Plasma-Surface Interactions at Atmospheric Pressure: Physical, Chemical and Biological Effects

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Introduction

Low temperature plasmas are characterized by complex, generally non-Maxwellian kinetics.

Multiple, often strongly interacting species: electrons/ions, neutral species, and photons.

Surfaces and multi-phase effects introduce important new challenges for plasma kinetic control, especially at atmospheric pressure.

Focus here on:
- ion/radical effects at surfaces via Molecular Dynamics
- multi-scale plasma-chemical kinetic SMD model for charged and neutral species, (including role of N₂ vibrational state, see Y. Sakiyama, Friday)
- multi-phase effects introduces new time and length scales into kinetics.
Hydrogenation and surface density changes in hydrocarbon films during erosion using Ar/H$_2$ plasmas

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Surfaces couple strongly to plasma and vice versa at low pressure

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*Predictive Control of Plasma Kinetics*
Ion activation energy delivered to wounds by atmospheric pressure dielectric-barrier discharges: sputtering of lipid-like surfaces


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Graph and diagram: C Sputter Yield per Ion vs. Energy (eV) for argon ions. The graph shows a sharp increase in sputter yield at low energies, peaking near 100 eV. The diagram illustrates the original lipid layers and the changes after exposure to 6 x 10¹⁶ cm⁻² 100 eV Ar⁺ ions.

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Predictive Control of Plasma Kinetics
Convolving IEDFs with Ar$^+$ Sputter Yields

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Predictive Control of Plasma Kinetics
Atmospheric Pressure Air: SMD Device Configuration

SMD = surface micro-discharge

- Frequency: 1-10 kHz
- Voltage: 1-10 kV<sub>pp</sub>
- Power: 0.01-1 W/cm<sup>2</sup>
- Distance to sample: 1-10 mm
- Exposure time: 1-1000 s

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SMD: 0-D SMD-neutral Mass Transfer Model

SMD:
\[
\frac{\partial n_{pls}}{\partial t} = \sum_j R_j - \frac{1}{d_{pls}} \Gamma_{pg}
\]

Neutral reactor:
\[
\frac{\partial n_{gas}}{\partial t} = \sum_j R_j + \frac{1}{d_{gas}} \Gamma_{pg}
\]

For charged particles:
\[
\Gamma_{pg} = 0
\]

For neutrals:
\[
\Gamma_{pg} = \frac{D_{gas}(n_{pls} - n_{gas})}{d_{gas}}
\]

Computational domain

- zero flux
- SMD: Neutral reactor

Treied surface

- zero flux
- Treated surface

- e.g. metal surface with diluted bacteria

- electrons
- ions
- neutrals

\[ E \rightarrow 10 \text{ ns} \]

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SMD: humid air plasma chemistry at/near R.T.

Negative particles: \( e, O^-, O_2^-, O_3^-, O_4^-, H^-, OH^-, NO^-, N_2O^-, NO_2^-, NO_3^- \)

Positive particles: \( N^+, N_2^+, N_3^+, N_4^+, O^+, O_2^+, O_4^+, NO^+, N_2O^+, NO_2^+, H^+, H_2^+, H_3^+, OH^+, H_2O^+, H_3O^+ \)

Neutrals: \( N, N^*, N_2, N_2^*, N_2^{**}, O, O^*, O_2, O_2^*, O_3, NO, N_2O, NO_2, NO_3, N_2O_5, H, H_2, OH, H_2O, HO_2, H_2O_2, HNO, HNO_2, HNO_3 \)


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Predictive Control of Plasma Kinetics
SMD: multiple time-scale phenomena

- Electron impact reactions
- Charge transfer, ion recombination
- Neutral reactions
- Applied voltage period
- Gas diffusion
- Exposure time

Simulation procedure:

- SMD (electrons, ions, neutrals)
  - Cycle-averaged reaction rates
- SMD (electrons, ions, neutrals)
- Neutral reactor (neutrals)

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Predictive Control of Plasma Kinetics
Multiple-timescale reactions in gas phase

- Power density: 0.1 W/cm² (low power mode)
- 56 species/626 reactions with multiple-time steps
- SMD region and gas gap
- Input parameter: pulse-like electric field for 1 ns

Charged particles (1 cycle=100 ms)

Neutrals (1-1000 s)

<table>
<thead>
<tr>
<th>Species</th>
<th>Density [m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>( 10^{17} )</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>( 10^{19} )</td>
</tr>
<tr>
<td>( \text{HO}_2 )</td>
<td>( 10^{18} )</td>
</tr>
<tr>
<td>( \text{HNO}_3 )</td>
<td>( 10^{23} )</td>
</tr>
<tr>
<td>( \text{HNO}_2 )</td>
<td>( 10^{21} )</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>( 10^{19} )</td>
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<tr>
<td>( \text{N}_2\text{O} )</td>
<td>( 10^{21} )</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_5 )</td>
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<tr>
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<tr>
<td>( \text{NO}_2 )</td>
<td>( 10^{22} )</td>
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<tr>
<td>( \text{NO} )</td>
<td>( 10^{19} )</td>
</tr>
<tr>
<td>( \text{O}_2^* )</td>
<td>( 10^{18} )</td>
</tr>
</tbody>
</table>
Model Predictions and Measurements

After 100 [s]

FTIR measurement (qualitative comparison)

200 scans for 60-120 [s]
From Gas-Phase to Liquid (Aqueous)-Phase

Additional Time- and Length-Scales

Equilibrium interfacial concentration:
Henry’s law constant [M/atm]

- \( \text{N}_2, \text{O}_2, \text{NO} \): \( \sim 0.001 \)
- \( \text{O}_3, \text{N}_2\text{O}, \text{NO}_2 \): \( \sim 0.01 \)
- \( \text{NO}_3, \text{N}_2\text{O}_5 \): \( \sim 1 \)
- \( \text{OH}, \text{HNO}_2 \): \( \sim 10 \)
- \( \text{HO}_2 \): \( \sim 1000 \)
- \( \text{H}_2\text{O}_2, \text{HNO}_3 \): \( \sim 100000 \)

Ref.: R. Sander, Max-Planck Institute of Chemistry (1999)
Aqueous-Phase RONS: Power Dependence

- **O$_3$**: indigo colorimetric method
- **H$_2$O$_2$**: electrochemical probe
- **HNO$_2$/HNO$_3$**: UV absorbance

- 150 ml PBS (pH~7.2)
- 5 min exposure

**Low power** → **Intermediate power**

<table>
<thead>
<tr>
<th>H$_2$O$_2$ (x10)</th>
<th>HNO$_2$</th>
<th>HNO$_3$</th>
<th>O$_3$</th>
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<tbody>
<tr>
<td>[mM]</td>
<td></td>
<td></td>
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<tr>
<td>0.00</td>
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<td>0.00</td>
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<tr>
<td>0.05</td>
<td>0.15</td>
<td>0.30</td>
<td>0.50</td>
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<td>0.10</td>
<td>0.30</td>
<td>0.60</td>
<td>0.80</td>
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<tr>
<td>0.15</td>
<td>0.45</td>
<td>0.90</td>
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</table>

**Graphical Data**

- Normalized ozone concentration $\times 10$
- Power density [W/cm$^2$]
- Power density range: 0.00 to 0.30 W/cm$^2$

**Graph Details**

- Ozone concentration
- Hydrogen peroxide concentration
- Nitric oxide concentrations
- Nitric acid concentration

**Legend**

- Low power
- Intermediate power
Aqueous-Phase Composition and Sterilization

- power density: 0.05-0.3 W/cm²
- exposure time: 5 min
- E. coli: ~10⁷ cfu/ml

Active species concentration

- O₃
- H₂O₂
- HNO₃
- HNO₂

Inactivation of E. coli

- Log Reduction
- PBS
- 0.75% NaCl

Active species concentration vs. power density [W/cm²]

Inactivation of E. coli vs. power density [W/cm²]
Bacterial (E. coli) Killing: Role of Liquid Mixing is Profound

![Graph showing the logarithmic reduction of bacterial (E. coli) kill with exposure time. Two conditions are compared: Vortexed and Not vortexed. The graph shows a clear linear increase in log reductions with increasing exposure time for both conditions. The PBS is 0.05 W/cm².](image-url)
Plasma Activated Water: Antibacterial Effects And Long Term Composition

Initial pH: 6.2

Chemical compounds:
- Nitrite (HNO$_2$)
- Nitrate (HNO$_3$)
- Hydrogen peroxide (H$_2$O$_2$)

pH vs. time graph:
- pH remains relatively constant over time.

Chemical compounds vs. time graph:
- Nitrite and nitrate levels decrease over time.
- Hydrogen peroxide levels increase over time.
- Initial pH: 6.2
Effects of Incubation Time: New Time Scales

20 min

0-7 days

incubation

E. coli

log reduction = \log_{10}\left(\frac{\text{initial number}}{\text{number of survivors}}\right)

3 hour incubation

15 minute incubation

Log Reduction CFU

Log Reduction CFU

Initial 1d 2d 4d 7d

Initial 30min 1d 2d 7d
Plasma Activated Water: Antibacterial Effects And Long Term Composition

\[ \text{log reduction} = \log_{10} \left( \frac{\text{initial number}}{\text{number of survivors}} \right) \]

**short-lived species?**

![Graph showing log reduction over time with E. coli](image)

![Graph showing concentration of hydrogen peroxide and nitrite/nitrate over time](image)
Plasma Activated Water: Antibacterial Effects And Long Term Composition

E. coli

20 min 0-7 days 3 h

Log Reduction CFU

Initial 1d 2d 4d 7d

Nitrite/nitrate [mM]

H₂O₂, HNO₂, HNO₃

Hydrogen peroxide [µM]

Time [hour]
Concluding Remarks

Atmospheric pressure, low temperature plasmas are particularly sensitive to the roles of *neutrals*, *surfaces* and *multi-phase effects*.

Gradients in time and space are often large.

Non-equilibrium $f(\varepsilon)$ couples electrons and neutrals – for example in vibrational distributions.

Another source of non-equilibrium effects can occur with photons: the higher densities in gases at atmospheric pressure, at surfaces and in liquids can lead to strong *photo-induced effects*: this will be explored in the future.
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