Plasma-liquid interactions: Separating electrolytic reactions from plasma/gas phase reactions

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Plasma-Water Interactions

Plasma Medicine

Nanomaterials Synthesis

Bulk Plasma Phase Reactions

Products formed in the bulk plasma phase will dissolve into solution.

Hydrogen peroxide:
\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

Nitric acid:
\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]


Electron Transfer Reactions

Free electrons from the plasma will reduce ions at the plasma-liquid interface.

**Metallic nanoparticle synthesis:**

**Reduction of ferricyanide:**

**Acidic water electrolysis:**

\[
\text{Ag}^+ + e^- \rightarrow \text{Ag}
\]

\[
\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{g})
\]
Bulk Plasma Reactions

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]


Electron Transfer Reactions

\[ \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag} \]
\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \]
**DC Microplasma Jet**

**Electrochemistry with a plasma cathode**

**Experimental setup**

Plasma jet injects free electrons into and aqueous solution.

Ar

Plasma jet

Pt foil anode

NaCl

\[ R_B \]

\[ 3 \text{ kV} \]

\[ \text{DC} \]

100 µm

\[ e^- \]
Competing Processes

Electrolytic reactions vs. bulk plasma reactions

**Water Electrolysis**

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \]

\[ 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2 \]

**Chlorine gas evolution**

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]

\[ \rightarrow \text{NaOH} \]

**Hydrogen peroxide**

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

**Nitric acid**

\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]

These effects can be quantified with pH measurements.
In air and N₂ acidification due to *nitric acid*

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{ NO}(g) \]
\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{ NO}_2(g) \]
\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]

Colorimetric tests indicated NO₃⁻ present in solution for air and N₂.

Potassium iodide titrations found H₂O₂ ~5 ppm for all cases.
Isolating Gas Phase Reactions

To isolate reactions, exhaust was bubbled into an external saline solution.

Exhaust OUT

O₂, N₂, Ar, or Air
IN

Saline Solution
Exhaust is bubbled through an external container of saline solution.

Plasma
Plasma is run in an empty cell.
pH Measurements of External Solution

Nitric acid is no longer produced for the case of ambient N₂ gas.

Colorimetric tests indicated NO₃⁻ present in solution for air only.
HNO$_3$ vs. NaOH Production Rates

**NaOH**

$\sim 5 \times 10^{-11} \text{ mol/s}$

![Graph showing NaOH production rates]

**HNO$_3$**

$\sim 8.6 \times 10^{-9} \text{ mol/s for air}$

$\sim 1.8 \times 10^{-9} \text{ mol/s for N}_2$

![Graph showing HNO$_3$ production rates]

**Faraday's law** predicts O$_2$ gas evolution at $3.9 \times 10^{-9} \text{ mol/s}$

HNO$_3$ produced at $1.8 \times 10^{-9} \text{ mol/s}$ → limited by O$_2$ production rate!
Summary

Final pH determined by competing reactions
(electron transfer vs. bulk plasma reactions)

1. In mixtures containing N$_2$/O$_2$, significant acidification from HNO$_3$

2. In mixtures without N$_2$ and O$_2$, electrolytic production of NaOH dominates

3. In all cases, small amounts of H$_2$O$_2$ (~5 ppm) produced does not significantly affect pH
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