Controlling Vibrationally Excited Nitrogen and Overall Plasma Chemistry with Surface Micro-discharge in Ambient Air

Yukinori Sakiyama and David B. Graves

Department of Chemical and Biomolecular Engineering
University of California at Berkeley
Outline

1. Surface micro-discharge (SMD)

2. Distribution of RONS at low-power
   • RONS in discharge layer and afterglow
   • Comparison with FTIR

3. Mode transition in afterglow
   • UV O$_3$ measurement
   • Fitting model with N$_2$ vibrational mode
   • Correlation with bactericidal effect

4. Concluding remarks
SMD: discharge characteristics


SMD = surface micro-discharge
(surface dielectric barrier discharge in ambient air at room temperature)

- Frequency: 1-10 kHz
- Voltage: 1-10 kV_{pp}
- Power: 0.01-1 W/cm^2
- Distance to sample: 1-10 mm
- Exposure time: 1-1000 s
**SMD: anti-microbial effect**

Various microbes on agar plate


E. coli on pig skin


untreated

30 s

gram positive/negative bacteria, spores, viruses, etc...

Plasma Science Center

*Predictive Control of Plasma Kinetics*
SMD: multi-scale phenomena

- 1 ns: pulse excitation, electron impact reactions
- 1 μs: charge transfer, recombination
- 1 ms: neutral reactions, applied voltage period, gas diffusion
- 1 s: exposure time
- 1000 s: SMD for biomaterial treatment

Ozonizer
Pollution control

SMD for biomaterial treatment

Plasma Science Center
Predictive Control of Plasma Kinetics
Modeling: domain and equations

- Humid air at 1 atm: 79% N₂, 20% O₂, 1% H₂O (30% relative humidity)
- Gas temperature: 300 K

\[
\frac{\partial n_p}{\partial t} = \sum_{j} k_j \prod n_{r,j} - \frac{\Gamma_{pg}}{d_p}
\]

\[
\Gamma_{pg} = \frac{D(n_p - n_g)}{(d_p + d_g)/2}
\]

\[
\frac{\partial n_g}{\partial t} = \sum_{j} k_j \prod n_{r,j} + \frac{\Gamma_{pg}}{d_g}
\]
Modeling: simulation procedure (solver: MATLAB)

Pulse-like electric field

$$|E| = E_0 \exp\left\{-(t / \tau_{\text{pls}})^2 / 2\right\}$$

Discharge layer (e, ion, neutral)  Afterglow (neutral) for single cycle $\tau_{\text{rep}}=100 \ \mu\text{s}$

Cycle-averaged reaction rates

Discharge layer (neutral)  Afterglow (neutral) for $\tau_{\text{gas}}=1 \ \text{s}$

Plasma Science Center
Predictive Control of Plasma Kinetics
Modeling: humid air plasma chemistry

- **53 species:**
  - electrons, 16 positive ions, 10 negative ions, and 26 neutrals

- **624 reactions**
  - 23 electron impact excitation/ionization
  - 84 electron recombination/attachment/detachment
  - 169 charge transfer and ion conversion
  - 231 ion-ion recombination
  - 116 neutral-neutral reactions

References

  etc., etc., etc…. 

---

Plasma Science Center

*Predictive Control of Plasma Kinetics*
Modeling: discharge layer at low power

Power density: 0.05 W/cm²
Peak density: ~$10^{19}$ m$^{-3}$

Positive ions at 1000 s

Negative ions at 1000 s

Plasma Science Center
Predictive Control of Plasma Kinetics
Modeling: neutrals still in transient after 1000 s

Power density: 0.05 W/cm²
Peak density: > $10^{19}$ m$^{-3}$

Cycle-averaged neutral density at 1000 s

![Graph showing cycle-averaged neutral density over time with labels for $O_x$, $N_xO_y$, $H_xN_yO_z$, and $O_xH_y$.]
Modeling: distributions of neutrals

Simulation at 100 [s]

FTIR measurement (qualitative comparison)

IR beam

200 scans for 60-120 [s]
Outline

1. Surface micro-discharge (SMD)

2. Distribution of RONS at low-power
   - RONS in discharge layer and afterglow
   - Comparison with FTIR

3. Mode transition in afterglow
   - UV O$_3$ measurement
   - Fitting model with N$_2$ vibrational mode
   - Correlation with bactericidal effect

4. Concluding remarks
Gas-phase ozone: modulation by power density


Plasma Science Center
Predictive Control of Plasma Kinetics
Mode transition: \( \text{N}_2 \) vibrational state


Energy transfer efficiency

Cumulative distribution function \((v > 12)\)
Mode transition: simplified fitted model

Governing equations

\[
\begin{align*}
\frac{dn_{O_3}}{dt} &= k_1 n_M n_O n_{O_2} - k_3 n_{NO} n_{O_3} - \frac{n_{O_3}}{\tau_{\text{dif}}} \\
\frac{dn_{NO}}{dt} &= k_2 n_{N_2(v)} n_O - k_3 n_{NO} n_{O_3} - k_4 n_O n_{NO} n_M - \frac{n_{NO}}{\tau_{\text{dif}}} \\
n_{N_2(v)} &= n_{N_2} F_{v>12} = n_{N_2} \exp\left(-\frac{12\Delta\varepsilon_v}{kT_v}\right) \\
T_v &= T_g + T_{v_{\text{max}}} \{1 - \exp(-t / \tau_v)\}
\end{align*}
\]

2 unknown variables
• \(n_{O_3}\) and \(n_{NO}\)

3 fitting parameters
• \(n_O, T_{v_{\text{max}}}, \tau_v\)

R1: \(O + O_2 + M \rightarrow O_3 + M\)
R2: \(N_2(v) + O \rightarrow NO + N\)
R3: \(O_3 + NO \rightarrow NO_2 + O_2\)
R4: \(O + NO + M \rightarrow NO_2 + M\)
Mode transition: $O_3$ model and $N_xO_y$ mode

fitted parameters: $n_O = 8 \times 10^{17} \text{ m}^{-3}$, $T_{v\text{max}} = 5000 \text{ K}$, $\tau_v = 2 \text{ s}$

Plasma Science Center
Predictive Control of Plasma Kinetics
Gas-phase ozone: bactericidal activity on agar plate

- **Low power (< 0.1 Wcm\(^2\))**
  - \(O_3\): increase
  - Low-R: increase

- **High power (> 1.0 Wcm\(^2\))**
  - \(O_3\): low
  - L-R: low

- **Intermediate power (0.1-1.0 Wcm\(^2\))**
  - \(O_3\): quenched
  - L-R: high

- **ozone is not responsible for inactivation?**
- **Nonlinear reaction on lipid membrane?**
Concluding Remarks

1. We developed multi-scale model of SMD. Our simulation results at low power (0.05 W/cm²) shows good agreement with our FTIR measurement.

2. We presented one example of modulating plasma chemistry in SMD. The modulation is achieved by controlling distribution functions of electrons and neutrals through pulsing of electric field.
Acknowledgements

Prof. G. Morfill (Max-Planck Institute)
Dr. T. Shimizu (Max-Planck Institute)

Prof. D. Clark (UC Berkeley)
M. Pavlovich (Ph.D. candidate, UC Berkeley)
H.-W. Chang (Ph.D. candidate, National Taiwan University)