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

Hayato Kawanami¹, Kohki Satoh¹,², Hidenori Itoh¹, Hideki Kawaguchi¹ (Muroran I. T.)
Igor Timoshkin³, Martin Given³ and Scott MacGregor³ (University of strathclyde)

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### Background

#### Plasma-treated water

- Many kinds of species are produced in plasma.
- Precursors of ROS/RNS can be produced in the discharge plasma in gas phase.
- These precursors dissolve into the water, and then $\text{H}_2\text{O}_2$, $\text{NO}_x^-$, etc., are produced.

![Diagram of discharge and water interaction](image)

#### Applications of plasma-treated water

- Kitano et al.\(^1\) and Takaki\(^2\) applied the plasma treated water for disinfection\(^1\) and stimulation of germination and plant growth\(^2\).

  ![Orange arrow](image)

  In these applications, $\text{H}_2\text{O}_2$ and $\text{NO}_x^-$ in the water play an important roll.

- For the effective use of the plasma-treated water in these applications, it is important to clarify the mechanism of $\text{H}_2\text{O}_2$ and $\text{NO}_x^-$ production.

### Objective

**To investigate the production processes of $\text{H}_2\text{O}_2$ and $\text{NO}_x^-$ in water exposed to a DC corona discharge.**

- We generated the DC corona discharge above deionised-water, and then investigate $\text{H}_2\text{O}_2$ and $\text{NO}_x^-$ concentrations.
- We also deduced the production processes of the $\text{H}_2\text{O}_2$ and $\text{NO}_x^-$.  

\(^1\) K. Kitano *et al.*: The 60th JSAP Spring Meeting, 29p-B7-8 (2013)  
Experimental set up & conditions

- **Background Gas**
  - Ar:O₂ = 40:60, 60:40, 80:20%
  - N₂:O₂ = 40:60, 60:40%
  - Flow rate: 2 L/min

- **Comb-shaped electrode**: comb-tooth clusters, each of which has 26 comb-tooth
- **Deionized water**: 100 mL
- **Distance between comb electrode and water**: 15 mm

- **Polarity**: Positive
- **Applied voltage**: ±14.7 ~ 15.4 kV
- **Discharge current**: 0.39 ~ 0.41 mA
- **Input power**: 6 W
- **Exposure time**: 15 min
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- Ar:O₂ = 40:60, 60:40, 80:20 %
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- Flow rate: 2 L/min

Sampling time: 3, 6, 9, 12 and 15 min
Chromatogram

The flow of HPLC analysis

- Liquid sample
- Column Separation
- Detector UV absorption

- retention time from injection to detection
- peak area concentration

Calibration using peak area

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Calibration using peak area
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Chromatogram of samples taken from the reactor

- **Ar-O$_2$ atmosphere** → only H$_2$O$_2$
- **N$_2$-O$_2$ atmosphere** → H$_2$O$_2$, NO$_2^-$ and NO$_3^-$
Increase of input energy

- $\text{H}_2\text{O}_2$ and $\text{NO}_3^-$ concentrations monotonously increase.
- $\text{NO}_2^-$ concentration is very low.
Increase of input energy

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- $\text{NO}_2^-$ concentration is very low.

At higher content of Ar or N$_2$

- $\text{H}_2\text{O}_2$ and $\text{NO}_3^-$ concentrations tend to increase.
**H₂O₂ production**

### Production of H₂O₂

- **OH + OH → H₂O₂**
- **O₃ + H₂O → H₂O₂ + O₂**

### Production of OH & O₃

- **H₂O + e(fast) → OH + O + e(slow)**
- **O₂ + e(fast) → O + O + e(slow)**
- **O + O₂ + M → O₃ + M**

**Higher content of Ar or N₂ in BG gas**

- H₂O₂ → increase
- O₃ → approximately equal

**H₂O₂ produced by O₃ may be constant.**

**H₂O₂ is mainly produced by OH.**
Photographs of discharge in Ar-O$_2$ and N$_2$-O$_2$ atmosphere

**H$_2$O$_2$**

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>H$_2$O$_2$ concentration (ppm)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Ar:O$_2$</td>
</tr>
<tr>
<td>40:60</td>
<td>3.70</td>
</tr>
<tr>
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<td>5.42</td>
</tr>
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<td>80:20</td>
<td>9.08</td>
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</table>

exposure time = 15 min
Photographs of discharge in Ar-O₂ and N₂-O₂ atmosphere

At high mixture ratio of Ar or N₂, corona discharge tends to extend.

The production of OH is promoted by following reaction,

\[
\text{H}_2\text{O} + \text{e} (\text{fast}) \rightarrow \text{OH} + \text{O} + \text{e} (\text{slow})
\]

The concentration of H₂O₂ increases.

\[
\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2
\]
Pollutant concentration (ppm)

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**Emission intensity**

- Ar-O₂ < N₂-O₂

⇒ The amount of OH in N₂-O₂ atmosphere must be larger than Ar-O₂ atmosphere.

**But**

The concentration of H₂O₂ in N₂-O₂ atmosphere is lower than that in Ar-O₂ atmosphere.

⇒ In N₂-O₂ atmosphere, OH is consumed for production of HNO₃

NO₂ + OH → HNO₃
NO$_3^-$ production

![Graph showing NO$_3^-$ production as a function of input energy and absorbance spectrum.](image)
**NO$_3^-$ production**

**Production of N$_2$O**

- $\text{HNO} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$
- $\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O}$
- $\text{N}_2 + \text{O} + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$

**Production of NO$_3^-$**

- $\text{HNO}_3 \rightarrow \text{NO}_3^- + \text{H}^+ \text{ (in water)}$
- $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$
**NO₃⁻ production**

**Production of N₂O**

\[
\text{HNO} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O} \\
\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O} \\
\text{N}_2 + \text{O} + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}
\]

**Production of NO₃⁻**

\[
\text{HNO}_3 \rightarrow \text{NO}_3^- + \text{H}^+ \text{ (in water)} \\
\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3
\]

N₂O may be produced by NO₂ so that NO₂ probably exist in the plasma in gas phase.

\[\downarrow\]

HNO₃ may be produced by NO₂.

\[\downarrow\]

NO₃⁻ can be produced by dissolving HNO₃ into water.
Conclusions

- We generated a DC corona discharge above water, measured H$_2$O$_2$ and NO$_x^-$ concentrations in the water, and deduced production processes of H$_2$O$_2$ and NO$_x^-$ in the water.

- H$_2$O$_2$ can be produced from OH through the following reactions.
  
  \[
  H_2O + e \rightarrow OH + H + e 
  \]
  
  \[
  OH + OH \rightarrow H_2O_2 
  \]

- H$_2$O$_2$ produced by O$_3$ is constant.

  \[
  O_3 + H_2O + e \rightarrow H_2O_2 + O_2 
  \]

- At higher content of Ar or N$_2$, discharge tends to extend; therefore, the production of H$_2$O$_2$ is promoted.

- In N$_2$-O$_2$ atmosphere, OH is consumed for the production of HNO$_3$ so that H$_2$O$_2$ concentration is lower than that of Ar-O$_2$ atmosphere.

  \[
  NO_2 + OH \rightarrow HNO_3 
  \]
Thank you for your attention.