value at $\xi = 0.05$, and then increases again, as $\xi$ increases from a small value to a large value. The $pH$ value of the plasma activated water, which is slightly changed to alkali without oxygen, decreases as $\xi$ increases.

Nonthermal plasma was proposed as a novel therapy for some incurable diseases1–6. Nonthermal plasma generates various kinds of reactive chemicals including reactive oxygen species (ROS) and reactive nitrogen species (RNS) in the liquid, and the consequent increase of intracellular ROS and RNS have been reported as main cause for various biological events. In recent studies, plasma activated water/media showed similar anticancer effects as direct nonthermal plasma treatment7,8. These reports support that those diseases may be cured by long lived ROS/RNS. H$_2$O$_2$ and ONOO$^-$ have been suggested as main players in plasma treated liquids8–10. However, still it is unclear why any artificial combination of H$_2$O$_2$ and NO$_2$ cannot make full biological effects as plasma does. Therefore, the effects of different compositions of reactive species in the plasma need to be investigated.

Nitrogen plasma is known to produce OH radicals easily according to the water bombardment of excited nitrogen molecules in a metastable state11. Though OH radicals from the liquid surface are hard to directly affect biological systems, the OH radicals are important source to generate H$_2$O$_2$ or ONOO$^-$. In addition, oxygen addition to the nitrogen gas causes dramatic changes in the chemistry of plasma treated water, resulting in differential biological responses12–15. Therefore, this article investigates influence of oxygen on generation of reactive species in nitrogen plasma.

In this study, detailed theoretical investigation of these chemical compounds is carried out in terms of different oxygen content ($1\sim25\%$). The steady-state density of the H, OH, HO$_2$, H$_2$O$_2$, NH, NH$_2$, NH$_3$, NO, HNO$_2$, and HNO$_3$ are calculated using major forty two chemical reactions (Table 1). Experimental measurements are also carried out in comparison with theoretical results. OH, NH$_4^+$, H$_2$O$_2$, NO$_3^-$, and pH are measured in deionized water treated with nonthermal plasma. Though our analysis does not show detail kinetics in a pico second range or detail spatial distributions in a micro meter range as other computational simulation studies, our steady-state solutions are well matched with experimental measurements. This is the first report showing the changes in the chemical species in water according to the O$_2$ mole fraction in N$_2$ plasma in both theoretical and experimental approaches. Densities of H, OH, H$_2$O$_2$, NH, NH$_2$, and NH$_3$ drastically reduced in the low level of O$_2$ mole fraction, but densities of O and HNO$_3$ increased according to O$_2$ mole fraction. Their relations with the pH will be discussed.

We calculated the changes in the chemical reactive species in water according to the O$_2$ mole fraction in accordance with experiments.

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The dominant chemical species in the plasma jet is a metastable state $N_2(A^3\Sigma_u^+)$.

### Table 1.

| Eq. Num. | Reaction | Rate coefficient | Ref. |
|----------|----------|------------------|------|
| 1        | $N_2 + e \rightarrow N_2(A^3\Sigma_u^+)$ | $\alpha_{N_2} = 6.4 \times 10^{-12} \text{cm}^3/\text{s}$ |
| 2        | $N_2 + e \rightarrow 2N$ | $k_N = 1 \times 10^{-12} \text{cm}^3/\text{s}$ |  
| 3        | $O_2 + e \rightarrow 2O$ | $k_O = 1.5 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 4        | $N_2(A^3\Sigma_u^+) + H_2O \rightarrow OH + H N_2$ | $\alpha_{OH} = 5 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 5        | $N_2(A^3\Sigma_u^+) + N_2 \rightarrow N_2 + N_2$ | $\alpha_{N_2} = 3 \times 10^{-12} \text{cm}^3$ |  
| 6        | $N_2(A^3\Sigma_u^+) + O_2 \rightarrow \text{products}$ | $\alpha_{O_2} = 2.5 \times 10^{-12} \text{cm}^3/\text{molecule/s}$ |  
| 7        | $OH + H + M \rightarrow H_2O + M$ | $\alpha_{OH} = 1.14 \times 10^{-10} \text{cm}^3/\text{molecule/s}$ |  
| 8        | $H + O_2 + M \rightarrow HO_2 + M$ | $\alpha_{HO_2} = 4.6 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 9        | $OH + OH + M \rightarrow H_2O_2 + M$ | $\alpha_{H_2O_2} = 1.78 \times 10^{-12} \text{cm}^3/\text{molecule/s}$ |  
| 10       | $OH + HO_2 \rightarrow H_2O + O_1$ | $\alpha_{OH} = 1.1 \times 10^{-10} \text{cm}^3/\text{s}$ |  
| 11       | $OH + H_2O \rightarrow HO_2 + H_2O$ | $\alpha_{HO_2} = 1.7 \times 10^{-12} \text{cm}^3/\text{s}$ |  
| 12       | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $\alpha_{H_2O_2} = 1.24 \times 10^{-12} \text{cm}^3/\text{molecules/s}$ |  
| 13       | $H_2O_2 + O \rightarrow HO_2 + OH$ | $\alpha_{HO_2} = 1.7 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 14       | $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$ | $1 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 15       | $H_2O_2 + H \rightarrow OH + H_2O$ | $4.2 \times 10^{-14} \text{cm}^3/\text{molecules/s}$ |  
| 16       | $H + N \rightarrow NH$ | $\alpha_{NH} = 1.3 \times 10^{-12} \text{cm}^3/\text{s}$ |  
| 17       | $NH + OH \rightarrow HNO + H$ | $\alpha_{HNO} = 3.3 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 18       | $NH + O \rightarrow OH + N$ | $\alpha_{OH} = 1.16 \times 10^{-11} \text{cm}^3/\text{molecules/s}$ |  
| 19       | $NH + O_2 \rightarrow \text{Products}$ | $\alpha_{OH} = 9.98 \times 10^{-12} \text{cm}^3/\text{molecules/s}$ |  
| 20       | $NH + NH \rightarrow NH_2 + N$ | $\alpha_{NH_2} = 4.3 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 21       | $NH_2 + OH \rightarrow NHOH$ | $\alpha_{NH_2OH} = 9.31 \times 10^{-11} \text{cm}^3/\text{s}$ |  
| 22       | $NH_2 + O \rightarrow H + HNO$ | $\alpha_{NH_2} = 7.4 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 23       | $O_3 + NH_2 \rightarrow H_2NOO$ | $\alpha_{H_2NOO} = 1.54 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 24       | $H + NH_2 \rightarrow NH_3$ | $\alpha_{NH_3} = 7.7 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 25       | $HNO_2 + NH_2 \rightarrow NH_3 + NO_2$ | $\alpha_{NH_3} = 6.4 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 26       | $NH_2 + O \rightarrow OH + NH_2$ | $\alpha_{NH_2} = 4.6 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 27       | $OH + NH_2 \rightarrow H_2O + NH_2$ | $\alpha_{H_2O_2} = 1.6 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 28       | $NH_2 + NO_2 \rightarrow HNO_2 + NH_2$ | $\alpha_{HNO_2} = 6 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 29       | $OH + N \rightarrow NO + H$ | $\alpha_{NO} = 4.7 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 30       | $N + O \rightarrow NO$ | $\alpha_{NO} = 2.39 \times 10^{-12} \text{cm}^3/\text{s}$ |  
| 31       | $N + O_2 \rightarrow NO + O$ | $\alpha_{NO} = 9.2 \times 10^{-17} \text{cm}^3/\text{molecule/s}$ |  
| 32       | $NO + H \rightarrow HNO$ | $\alpha_{HNO} = 1.56 \times 10^{-12} \text{cm}^3/\text{molecules/s}$ |  
| 33       | $NO + OH \rightarrow HNO_2$ | $\alpha_{HNO_2} = 1.78 \times 10^{-11} \text{cm}^3/\text{s}$ |  
| 34       | $HNO_2 + OH \rightarrow H_2O + NO_2$ | $\alpha_{H_2O_2} = 5.95 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 35       | $NO + O \rightarrow NO_2$ | $\alpha_{NO_2} = 2.6 \times 10^{-12} \text{cm}^3/\text{molecules/s}$ |  
| 36       | $NO + HO_2 \rightarrow OH + NO_2$ | $\alpha_{NO_2} = 8.85 \times 10^{-13} \text{cm}^3/\text{molecules/s}$ |  
| 37       | $NO_2 + H \rightarrow H + NO_2$ | $\alpha_{NO_2} = 1.47 \times 10^{-10} \text{cm}^3/\text{molecules/s}$ |  
| 38       | $NO_2 + OH \rightarrow HNO_2$ | $\alpha_{HNO_2} = 8.81 \times 10^{-13} \text{cm}^3/\text{s}$ |  
| 39       | $NO_2 + O_2 \rightarrow NO + O_2$ | $\alpha_{NO_2} = 1.03 \times 10^{-15} \text{cm}^3/\text{molecules/s}$ |  
| 40       | $HO_2 + NO + NO_2$ | $\alpha_{NO_2} = 4.58 \times 10^{-12} \text{cm}^3/\text{molecules/s}$ |  
| 41       | $HNO_2 + OH \rightarrow H_2O + NO_2$ | $\alpha_{HNO_2} = 1.5 \times 10^{-13} \text{cm}^3/\text{s}$ |  

### Results

#### Theoretical Approaches - Chemical species generated in plume of $N_2$ plasma jet with $O_2$.

Various chemical species are generated from the $N_2$ plasma jet by changing the $O_2$ content in the plasma. The most predominant chemical species in the plasma jet is a metastable state $N_2(A^3\Sigma_u^+)$ of excited nitrogen molecules. The rate coefficient $\alpha_{N_2}$ is expressed as:

$$\alpha_{N_2}(T_e) = 2.25 \times 10^{-10} \sqrt{T_e} (6.8 + 2T_e) \exp \left(-\frac{6.8}{T_e}\right)$$

(1)

where, $T_e$ is the electron temperature in a unit of eV. Dissociation coefficient of $N_2$ by electrons is given by:

$$k_N(T_e) = 4.26 \times 10^{-10} \sqrt{T_e} (10 + 2T_e) \exp(-10/T_e)$$

(2)

Meanwhile, the dissociation coefficient of $O_2$ by electrons is given by:

$$k_O(T_e) = 1.03 \times 10^{-15} \sqrt{T_e} (30 + 2T_e) \exp(-10/T_e)$$

(3)
The rate coefficients in Eqs (1–3) increase drastically as the electron temperature \( T_N \) increases. The reaction coefficients in Eqs (1–3) are given by \( \alpha_N = 6.40 \times 10^{-12}, \) \( K_N = 1 \times 10^{-12}, \) and \( k_0 = 1.5 \times 10^{-11} \) cm\(^3\)/s for \( T_e = 1 \) eV, a typical value of non-thermal plasma.

The excited nitrogen molecules \( N_2^* \) return back to the ground state when contact with \( N_2, \) according to \( N_2 (A^2\Sigma_{u}^+) \rightarrow N_2 + N_2 \) with its reaction coefficient of \( \alpha_{N2} = 3 \times 10^{-18} \) cm\(^3\)/molecule/s\(^{16}\). The \( N_2^* \) returns back to the ground state in contact with \( O_2, \) according to \( N_2(A^2\Sigma_{u}^+) \rightarrow O_2 \) to products with its reaction coefficient of \( \alpha_{O_2} = 2.5 \times 10^{-12} \) cm\(^3\)/molecule/s\(^{10}\). The \( N_2^* \) disappears in contact with water molecules\(^{12}\) with a dissociation coefficient of \( \alpha_{O_2} = 5 \times 10^{-14} \) cm\(^3\)/s\(^{16}\). In these reactions, gas composition in jet is very important. If the ambient neutral density in the atmospheric pressure at room temperature is \( n_0, \) the \( N_2 \) and \( O_2 \) density in the entering gas can be expressed with oxygen mole fraction \( \xi. \) The \( O_2 \) density \( n_{O_2} \) is \( n_0 \) and the \( N_2 \) density \( n_{N_2} \) is \( (1 - \xi) n_0. \) When the water molecules from the water surface are entering into this mixed gas with its mole fraction of \( \zeta, \) the \( H_2O \) density \( n_{H_2O} \) is \( \zeta n_0. \) The rate equation of the metastable state density \( n_{N_2^*} \) can be calculated from

\[
\frac{dn_{N_2^*}}{dt} = \alpha_{N2^*}(1 - \xi)(1 - \zeta)n_p n_p - \left[ \alpha_{N2} (1 - \xi) + \alpha_{O_2} (1 - \xi) + \alpha_{OH} \xi n_p n_{N_2^*} \right]
\]

where \( n_p \) is plasma electron density. The saturation time constant \( \tau_{N_2^*} \) of the metastable state molecules is \( \tau_{N_2^*} = \frac{\alpha_{N2}(1 - \xi)n_0 + \alpha_{O_2}(1 - \xi)n_0 + \alpha_{OH} \xi n_0}{(1 - \xi) [ \xi n_{H_2O} + \xi n_{H_2O_2} ]}. \) Here, \( n_{H_2O_2} \) is the water density, and \( \tau_{N_2^*} \) is the flux of \( N_2 \) entering into water, when a nitrogen plasma jet injects to a water surface. The \( N_2 \) density \( n_{N_2} \) is \( (1 - \xi) n_0 \), the \( N_2 \) density \( n_{N_2} \) is \( (1 - \xi) n_0 \).

Penetration mechanism of \( N_2^* \) in a metastable state into water. We investigate the penetration properties of \( N_2^* \) entering into water, when a nitrogen plasma jet injects to a water surface. The \( N_2^* \) in the plasma jet may continuously bombard on the water surface, diffuse into water, and generate hydroxyl molecules through a reaction with water molecules\(^{11}\) with a dissociation coefficient of \( \alpha_{OH} = 5 \times 10^{-14} \) cm\(^3\)/s\(^{16}\). Then, the diffusion equation of the \( N_2^* \) in steady-state is given by

\[

\frac{dn_{N_2^*}}{dt} = \alpha_{N2^*}(1 - \xi)(1 - \zeta)n_p n_p - \left[ \alpha_{N2}(1 - \xi) + \alpha_{O_2}(1 - \xi) + \alpha_{OH} \xi n_p n_{N_2^*} \right]
\]

where \( n_p \) is plasma electron density. The saturation time constant \( \tau_{N_2^*} \) of the metastable state molecules is \( \tau_{N_2^*} = \frac{\alpha_{N2}(1 - \xi)n_0 + \alpha_{O_2}(1 - \xi)n_0 + \alpha_{OH} \xi n_0}{(1 - \xi) [ \xi n_{H_2O} + \xi n_{H_2O_2} ]}. \) Here, \( n_{H_2O} \) is the water density, and \( \tau_{N_2^*} \) is the flux of \( N_2^* \) defined by \( \Gamma_{N_2} = \nabla \cdot n_{N_2^*}. \) The symbol \( D \) is the diffusion constant of the \( N_2^* \).

\[
\frac{dn_{N_2^*}}{dt} = \alpha_{N2^*}(1 - \xi)(1 - \zeta)n_p n_p - \left[ \alpha_{N2}(1 - \xi) + \alpha_{O_2}(1 - \xi) + \alpha_{OH} \xi n_p n_{N_2^*} \right]
\]

The solution to Eq. (6) is \( n_{N_2^*} = n_{N_0} \exp(-\kappa n_{N_2^*}). \) The density decay length \( \lambda_N \) is calculated to be \( 15 \) nm. This means that all \( N_2^* \) will be instantaneously converted to hydroxyl and hydrogen atoms.

Generation of \( H_2O, HO_2, HO, \) and \( H_2O_2 \) molecules in water. The OH and H molecules that were formed from the disappearance of \( N_2^* \) at the water surface make consequence reactions to generate \( H_2O, HO_2, \) and \( H_2O_2. \) There are many ways to eliminate the \( H_2O \) in the water, including \( OH + H + M \rightarrow H_2O + M \) with its rate coefficient of \( \alpha_{H_2O} = 4.38 \times 10^{-30}(T_e/T)^2 \) cm\(^3\)/molecule/s from \( T = 300 \) K\(^{19}\) and \( H + O_2 + M \rightarrow H_2O + M \) with its reaction coefficient of \( \alpha_{H_2O} = 1.78 \times 10^{-15}(T_e/T)^3 \) cm\(^3\)/molecule/s from \( T = 300 \) K\(^{16}\) and \( \alpha_{H_2O} = 5.71 \times 10^{-32}(T_e/T)^4 \) cm\(^3\)/molecule/s from \( T = 300 \) K\(^{18}\). Here \( M \) is the neutral particles. There is a considerable difference of \( \alpha_{H_2O} \) in the references. However, we use \( \alpha_{H_2O} \) in ref.\(^{19}\) in the subsequent analysis. Some of the \( H_2O \) molecules generated from the \( N_2^* \) may diffuse into water, and some of them may diffuse into gas. But most of them may disappear, forming \( H_2O \) and \( H_2O_2, \) due to the very high concentration of \( OH \) molecules in the water surface. Therefore, in the steady-state case, the \( H_2O \) density can be calculated to be

\[
\alpha_{OH} n_{N_2} n_{H_2O} - \alpha_{H_2O} n_{OH} n_{H_2O} - \alpha_{H_2O} n_{H_2O} - \alpha_{H_2O} n_{H_2O} = 0
\]

where \( \alpha_{OH} \) is the ratio of OH density to the ambient air density \( n_0. \)

There are many ways of disappearance of hydroxyl molecules. The dominant reactions of OH eliminations are forming \( H_2O_2 \) with its reaction coefficient of \( \alpha_{H_2O_2} = 6.83 \times 10^{-31}(T_e/T)^8 \) cm\(^3\)/molecule/s from \( T = 300 \) K\(^{19}\), and combining with \( HO \) with its reaction coefficient of \( \alpha_{H_2O_2} = 4.8 \times 10^{-14} \) exp\((249/T) \) cm\(^3\)/s\(^{14}\). Therefore, in the steady-state case, we obtain:

\[
k_{OH}(T_e) = 4.2 \times 10^{-9} \exp(-5.6/T_e)
\]
\[ \alpha_{OH} n_{N2} + n_{H2O} - \alpha_{H2O} n_{OH} - \alpha_{H2O} n_{OH} = 0 \] (8)

The major sources of HO₂ radical composition are H + O₂ + M → HO₂ + M with its reaction coefficient of \( \alpha_{OH} = 4.6 \times 10^{-13} \) cm³/mole/s, and combination of OH and H₂O₂ with its reaction coefficient of \( \alpha_{H2O} = 1.7 \times 10^{-12} \) cm³/mole/s. The decay of HO₂ can be represented by OH + HO₂ → H₂O + O₂, with its reaction coefficient of \( \alpha_{H2O} = 4.8 \times 10^{-11} \exp(294/T) = 1.1 \times 10^{-10} \) cm³/mole/s, which is one of the major destruction mechanism of OH radical. The density of \( n_{H2O} \) radical in steady state can be obtained from:

\[ \alpha_{H2O} n_{H2O} + \alpha_{H2O} n_{H2O} - \alpha_{H2O} n_{OH} n_{H2O} = 0 \] (9)

The hydrogen peroxide (H₂O₂) molecules are generated from the hydroxyl combination of OH + OH + M → H₂O₂ + M, and are eliminated by reaction of OH + H₂O₂ → HO₂ + H₂O, which are balanced by \( \alpha_{H2O} n_{OH} = \alpha_{H2O} n_{OH} n_{H2O} \), so the normalized H₂O₂ density can be obtained as:

\[ x_{H2O2} = \frac{n_{H2O2}}{n_0} = \frac{(\alpha_{H2O}/\alpha_{H2O2})x_{OH}}{10 x_{OH}}. \] (10)

And the Eq. (9) is rewritten as to make the normalized HO₂ density as:

\[ \alpha_{H2O} n_{H2O} + \alpha_{H2O} n_{H2O}^2 - \alpha_{H2O} n_{OH} n_{H2O} = 0 \] (11)

\[ x_{H2O} = \frac{(\alpha_{H2O}/\alpha_{H2O2})x_{OH} + \alpha_{OH} x_{OH} (\alpha_{H2O2} x_{OH})}{10 x_{OH} + 0.026 x_{OH} \xi / x_{OH}}. \] (12)

However, when the hydroxyl density is very small, H₂O₂ may be generated from the reaction of HO₂ + HO₂ → H₂O₂ + O₂ with its reaction coefficient of \( \alpha_{H2O} = 1.24 \times 10^{-12} \) cm³/mole/s, and disappeared by the reaction of H₂O₂ + O → HO₂ + OH with its reaction coefficient of \( \alpha_{H2O} = 1.7 \times 10^{-12} \) cm³/mole/s, by H₂O₂ + OH → H₂O + O₂ with its reaction coefficient of \( 1 \times 10^{-11} \) cm³/mole/s, and by the reaction of H₂O₂ + H → OH + H₂O with its reaction coefficient of \( 4 \times 10^{-11} \) cm³/mole/s. Then normalized H₂O₂ density can be obtained as:

\[ x_{H2O2} = \frac{n_{H2O2}}{n_0} = \left[ \frac{(\alpha_{H2O}/\alpha_{H2O2})x_{OH} + \alpha_{H2O} x_{OH}^2 (\alpha_{H2O2} x_{OH})}{1 + 0.001 x_{OH} / (10 x_{OH} + 0.729 x_{H2O2} x_{OH} / (1 + 0.001 x_{OH} x_{OH} + 0.588 x_{H2O2} x_{OH} + 0.0247 x_{OH}^2 x_{OH})} \right]. \]

Making use of Eqs. (5, 7, 8 and 11), we obtain the normalized OH density equation as:

\[ x_{OH} = \frac{n_{OH}}{n_0} = \frac{b - c}{c + b} \]

where, the constants b and c are defined by:

\[ b = 4.7 \times 10^{-3} \xi ; \quad c = 1.76 \times 10^{-8} \left( 1 - \xi \right) \left( 1 - \xi \right) \eta \]

The meaningful solution of Eq. (13) is \( x_{OH} = n_{OH}/n_0 = \sqrt{b^2 + c} - c \).

Hydrogen atoms are generated through a reaction between the excited nitrogen and water molecules, and N + OH → NO + H, but the reaction between the excited nitrogen and water molecules prevails, due to the high concentration of water. The major elimination of H atoms is H + O₂ + M → HO₂ + M with its reaction coefficient of \( \alpha_{OH} = 5.71 \times 10^{-13} (T/300)^{1/2} \) cm³/mole/s, at \( T = 300 \) K, and forming water by hydrogen atom and hydroxyl with a reaction coefficient of \( \alpha_{H2O} = 1.1 \times 10^{-12} \) cm³/mole/s, establishing the hydrogen atom density of \( n_H = \alpha_{OH} n_{N2} \), which can be further simplified to:

\[ x_H = \frac{n_H}{n_0} = 5.89 \frac{(1 - \xi)(1 - \xi)}{(\xi + 108 x_{OH}) (\xi + 0.026 \xi) / x_{OH}} \] (15)

being the normalized H atom density.

Figure 1 shows plots of the normalized density of OH, H, and HO₂ molecules, \( x_{OH} x_{H} x_{OH} \), which are normalized by the neutral density at ambient air \( n_a = 2.6 \times 10^{19} \) cm⁻³. We assume the water density near the water surface is \( \xi = 0.60 \) (60%), where most of the OH molecules are generated and diffused into water. On the other hand, the H atoms participating in chemical reactions with O and N atoms are borne far away from the water surface, where the water density is about \( \xi = 0.25 \). The OH molecular density and H atom density decrease as the O₂ mole fraction \( \xi \) increases from zero to 0.25. On the other hand, the HO₂ density increases drastically as the \( \xi \) increases to 0.25.

**Generation of reactive NH, NH₂, and NH₃ molecules in water.** For generation of reactive nitrogen species (RNS), the generation of N atom is necessary. Electrons in the N₂ plasma generate N atoms by impact dissociation of N₂. The N atoms in the plasma jet may disappear according to the reaction of N + O₂ → NO + O with its reaction coefficient of \( \alpha_{NO} = 9.22 \times 10^{-15} \) cm³/mole/s, to the reaction of N + O → NO with its reaction coefficient of \( \alpha_{NO} = 2.39 \times 10^{-15} \) cm³/mole/s, to the reaction between hydroxyl and nitrogen atom with its reaction coefficient of \( \alpha_{NO} = 4.7 \times 10^{-11} \) cm³/mole/s, and to the reaction between hydrogen and nitrogen atoms with a reaction coefficient of \( \alpha_{NO} = 1.3 \times 10^{-12} \) cm³/mole/s. But most of the OH molecules and H atoms are generated near the water surface. On the other hand, the N atoms are generated at the beginning of plasma jet far away from the water surface. Therefore, the OH molecules and H atoms may not actively participate in the disappearance process of N atoms. Thus the rate equation of the nitrogen atom density \( n_N \) is calculated from
where the N atom density may not saturate in the plasma column, because of insufficient O₂ mole fraction. The rate equation of oxygen atom density $n_O$ is given by:

$$\frac{dn_O}{dt} = 2k_O(1 - \xi)(1 - \zeta)n_On_P - (\alpha_{O2N}\xi n_0 + \alpha_{NO}n_O)n_N$$

where, the O atom density also may not saturate in the plasma jet, continuously growing with time. Assuming the electron temperature of $T_e = 1$ eV, we find from the above two equations that the N and O atom normalized densities are $x_N = 2 \times 10^{-4} (1 - \xi)(1 - \zeta)n_0/\text{cm}^3$ and $x_O = 3 \times 10^{-3} (1 - \zeta)n_0/\text{cm}^3$ at $t = 100 \mu s$, respectively.

Figure 2 shows plots of the normalized nitrogen ($x_N$) and oxygen ($x_O$) atoms densities versus oxygen molecular mole fraction of $\xi$. As the oxygen molecular mole fraction of $\xi$ increases, the nitrogen atom density $x_N$ increases drastically. However, in the entire range of the oxygen mole fraction, the nitrogen atom density is almost constant.

The NH generation process is forming NH by combination of nitrogen and hydrogen atoms, while the major contributions to NH dissociation are the reaction between NH and hydroxyl forming HNO with a reaction coefficient of $\alpha_{HNO} = 3.32 \times 10^{-11} \text{cm}^3/\text{s}^{28}$, the reaction between NH and oxygen atom with the reaction coefficient of $\alpha_{OH} = 1.16 \times 10^{-11} \text{cm}^3/\text{molecules}/\text{s}^{28}$, and the reaction of NH + O₂ → Products with its reaction coefficient of $\alpha_{NO} = 9.98 \times 10^{-15} \text{cm}^3/\text{molecules}/\text{s}^{28}$, establishing the steady-state value of $n_{NH} = (\alpha_{NH}/\alpha_{HNO}) (n_Hn_N/n_O + \alpha_{OH}n_O/\alpha_{HNO} + \alpha_{NO}n_O/\alpha_{HNO})$ rather quickly; therefore, the normalized NH density is expressed...
as \( x_{\text{NH}_3} = 3.9 \times 10^{-2}, x_{\text{NO}_2} = 0.35 x_O + 0.0003 (1 - x_O) \), which is usually less than the N atom density. Combination of two NH molecules form NH2, with a reaction coefficient of \( \alpha_{\text{NH}_2} = 4.3 \times 10^{-13} \text{cm}^3/\text{molecules/s} \), and NH2 molecules are eliminated by reaction between NH2 and OH forming HNO2 with a reaction coefficient of \( \alpha_{\text{HNO}_2} = 9.31 \times 10^{-11} \text{cm}^3/\text{molecules/s} \), by the reaction of NH2 and O forming HNO with its reaction coefficient of \( \alpha_{\text{HNO}} = 7.47 \times 10^{-11} \text{cm}^3/\text{molecules/s} \), and by the reaction of O + NH2 – H2NOO with a reaction coefficient of \( \alpha_{\text{H}_2\text{NOO}} = 1.54 \times 10^{-15} \text{cm}^3/\text{molecules/s} \), leading to a steady-state value of \( n_{\text{H}_2\text{NOO}} = (\alpha_{\text{H}_2\text{NOO}}/\alpha_{\text{HNO}_2}) \left( n_{\text{H}_2\text{NOO}} + \alpha_{\text{H}_2\text{NOO}} n_{\text{O}} + \alpha_{\text{H}_2\text{NOO}} n_{\text{O}} n_{\text{H}} \right) \), which can be expressed as \( x_{\text{H}_2\text{NOO}} = n_{\text{H}_2\text{NOO}} / n_O = 4.62 \times 10^{-3} x_{\text{NH}_2}/(x_O + 0.8 x_O + 1.65 \times 10^{-2} (1 - x_O)) \). The ammonia molecules are generated from the reaction of H + NH2 – H2N with its reaction coefficient of \( \alpha_{\text{H}_2\text{N}} = 7.7 \times 10^{-11} \text{cm}^3/\text{molecules/s} \), and the reaction between HNO, and NH2 forming NH3 with its reaction coefficient of \( \alpha_{\text{H}_2\text{N}+} = 3.64 \times 10^{-13} \text{cm}^3/\text{molecules/s} \). Meanwhile, the ammonia may be eliminated by the reaction of NH3 and O with its reaction coefficient of \( \alpha_{\text{H}_2\text{N}+} = 4.69 \times 10^{-17} \text{cm}^3/\text{molecules/s} \), by the reaction between OH and NH3 with its reaction coefficient of \( \alpha_{\text{H}_2\text{N}+} = 1.6 \times 10^{-13} \text{cm}^3/\text{molecules/s} \), and by the reaction of NH2 and NO forming HNO2 with its reaction coefficient of \( \alpha_{\text{H}_2\text{NO}+} = 6 \times 10^{-18} \text{cm}^3/\text{molecules/s} \), leading to a steady-state value of the normalized ammonia density of \( x_{\text{NH}_3} = n_{\text{NH}_3}/n_O = 481(x_H + 0.0047 n_{\text{H}_2\text{NO}}) x_{\text{NH}_3} / (x_O + 0.000293 x_O) \), where \( x_{\text{H}_2\text{NO}} \) is the normalized density of nitric acid HNO2.

Figure 3 shows plots of the normalized densities of NH, NH2, and NH3 molecules in terms of the oxygen mole fraction of \( \xi \). Ammonia (NH3) is well generated in the N2 plasma, due to the abundance of H atoms. However, this compound disappears very quickly, as the O2 mole fraction increase. Nevertheless, ammonia generated in the nitrogen plasma jet dissolves into water forming ammonia water, which is a weak alkali.

**Figure 3.** Plots of normalized densities of NH, NH2, and NH3 molecules versus the oxygen mole fraction of \( \xi \). NH, NH2, and Ammonia (NH3) are well generated in the nitrogen plasma, due to the abundance of hydrogen atoms. However, as the oxygen mole fraction increases, they disappear very quickly. Nevertheless, ammonia generated in the nitrogen plasma jet dissolves into water forming ammonia water, which is a weak alkali.

**Generation of reactive NO, HNO2, and HNO3 molecules in water.** We must investigate the nitric oxide behaviors in the environment of high concentration of H atoms in the vicinity of the water surface. Nitric monoxide is formed by the reaction of N + OH – NO + H, by the reaction of N + O – NO + O, and by the reaction of NO + O – NO2 + O with its reaction coefficient of \( \alpha_{\text{NO}+} = 9.22 \times 10^{-17} \text{cm}^3/\text{molecules/s} \), but its disappearance may be the reaction of NO and H forming HNO with its reaction coefficient of \( \alpha_{\text{NO}H} = 1.56 \times 10^{-12} \text{cm}^3/\text{molecules/s} \), and the reaction of NO and OH forming HNO2 with a reaction coefficient of \( \alpha_{\text{NO}_{2}H} = 1.78 \times 10^{-14} \text{cm}^3/\text{molecules/s} \). In this case, the nitrogen monoxide density is given by \( n_{\text{NO}} = (\alpha_{\text{NO}+}/\alpha_{\text{NO}H}) n_{\text{OH}} + n_O + \alpha_{\text{NO}_{2}H} n_O n_{\text{H}} / (n_O + \alpha_{\text{NO}_{2}H} n_O n_{\text{H}} + \alpha_{\text{NO}H} n_{\text{O}} n_{\text{H}} + \alpha_{\text{NO}_{2}H} n_O n_{\text{H}}) \), which can be expressed as \( x_{\text{NO}} = 30.1 x_O + 0.0051 x_O + 0.000002 x_O / (x_H + 11.4 x_O + 1.67 x_O) \). The nitrous acid HNO2 is destroyed due by the reaction of HNO2 and OH with a reaction coefficient of \( \alpha_{\text{H}_2\text{NO}_{2}+} = 5.95 \times 10^{-15} \text{cm}^3/\text{molecules/s} \), resulting to the steady-state value of the HNO2 density of \( n_{\text{H}_2\text{NO}_{2}} = 3 n_{\text{NO}} \). The leading reactions of NO2 formation are the reaction of NO + O – NO2 + O with its reaction coefficient of \( \alpha_{\text{NO}_{2}} = 2.6 \times 10^{-12} \text{cm}^3/\text{molecules/s} \), the reaction between HNO2 and OH forming NO3, and the reaction of HNO2 and O forming NO3, with their reaction coefficient of \( \alpha_{\text{H}_2\text{NO}_{2}+} = 8.85 \times 10^{-12} \text{cm}^3/\text{molecules/s} \). The leading elimination of NO3 is the reaction of NO3 and H with its reaction coefficient of \( \alpha_{\text{OH}_{3}+} = 1.47 \times 10^{-16} \text{cm}^3/\text{molecules/s} \), and the reaction of NO3 with OH forming HNO3, with its reaction coefficient of \( \alpha_{\text{H}_2\text{O}_{3}H} = 8.81 \times 10^{-11} \text{cm}^3/\text{molecules/s} \), the reaction of NO3 + O – OH3 + NO with its reaction coefficient of \( \alpha_{\text{O}_{2}H} = 1.03 \times 10^{-11} \text{cm}^3/\text{molecules/s} \), and the reaction of H2O3 + NO3 – H2O3NO3, with its reaction coefficient of \( \alpha_{\text{H}_2\text{O}_{3}H} = 4.58 \times 10^{-12} \text{cm}^3/\text{molecules/s} \). Therefore, the steady-state value of NO2 density is given by \( n_{\text{NO}_2} = (\alpha_{\text{H}_2\text{O}_{3}H}/\alpha_{\text{OH}_{3}+}) (3 n_{\text{OH}} + 3 n_{\text{O}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} n_{\text{H}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} n_{\text{H}} n_{\text{O}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} n_{\text{H}} n_{\text{O}} n_{\text{H}}) / n_{\text{NO}} n_{\text{H}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} n_{\text{H}} + \alpha_{\text{H}_2\text{O}_{3}H} n_{\text{O}} n_{\text{H}} n_{\text{O}} n_{\text{H}} \), which is expressed as \( x_{\text{NO}_2} = 0.0405 (3 x_O + 0.437 x_O + 1.5 x_{\text{NO}_2} x_O + 0.6 x_O + 0.07 x_O + 0.0312 x_O) \). The nitric acid (HNO3) can be eliminated by the reaction of HNO3 with OH forming NO3, with a reaction coefficient of \( \alpha_{\text{H}_2\text{O}_{3}H} = 1.5 \times 10^{-13} \text{cm}^3/\text{molecules/s} \), leading to \( x_{\text{H}_2\text{O}_{3}H} = 587 x_{\text{NO}_2} \) and resulting in a very high concentration of nitric acid. We remind the reader that the H atom density \( n_{\text{H}} \) is very high for a small mole fraction of oxygen, so that in general, the nitric oxide densities for a small mole fraction of O2 are very low. Therefore, the nitric acid density of \( n_{\text{HNO}_3} \) is low for a small mole fraction of oxygen. On the other hand, the nitric acid density at a high mole fraction of O2 is very high for a high value of nitric oxide density.

Figure 4 shows estimations of the nitric acid compounds in terms of the O2 mole fraction. The nitric acid density \( x_{\text{HNO}_3} \) is low at a small mole fraction of oxygen, but its intensity increases to a peak value of around \( \xi \approx 0.2 \), and then decreases, as the \( \xi \) increases. Meanwhile, the densities of HNO3 and NO are at moderate levels in the
the densities of HNO\(_2\) and NO are at a moderate level. The entire range of the oxygen mole fraction shows the expression in Eq. (14) in terms of the O\(_2\) mole fraction \(\xi\). The theoretical result obtained from Fig. 4 at a very small value of the O\(_2\) mole fraction \(\xi\) is 10\(^{-4}\), being alkali. On the other hand, the intensity of nitric acid is strong for the O\(_2\) mole fraction of \(\xi \geq 0.01\), turning the plasma activated water to acidic.

**Experimental Approaches**

We compare the theoretical results with the experimentally measured data. Figure 5 is a plot of the OH density in deionized water activated by the N\(_2\) plasma jet. Most of the hydroxyl molecules are generated at water surface, and some of them can penetrate into water. We do not know what fraction of hydroxyl molecules are injected into the water. Therefore, the theoretical result obtained from \(x_{OH} = n_{OH}/n_0 = \sqrt{b^2 + c - b}\) is least-squared-fitted to the experimental data, where the symbols \(b\) and \(c\) are expressed in Eq. (14) in terms of the O\(_2\) mole fraction \(\xi\). Typical error bar is shown in the data at \(\xi = 0.003\), where the size of the error bar due to the experimental process is about 8% of its measurement value. Every experimental datum was determined by three times of measurements. Figure 5 clearly shows that the hydroxyl density is strong at a small \(\xi\), but it quickly disappears as \(\xi\) increases to 0.2, corresponding to the O\(_2\) mole fraction of air.

Figure 6 is the experimental data of the NH\(_4\)\(^+\) ion concentration in water in terms of the O\(_2\) mole fraction \(\xi\). Based on a previous report [38], we assume that the ammonia of NH\(_3\) may dissolve into water forming ammonia water, where NH\(_4\)\(^+\) ions may be generated. The concentration of NH\(_4\)\(^+\) ions plays an important role in determination of pH value in water. Therefore, the theoretical result (curve) of ammonia obtained from \(x_{NH_3} = n_{NH_3}/n_0 = 481(x_{OH} + 0.0047n_{HNO_3})x_{H_2O_2}/(x_{OH} + 0.000293x_{n})\) or from Fig. 3 will be least-squared-fitted to the experimental data of NH\(_4\)\(^+\) concentration. The vertical axis in the right represents the ammonia concentration in the plasma jet in ppm unit. The typical error bar is shown in the data at \(\xi = 0.01\), where the size of the error bar due to the experimental process is about 11% of its measurement value. The experimental data follows the trend of the theoretical results. The ammonia concentration decreases as \(\xi\) increases to 0.2.

Figure 7 is the experimental data of the NO\(_2\) ion concentration in water, in terms of the O\(_2\) mole fraction \(\xi\). The theoretical results (curve) obtained from Fig. 4 in terms of HNO\(_3\) are also plotted in this figure, reasonably assuming that the nitric acid of HNO\(_3\) is dissolving into water. The theoretical results are least-squared-fitted to the experimental data. The typical error bar is shown in the data at \(\xi = 0.05\), where the size of the error bar due to the experimental process is about 10% of its measurement value. It is obvious from Fig. 7 that the experimental data and theoretical result indicate the increase of nitric acid as \(\xi\) increases to 0.2. However, the theoretical curve in Fig. 4 indicates that as the \(\xi\) increases beyond 0.2, the nitric acid (HNO\(_3\)) decreases drastically.

One of the most important reactive chemicals in water is the H\(_2\)O\(_2\) generated from N\(_2\) plasma jet. Figure 8 shows a plot of the measurement data (dots) of the H\(_2\)O\(_2\) in water activated by a N\(_2\) plasma jet with changing O\(_2\) mole fraction of \(\xi\). The theoretical curve obtained from \(x_{H_2O_2} = n_{H_2O_2}/n_0 = [10x_{OH} + 0.729x_{HNO_2}/x_{OH}]/(1 + 0.001x_{OH} + 0.588x_{HNO_2}/x_{OH} + 0.0247y_{H_2O_2}/x_{OH})\) is least-squared-fitted to the experimental data. The typical error bar is shown in the data at \(\xi = 0.005\), where the size of the error bar due to the experimental process is about 9% of its measurement value. The intensity of the H\(_2\)O\(_2\) is very high at a small value of \(\xi\), where a relatively high intensity of hydroxyl generates H\(_2\)O\(_2\), as expected from Fig. 1. But similar to the hydroxyl density, its intensity decreases.
as $\xi$ increases. However, the $\text{H}_2\text{O}_2$ density increases again as $\xi$ increases to a large value. The rebounding increase of $\text{H}_2\text{O}_2$ at a large value of $\xi$ is caused by a strong surge of $\text{HO}_2$ molecules shown in Fig. 1, which generate $\text{H}_2\text{O}_2$ molecules. Therefore, the density of $\text{H}_2\text{O}_2$ decreases, reaches its minimum value at $\xi = 0.05$, and then increases again, as the $\xi$ increases from a small value to a large value. The experimental data follow the trend of the theoretical results. As the oxygen mole fraction increases to $\xi = 0.2$, the ammonia concentration decreases.

Discussion

The purpose of this study is the investigation of the influence of $\text{O}_2$ on the generation of reactive chemical species from a $\text{N}_2$ plasma jet near a water surface. The most abundant reactive species in a $\text{N}_2$ plasma jet is the excited

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**Figure 5.** Plot of hydroxyl density in deionized water activated by the nitrogen plasma jet versus the oxygen mole fraction of $\xi$. Dots in the figure are the experimental data from the averaged value of three times of measurements. The hydroxyl molecules are mostly generated at water surface, and some of them can penetrate into water. The theoretical result (curve) obtained from $x_{\text{OH}} = n_{\text{OH}}/n_0 = \sqrt{b^2 + c - b}$ is least-squared-fitted to the experimental data, where the symbols $b$ and $c$ are expressed in Eq. (14) in terms of the oxygen mole fraction $\xi$. The typical error bar is shown in the data at the oxygen mole fraction $\xi = 0.003$, where the size of the error bar due to the experimental process is about 8% of its measurement value. At a small mole fraction of oxygen, the hydroxyl density is strong; but as the oxygen mole fraction increase to 0.2, corresponding to the oxygen mole fraction of air, it quickly disappears.

**Figure 6.** Plot of experimental data of $\text{NH}_4^+$ ion concentration in water versus oxygen mole fraction of $\xi$. The ammonia of $\text{NH}_3$ may dissolve into water forming ammonia water, where $\text{NH}_4^+$ ions may be generated. The theoretical result (curve) of ammonia obtained from $x_{\text{NH}_3} = n_{\text{NH}_3}/n_0 = 481(x_{\text{H}} + 0.0047n_{\text{H}_2}\text{O}_3)x_{\text{OH}}/\left(x_{\text{OH}} + 0.000293x_{\text{O}}\right)$ or from Fig. 3 is least-squared-fitted to the experimental data of $\text{NH}_4^+$ concentration. The typical error bar is shown in the data at the oxygen mole fraction $\xi = 0.01$, where the size of the error bar due to experimental process is about 11% of its measurement value. The experimental data follows the trend of the theoretical results. As the oxygen mole fraction increases to $\xi = 0.2$, the ammonia concentration decreases.
nitrogen molecules in the metastable state of N$_2^*$, which in turn dissociate water molecules, generating hydroxyl (OH) molecules and hydrogen atoms near the water surface. A presence of oxygen molecules may obstruct the dissociation mechanism of water molecules by the excited nitrogen molecules. In this regard, we theoretically and experimentally investigate the reactive chemical species in nitrogen plasma by changing the O$_2$ mole fraction of $\xi$.

Various chemical compounds are fabricated from N$_2^*$ and water molecules in plasma jet with varying O$_2$ content. Detailed theoretical investigation of these chemical compounds is carried out in terms of different O$_2$ content. Hydroxyl molecules and hydrogen atoms are well fabricated near the water surface by a nitrogen plasma jet without oxygen. But Fig. 1 shows that the densities of those species decrease as $\xi$ increases. On the other hand, the density of the hydrogen dioxide increases drastically as $\xi$ increases, turning the hydroxyl molecules into water. Due to the high density of hydrogen atoms, the ammonia intensity is relatively high at a small value of $\xi$. But Fig. 3 shows that the ammonia density ($\lambda$NH$_3$) decreases drastically as $\xi$ increases. Nitrogen monoxide (NO) is one of the important molecules related to a signaling material in cells. Figure 4 shows that the density of nitrogen monoxide is at a moderate level over the entire range $\xi \leq 0.2$. Nitric acid (HNO$_3$) starts from a negligibly small value, increases to a peak value at $\xi \approx 0.2$, and then decreases, as $\xi$ increases to a large value.

Electrons in plasma jet may have active roles in electron-impact ionization, excitation, dissociations, etc. There are hundreds chemical reactions of N, H, O elements in "plasma and humid air" or "plasma at water boundary" with electrons involved. Some of these reactions may play important roles. Investigating all of these reactions may be beyond the scope of this article. We therefore consider the most important reactions associated with negative affinity of oxygen. As a first example, water molecules made of oxygen may undergo a dissociative...
Attachment by the reaction of $e + H_2O \rightarrow H^+ + OH$ with the dissociative-attachment coefficient of $\alpha_{da}$. This reaction is important because of hydroxyl production. However, the excitation cross section of nitrogen molecules is one order in magnitude larger than the dissociative-attachment cross section of water, thereby estimating to be $\alpha_{SE} = 6.4 \times 10^{-12} \text{cm}^3/\text{s}$ and $\alpha_{da} = 9 \times 10^{-13} \text{cm}^3/\text{s}$ at $T_e = 1 \text{ eV}$. The dominant gas in the plasma jet is nitrogen molecules so that the density of the metastable state $N_2^*$ is $2.6 \times 10^{16}/\text{cm}^3$ due to a long lifetime, dissociating water molecules by reaction of $N_2(A_3 \Sigma_u^+)$ and $H_2O$ with a dissociation coefficient of $\alpha_{OH} = 5 \times 10^{-14} \text{cm}^3/\text{s}$. The other important reaction of the electron affinity is the dissociative attachment of oxygen molecules by $e + O_2 \rightarrow \text{O}^+ + \text{O}$ with dissociative attachment coefficient of $k_{da}$ which is less than one fifth of $k_d$ in Eq. (3) at $T_e = 1 \text{ eV}$.

Experimental measurements of the reactive chemical species in the plasma activated water were also carried out by comparison with the theoretical results. This identified that hydroxyl molecules are mostly generated at water surface, and some of them can penetrate into water. The hydroxyl molecular density reaches its maximum without oxygen, and decreases to zero, as $\xi$ increases to 0.25, showing that the theoretical prediction agrees reasonably well with the experimental data. The theoretical results and experimental data also indicate that the density of the ammonia of NH$_3$ also decreases as $\xi$ increases to 0.25. On the other hand, theory and experiment show that the density of the NO$_3$ increases drastically as $\xi$ increases to 0.25. The density of hydrogen peroxide in plasma activated water was measured. The hydrogen peroxide density decreases, reaches its minimum value at $\xi = 0.05$, and then increases again, as $\xi$ increases from a small value to a large value. Although the experimental data of the hydrogen peroxide follow the theoretical trend, there are considerable deviations from the theoretical curve. Further study is therefore recommended in future to resolve this difference. The pH value of the water activated by the N$_2$ plasma jet is experimentally measured. The pH value of the plasma activated water, which is slightly alkali without oxygen, decreases to three as $\xi$ increases to 0.25, which can be expected by the nitric acid in Fig. 4, and was also confirmed by experiments. The pH of ambient air is about 0.2, so that the pH value of water activated by the air plasma is acidic, with $pH \approx 3$.

**Method**

**Generation of the nitrogen plasma jet.** A nonthermal plasma device is operated at atmospheric pressure inside a vacuum chamber filled with N$_2$ gas. The plasma jet system is powered by a 60 Hz AC power supply using a neon transformer (FPN-1000, Daekwang Electric Co.). The inner electrode is a stainless-steel cylinder with an inner and outer diameters of 1.2 mm and 1.4 mm respectively, which is covered by a quartz tube with an outer diameter of 3.2 mm. The outer electrode is fabricated from stainless steel, and is centrally perforated with a hole of 1 mm, through which the plasma jet is ejected to the water surface in a dish surrounded by N$_2$ gas. The microdischarges in the porous alumina between inner and outer electrodes evolved into a plasma jet as the applied power increased. Significant changes in the discharge voltage and current waveforms were observed during the process of the evolution to the plasma jet. The current pulses were of short durations of 30–100 ns in the close-up image. They had repetition rates of 10–400 kHz and amplitudes reaching a few amperes and the discharge voltage of a few kV. This indicates that even at a frequency as low as 60 Hz, the plasma that evolves from a large amount of microdischarge inside a porous dielectric can have characteristics that are similar to those generated at several hundreds of kilohertz. The ratios of nitrogen and oxygen gases are controlled by a mass flow controller (GMC 1200, Atovac), and the total gas flow rate through the device is 1 liter per minute (lpm). In order to avoid the

![Figure 9](image-url)
influence of O$_2$ in the surrounding air, the experiment is carried out in a glove box, where the O$_2$ concentration is kept at less than 1%.

One of the most important issues in plasma jet is plasma properties represented by the electron temperature $T_e$ and density $n_e$, which can vary very sensitively by oxygen mole fraction. The electron temperature increases as the oxygen mole fraction increases, whereas the electron density decreases instead. The electron temperature $T_e$ and density $n_e$ may also be functions of measurement time and space in the plasma jet. We measured the electron temperature and density very close to the jet injection point near the electrodes. The electron temperature $T_e$ is measured to be approximately 0.5 eV for $\xi = 0$ and 1.5 eV for $\xi = 0.2$, consistent to data in refs.\cite{42,43}, whose experimental setups are very similar configuration to the present experiment. We therefore assume the electron temperature to be $T_e = 1$ eV in analytical calculation in our theoretical model. On the other hand, the plasma electron density varies in wide range according to the measurement point in the plasma jet, although the plasma density decreases drastically as the oxygen mole fraction increases, as expected. The electron density for $\xi = 0.2$ (air) is significantly less than that for $\xi = 0$ (nitrogen only) and is localized near electrodes even for higher discharge voltage due to electron attachment of oxygen molecules. The theoretical results in the analytical calculation based on the assumption of the electron density to be $n_e = 10^{15}$ cm$^{-3}$ are least-square-fitted to the experimental data in qualitative comparison, observing agreement between theoretical trend and experimental data. A study of plasma evolution in time and space for a given oxygen mole fraction is beyond the scope of present research and will be left for future work for customized investigation of individual experimental configurations.

Measurement of various chemical species and their pH values in water. The deionized (DI) water is deoxygenized by N$_2$ purging before experiments, and 1 ml DI water is placed 5 mm below the electrode. DI water is treated with nonthermal plasma for 3 minutes, and the concentrations of OH∙, H$_2$O$_2$, NO$_2$ and NO$_3$ are measured. For OH⁻ radical measurement, tert-butyl alcohol (TBA) that specifically reacts with OH⁻ to become fluorescent hydroxyl-terephthallic (HTA) is used. Both TBA (185361, Sigma-Aldrich Co) and HTA (752525, Aldrich) are solved in 35 mM NaOH solution to make 10 mM solutions, and the diluted HTA solution in TA solution is used as a standard to quantify OH⁻ impinging on the TA solutions. The fluorescence intensity is measured using a spectrophotometer with a filter set of 340/420 nm (ex/em). For H$_2$O$_2$ measurement, Amplex UltraRed reagent (A36006, Invitrogen) is used following the manufacturer’s protocol. NO$_3$ ion concentration is measured using a spectrophotometer with a filter set of 340/420 nm (ex/em). For H$_2$O$_2$ measurement, Amplex UltraRed reagent (A36006, Invitrogen) is used following the manufacturer’s protocol. NO$_3$ ion concentrations are detected by ion chromatography method.

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Acknowledgements
This research was supported by Leading Foreign Research Institute Recruitment Program through the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (NRF-2016K1A4A3914113), and funded by NRF (NRF-2016R1A1A05005431). This work was also partially supported by Korea Technology Information Promotion Agency (SME-C0566231).

Author Contributions
H.S.U. and S.H.K. wrote the manuscript, performed the study and interpreted the results. K.Y.B. and E.H.C. supervised the study and provided assistance with experiment. E.H.C. contributed the materials.

Additional Information
Competing Interests: The authors declare no competing interests.

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