Investigation of Active Species in Atmospheric-pressure Argon Plasma-jet

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Background & Objective

Plasma-jet

- Plasma is generated between electrodes by a dielectric barrier discharge in a tube.
- The plasma is pushed out of the tube by feed gas, allowing the plasma to reach a solid and liquid surface easily.

Plasma-jet can be applied to plasma medicine\(^1\) and disinfection\(^2\).

ROS/RNS (Reactive Oxygen Species/Reactive Nitrogen Species) such as OH, H\(_2\)O\(_2\) and NO\(_x\) are regarded as important species, and these are produced by dissolving of active species produced in plasma-jet in a liquid.

Objective

To investigate active species in plasma-jet and ROS/RNS in deionised-water exposed to the plasma-jet.

- We generated an Ar plasma-jet, and carried out the optical emission spectroscopy of the plasma-jet on the central axis of the plasma-jet. We also measured spatially resolved optical emission spectra along the plasma-jet.
- We exposed deionised-water to the plasma-jet, and analysed ROS/RNS dissolved in the deionised-water using liquid chromatograph.

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\(^{1}\) S. Hamaguchi: J. Plasma Fusion Res., 87, 10 (2011) 696
Experimental apparatus & conditions

- **Ar (10 L/min)**
- Copper tube (\(\phi 3 \times 2\) mm)
- Aluminium sheet
- 10 mm
- Air (0 or 0.1 L/min)
- Glass tube (\(\phi 6 \times 3\) mm)
Experimental apparatus & conditions

Power supply
- Applied voltage: AC 13 kV
- Frequency: 17 kHz
- Input power: 4 W

Photograph
- Before
- Ar
- Ar/Air

Diagram:
- Copper tube (φ 3 x 2 mm)
- Aluminum sheet
- Glass tube (φ 6 x 3 mm)
- Ar (10 L/min)
- Air (0 or 0.1 L/min)

Voltage and time graph:
- Voltage vs. time for AC supply.
Experimental apparatus & conditions

**Power supply**
- Applied voltage: AC 13 kV_{p-p}
- Frequency: 17 kHz
- Input power: 4 W

![Voltage waveform](image)

**Photograph**
- before
- Ar
- Ar/Air

![Photograph](image)

**Spectrometre**
- VIS/IR region
  - resolution: 0.31 nm
  - range: 660 ~ 1070 nm
- UV/VIS region
  - resolution: 0.33 nm
  - range: 230 ~ 670 nm
Experimental apparatus & conditions

**Power supply**
- Applied voltage: AC 13 kV\textsubscript{p-p}
- Frequency: 17 kHz
- Input power: 4 W

**Voltage vs Time Graph**

**Photograph**
- Before
- Ar
- Ar/Air

**Spectrometre**
- VIS/IR region
  - Resolution: 0.31 nm
  - Range: 660 ~ 1070 nm
- UV/VIS region
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  - Range: 230 ~ 670 nm
Experimental apparatus & conditions

Power supply
- Applied voltage: AC 13 kV_{p-p}
- Frequency: 17 kHz
- Input power: 4 W

Photograph
- before
- Ar
- Ar/Air

HPLC condition
- column: IC NI-424
- eluent: CH₃COOH (3.0 mmol/L) + KOH (2.25 mmol/L) (pH = 5.6)
- detector: UV (at 220nm)
- sampling time: 3, 6, 9, 12, 15 min

Ar (10 L/min)
- copper tube (φ 3 x 2 mm)
- aluminium sheet
- glass tube (φ 6 x 3 mm)
- Air (0 or 0.1 L/min)

High Performance Liquid Chromatograph
- Vial
- Autosampler

Ar/Air
- 15 mm
- 65 mm
- deionised water (200mL)
1. Optical emission spectroscopy of the plasma-jet
Emission spectra (in VIS/IR region)

- Ar I (4p → 4s)
- O (3p → 3s)

In Ar:
- Ar I(4p), O(3p)

In Ar/Air (= 100/1):
- Ar I(4p), O(3p)
Emission spectra (in UV/VIS region)

**in Ar**

Ar I(4p, 5p), O(3p), N\(_2\)(C\(^3\)Π\(_u\)), OH(A\(^2\)Σ\(^+\))

**in Ar/Air (= 100/1)**

Ar I(4p, 5p), O(3p), N\(_2\)(C\(^3\)Π\(_u\)), OH(A\(^2\)Σ\(^+\)), NO(A\(^2\)Σ\(^+\))
Spatially resolved emission intensity (Ar, N\textsubscript{2}, OH)
Spatially resolved emission intensity (Ar, N\textsubscript{2}, OH) in Ar

- **Between electrodes**
  \[
  \text{Ar} + e_{\text{fast}} \rightarrow \text{Ar}^\ast(\text{meta}) \text{ or } \text{Ar}^\ast + e_{\text{slow}} \quad (\varepsilon = 11.6 \text{ eV})
  \]

- **Inside of tube**
  \[
  \text{Ar}^\ast \leftrightarrow \text{Ar}^\ast(\text{meta}) + h\nu
  \]

- **Outside of tube (surface of plasma-jet)**
  \[
  \text{N}_2(X) + \text{Ar}^\ast(\text{meta}) \rightarrow \text{N}_2(C) + \text{Ar} \quad (\varepsilon = 11.0 \text{ eV})
  \]
  \[
  \text{H}_2\text{O} + \text{Ar}^\ast(\text{meta}) \rightarrow \text{OH}(A) + \text{H} + \text{Ar} \quad (\varepsilon = 9.1 \text{ eV})
  \]

  - Collision probability between \text{Ar}^\ast(\text{meta}) and ambient air increases with the distance.
  - The density of \text{Ar}^\ast(\text{meta}) decreases and the densities of \text{N}_2 and \text{OH} increase with the distance by energy transfer from \text{Ar}^\ast(\text{meta}) to ambient air.

  ![Diagram](image)

  The emission intensity of \text{Ar} monotonously decreases, and the emission intensities of \text{N}_2 and \text{OH} increase and then decrease.
Spatially resolved emission intensity (Ar, N\textsubscript{2}, OH) in Ar/Air

- Between electrodes
  \[ \text{Ar} + e_{\text{fast}} \rightarrow \text{Ar}^* (\text{meta}) \text{ or } \text{Ar}^* + e_{\text{slow}} \quad (\varepsilon = 11.6 \text{ eV}) \]

- Inside of tube (with air mixture)
  \[ \text{Ar}^* \leftrightarrow \text{Ar}^* (\text{meta}) + h\nu \]
  \[ \text{N}_2(X) + \text{Ar}^* (\text{meta}) \rightarrow \text{N}_2(C) + \text{Ar} \quad (\varepsilon = 11.0 \text{ eV}) \]
  \[ \text{H}_2\text{O} + \text{Ar}^* (\text{meta}) \rightarrow \text{OH}(A) + \text{H} + \text{Ar} \quad (\varepsilon = 9.1 \text{ eV}) \]

- The densities of N\textsubscript{2} and OH in the tube increase.
- The productions of N\textsubscript{2} and OH in the outside of the tube are negligible.

\[ \Rightarrow \] The emission intensities of Ar, N\textsubscript{2} and OH monotonously decrease.
2. ROS/RNS measurement in deionised-water after plasma-jet exposure
Identification of ROS/RNS in deionised-water after plasma-jet exposure

- 15 min exposure (Ar)

- Injection shock
Identification of ROS/RNS in deionised-water after plasma-jet exposure

15 min exposure (Ar)
reference
H$_2$O$_2$ (0.88 ppm)
NO$_2^-$ (0.50 ppm)
NO$_3^-$ (0.62 ppm)

injection shock
needle wash solution
dissolved oxygen
Production in plasma and ROS/RNS production

Production in plasma-jet

\[ \text{N}_2 + \text{Ar}^* (\text{meta}) \Rightarrow \text{N} + \text{N} + \text{Ar} \quad (\varepsilon = 9.8 \text{ eV}) \]
\[ \text{O}_2 + \text{Ar}^* (\text{meta}) \Rightarrow \text{O} + \text{O} + \text{Ar} \quad (\varepsilon = 5.2 \text{ eV}) \]
\[ \text{H}_2\text{O} + \text{Ar}^* (\text{meta}) \Rightarrow \text{OH} + \text{H} + \text{Ar} \quad (\varepsilon = 5.1 \text{ eV}) \]

ROS/RNS Production in gas-phase

\[ \text{OH} + \text{OH} \Rightarrow \text{H}_2\text{O}_2 \quad (k = 2.6 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{N} + \text{O} + \text{M} \Rightarrow \text{NO} + \text{M} \quad (k = 3.8 \times 10^{-33} \text{ cm}^6/\text{s}) \]
\[ \text{NO} + \text{O} \Rightarrow \text{NO}_2 \quad (k = 3.0 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO} + \text{OH} \Rightarrow \text{HNO}_2 \quad (k = 3.3 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{O} \Rightarrow \text{NO}_3 \quad (k = 2.3 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{OH} \Rightarrow \text{HNO}_3 \quad (k = 2.8 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{NO}_3 \Rightarrow \text{N}_2\text{O}_5 \quad (k = 1.9 \times 10^{-12} \text{ cm}^3/\text{s}) \]

RNS Production in deionised-water

\[ 2\text{NO}_2 + \text{H}_2\text{O} \Rightarrow \text{HNO}_2 + \text{HNO}_3 \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \Rightarrow 2\text{HNO}_3 \]
**Production in plasma and ROS/RNS production**

**Production in plasma-jet**

\[
\begin{align*}
N_2 + Ar^*(meta) & \rightarrow N + N + Ar \quad (\epsilon = 9.8 \text{ eV}) \\
O_2 + Ar^*(meta) & \rightarrow O + O + Ar \quad (\epsilon = 5.2 \text{ eV}) \\
H_2O + Ar^*(meta) & \rightarrow OH + H + Ar \quad (\epsilon = 5.1 \text{ eV})
\end{align*}
\]

**ROS/RNS Production in gas-phase**

\[
\begin{align*}
OH + OH & \rightarrow H_2O_2 \quad (k = 2.6 \times 10^{-11} \text{ cm}^3/\text{s}) \\
N + O + M & \rightarrow NO + M \quad (k = 3.8 \times 10^{-33} \text{ cm}^6/\text{s}) \\
NO + O & \rightarrow NO_2 \quad (k = 3.0 \times 10^{-11} \text{ cm}^3/\text{s}) \\
NO + OH & \rightarrow HNO_2 \quad (k = 3.3 \times 10^{-11} \text{ cm}^3/\text{s}) \\
NO_2 + O & \rightarrow NO_3 \quad (k = 2.3 \times 10^{-11} \text{ cm}^3/\text{s}) \\
NO_2 + OH & \rightarrow HNO_3 \quad (k = 2.8 \times 10^{-11} \text{ cm}^3/\text{s}) \\
NO_2 + NO_3 & \rightarrow N_2O_5 \quad (k = 1.9 \times 10^{-12} \text{ cm}^3/\text{s})
\end{align*}
\]

**RNS Production in deionised-water**

\[
\begin{align*}
2NO_2 + H_2O & \rightarrow HNO_2 + HNO_3 \\
N_2O_5 + H_2O & \rightarrow 2HNO_3
\end{align*}
\]
Production in plasma and ROS/RNS production

Production in plasma-jet

\[ \text{N}_2 + \text{Ar}^*(\text{meta}) \rightarrow \text{N} + \text{N} + \text{Ar} \quad (\varepsilon = 9.8 \text{ eV}) \]
\[ \text{O}_2 + \text{Ar}^*(\text{meta}) \rightarrow \text{O} + \text{O} + \text{Ar} \quad (\varepsilon = 5.2 \text{ eV}) \]
\[ \text{H}_2\text{O} + \text{Ar}^*(\text{meta}) \rightarrow \text{OH} + \text{H} + \text{Ar} \quad (\varepsilon = 5.1 \text{ eV}) \]

ROS/RNS Production in gas-phase

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (k = 2.6 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M} \quad (k = 3.8 \times 10^{-33} \text{ cm}^6/\text{s}) \]
\[ \text{NO} + \text{O} \rightarrow \text{NO}_2 \quad (k = 3.0 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO} + \text{OH} \rightarrow \text{HNO}_2 \quad (k = 3.3 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{O} \rightarrow \text{NO}_3 \quad (k = 2.3 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \quad (k = 2.8 \times 10^{-11} \text{ cm}^3/\text{s}) \]
\[ \text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5 \quad (k = 1.9 \times 10^{-12} \text{ cm}^3/\text{s}) \]

RNS Production in deionised-water

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]
We generated an Ar plasma-jet, and carried out spatially resolved optical emission spectroscopy of the plasma-jet.

- The emissions of Ar, OH, N\textsubscript{2} and O are observed, and that of NO is observed only when air is mixed into the plasma-jet.

- The emission intensities of OH and N\textsubscript{2} increase and then decrease, because Ar\textsuperscript{*}(meta) energy is transferred to ambient air.

We exposed deionised-water to the plasma-jet, and analysed ROS/RNS dissolved in the deionised-water.

- H\textsubscript{2}O\textsubscript{2}, NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} are dissolved in the deionised-water after the plasma-jet exposure, and air mixture into the plasma-jet leads RNS production.
Thank you for your attention!