Modeling and Diagnostics of Atmospheric Pressure Surface Microdischarge Plasma Chemistry

David B. Graves, Yuki Sakiyama,* and Matt Pavlovich
Department of Chemical & Biomolecular Engineering,
University of California, Berkeley, CA 94720

* Currently at Lam Research Corporation, Portland, OR

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Indirect Dielectric Barrier Discharges in Air

Surface microdischarge or SMD

View from below

~ 5 cm

Different type of model approach used to predict chemistry – dealing with highly disparate time scales
How to Model the Physics and Chemistry?

- Separate plasma zone near mesh from ‘downstream’ region
- Treat each zone as well-mixed, connected by diffusion
- Develop appropriate iteration scheme between ‘fast’ plasma and ‘slow’ diffusion/reaction
Coupled, Well-Mixed Zones

Discharge layer (electrons, ions, neutrals)

$$\frac{\partial n_p}{\partial t} = \sum k_j \prod n_{r,j} - \frac{\Gamma_{pg}}{d_p}$$

Neutral gas domain (neutrals (b))

$$\frac{\partial n_g}{\partial t} = \sum k_j \prod n_{r,j} + \frac{\Gamma_{pg}}{d_g}$$

Charged species confined here; short and long-lived species generated

Long-lived reactive neutral species interact with substrate here and can affect plasma
Simulation Scheme

- Spatially uniform, Gaussian E-field pulse (FWHM 10 ns) repeated at 10 kHz in discharge layer
- Field amplitude adjusted to maintain period-averaged power at experimental value (e.g. 0.05 W/cm²)
- 53 species/624 rxns in humid air: 79% N₂; 20% O₂; 1% H₂O
- MATLAB ODE solver used
Modeling: multiple time-scale phenomena

- 100 ns: electron impact reactions, charge transfer, ion recombination
- 1 ms: neutral reactions
- 1 s: applied voltage, period, gas diffusion
- 100 s: exposure time

Simulation procedure

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

<table>
<thead>
<tr>
<th>Category</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positively charged</td>
<td>$N^+$, $N_2^+$, $N_3^+$, $N_4^+$, $O^+$, $O_2^+$, $O_4^+$,</td>
</tr>
<tr>
<td>particles</td>
<td>$NO^+$, $N_2O^+$, $NO_2^+$,</td>
</tr>
<tr>
<td>Negatively charged</td>
<td>$e$, $O^-$, $O_2^-$, $O_3^-$, $O_4^-$,</td>
</tr>
<tr>
<td>particles</td>
<td>$NO^-$, $N_2O^-$, $NO_2^-$,</td>
</tr>
<tr>
<td>Neutral species</td>
<td></td>
</tr>
<tr>
<td>Group (a)</td>
<td>$N(^2D)$, $N_2(A^3\Sigma)$,</td>
</tr>
<tr>
<td></td>
<td>$N_2(B^3\Pi)$, $O(^1D)$, $H$</td>
</tr>
<tr>
<td>Group (b)</td>
<td>$N$, $O$, $O_2(a^1\Delta)$, $O_3$, $NO$,</td>
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<tr>
<td></td>
<td>$N_2O$, $NO_2$, $NO_3$, $N_2O_3$,</td>
</tr>
<tr>
<td></td>
<td>$N_2O_4$, $N_2O_5$, $H_2$, $OH$, $HO_2$,</td>
</tr>
<tr>
<td></td>
<td>$H_2O_2$, $HNO$, $HNO_2$, $HNO_3$, $N_2$, $O_2$, $H_2O$</td>
</tr>
</tbody>
</table>
Table 2. A list of reactions and the rate constants.

<table>
<thead>
<tr>
<th>Index</th>
<th>Reaction</th>
<th>Rate constant ( a )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>( e + N_2 \rightarrow N(^2D) + N + e )</td>
<td>( 3.99 \times 10^{-17} \varepsilon^{2.24} \exp(-9.10/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R2)</td>
<td>( e + N_2 \rightarrow N_2(A^3\Sigma) + e )</td>
<td>( 3.34 \times 10^{-16} \varepsilon^{-0.06} \exp(-8.50/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R3)</td>
<td>( e + N_2 \rightarrow N_2(B^3\Pi) + e )</td>
<td>( 8.44 \times 10^{-15} \varepsilon^{-0.33} \exp(-9.15/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R4)</td>
<td>( e + N_2 \rightarrow N_2^+ + e + e )</td>
<td>( 1 \times 10^{-16} \varepsilon^{1.90} \exp(-14.6/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R5)</td>
<td>( e + N \rightarrow N(^2D) + e )</td>
<td>( 5.06 \times 10^{-15} \exp(-10.8/\varepsilon^{3.95}) )</td>
<td>b</td>
</tr>
<tr>
<td>(R6)</td>
<td>( e + N \rightarrow N^+ + e + e )</td>
<td>( 1.45 \times 10^{-17} \varepsilon^{2.58} \exp(-8.54/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R7)</td>
<td>( e + O_2 \rightarrow O + O + e )</td>
<td>( 2.03 \times 10^{-14} \varepsilon^{-0.10} \exp(-8.47/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R8)</td>
<td>( e + O_2 \rightarrow O(^1D) + O + e )</td>
<td>( 1.82 \times 10^{-14} \varepsilon^{-0.13} \exp(-10.7/\varepsilon) )</td>
<td>b</td>
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<tr>
<td>(R9)</td>
<td>( e + O_2 \rightarrow O_2(a^1\Delta) + e )</td>
<td>( 1.04 \times 10^{-15} \exp(-2.59/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R10)</td>
<td>( e + O_2 \rightarrow O_2^+ + e + e )</td>
<td>( 9.54 \times 10^{-12} \varepsilon^{-1.05} \exp(-55.6/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R11)</td>
<td>( e + O_3 \rightarrow O + O_2 + e )</td>
<td>( 1.78 \times 10^{-12} \varepsilon^{-0.614} \exp(-11.5/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R12)</td>
<td>( e + O \rightarrow O(^1D) + e )</td>
<td>( 7.46 \times 10^{-15} \exp(-5.58/\varepsilon^{1.47}) )</td>
<td>b</td>
</tr>
<tr>
<td>(R13)</td>
<td>( e + O \rightarrow O^+ + e + e )</td>
<td>( 4.75 \times 10^{-15} \varepsilon^{0.614} \exp(-22.1/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R14)</td>
<td>( e + H_2O \rightarrow H_2O^+ + e + e )</td>
<td>( 9.65 \times 10^{-18} \varepsilon^{2.53} \exp(-8.99/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R15)</td>
<td>( e + H_2O \rightarrow OH^+ + H + e + e )</td>
<td>( 9.89 \times 10^{-12} \varepsilon^{-1.64} \exp(-67.6/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R16)</td>
<td>( e + H_2O \rightarrow H^+ + OH + e + e )</td>
<td>( 7.45 \times 10^{-15} \varepsilon^{0.34} \exp(-54.2/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R17)</td>
<td>( e + H_2O \rightarrow O^+ + H_2 + e + e )</td>
<td>( 7.4 \times 10^{-16} \varepsilon^{0.45} \exp(-55.5/\varepsilon) )</td>
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<tr>
<td>(R18)</td>
<td>( e + H_2O \rightarrow H^+_2 + O + e + e )</td>
<td>( 8.49 \times 10^{-15} \varepsilon^{-1.23} \exp(-74.0/\varepsilon) )</td>
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</tr>
<tr>
<td>(R19)</td>
<td>( e + H_2O \rightarrow OH + H + e )</td>
<td>( 5.15 \times 10^{-15} \varepsilon^{0.62} \exp(-10.9/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R20)</td>
<td>( e + H_2O \rightarrow H_2 + O^+ + e + e )</td>
<td>( 5.19 \times 10^{-18} \varepsilon^{1.2} \exp(-13.8/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R21)</td>
<td>( e + H_2 \rightarrow H + H + e )</td>
<td>( 3.29 \times 10^{-10} \varepsilon^{0.578} \exp(-7.56/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R22)</td>
<td>( e + H_2 \rightarrow H^+ + e + e )</td>
<td>( 4 \times 10^{-17} \varepsilon^{2.13} \exp(-14.9/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R23)</td>
<td>( e + N_2O_5 \rightarrow NO_2^+ + NO_3 + e + e )</td>
<td>( 2.43 \times 10^{-17} \varepsilon^{2.77} \exp(-5.62/\varepsilon) )</td>
<td>b</td>
</tr>
<tr>
<td>(R24)</td>
<td>( e + N^+ + M \rightarrow N + M )</td>
<td>( 3.12 \times 10^{-35} / T_e^{1.5} )</td>
<td>[9]</td>
</tr>
<tr>
<td>(R25)</td>
<td>( e + N_2^+ \rightarrow N + N )</td>
<td>( 1.66 \times 10^{-12} / T_e^{0.7} )</td>
<td>[9]</td>
</tr>
<tr>
<td>(R26)</td>
<td>( e + N_2^+ \rightarrow N(^2D) + N )</td>
<td>( 1.5 \times 10^{-12} / T_e^{0.7} )</td>
<td>[9]</td>
</tr>
<tr>
<td>(R27)</td>
<td>( e + N_2^+ + M \rightarrow N_2 + M )</td>
<td>( 3.12 \times 10^{-35} / T_e^{1.5} )</td>
<td>[9]</td>
</tr>
<tr>
<td>(R28)</td>
<td>( e + N_3^+ \rightarrow N_2 + N )</td>
<td>( 3.46 \times 10^{-12} / T_e^{0.5} )</td>
<td>[11]</td>
</tr>
<tr>
<td>(R29)</td>
<td>( e + N_4^+ \rightarrow N_2 + N_2 )</td>
<td>( 4.73 \times 10^{-11} / T_e^{0.53} )</td>
<td>[9]</td>
</tr>
<tr>
<td>(R30)</td>
<td>( e + O^+ + M \rightarrow O + M )</td>
<td>( 3.12 \times 10^{-35} / T_e^{1.5} )</td>
<td>[11]</td>
</tr>
<tr>
<td>(R31)</td>
<td>( e + O_2^+ \rightarrow O + O )</td>
<td>( 1.68 \times 10^{-11} / T_e^{0.7} )</td>
<td>[11]</td>
</tr>
<tr>
<td>(R32)</td>
<td>( e + O_2^+ \rightarrow O + O(^1D) )</td>
<td>( 1.24 \times 10^{-11} / T_e^{0.7} )</td>
<td>[11]</td>
</tr>
</tbody>
</table>

... + > 600 reactions
Charged Species in Discharge Layer During Pulse

(a) Density of positive ions, negative ions, and electrons.

(c) Density of various charged species as a function of time.

(f) Density of specific charged species as a function of time.
Neutral Species in Discharge Layer During Pulse
Time Evolution of Neutral Species in Diffusion Layer
Cycle-Averaged Neutral Species

Discharge region

- $H_2$
- $N$
- $O$
- $OH$
- NO
- $O_2(a^1Δ)$
- HO$_2$
- H$_2$O$_2$
- N$_2$O
- NO$_2^+$
- NO$_3^-$
- HNO$_2$
- NO$_3$
- HN$O_3$
- N$_2$O$_5$

Diffusion region

- $H_2$
- H$_2$O$_2$
- N$_2$O
- NO$_2$
- NO$_3$
- HNO$_2$
- NO$_3$
Solution Iteration Schemes: *Tight Coupling*

**discharge layer**  
(C, S, L)  

**afterglow**  
( L )  

C: Charged species  
S: Short-lived neutrals  
L: Long-lived neutrals

1000 times

*Tight coupling*: accurate but slow

Solution Iteration Schemes: One-Way Coupling

One-way coupling: rapid but is accuracy ok?

C: Charged species
S: Short-lived neutrals
L: Long-lived neutrals
Solution Iteration Schemes: **Weak Coupling**

- **discharge layer** $(C, S, L)$
- **afterglow** $(L)$

C: Charged species
S: Short-lived neutrals
L: Long-lived neutrals

- **Weak coupling**: best compromise between accuracy and cost
Cycle-Averaged Neutral Species in Diffusion Region Using Different Iteration Schemes

Note major discrepancies
SMD-Water Treatment

- Air SMD plasma shows antimicrobial effects when interacting with water
- Plasma-created species must transport to water and enter water phase: this involves many new processes and reactions
- Crucially important for plasma-biological applications since water generally involved

Long-Lived Antimicrobial Plasma-Activated Water

- Air SMD plasma-activated water remains antimicrobial for many days.
- This effect requires acidic pH (~ pH 3) and relatively long incubation times (~ 3 hours).
- Later work showed that at lower power, air plasma creates copious amounts of O$_3$; if mixed into water, O$_3$ can be very rapidly antimicrobial at any pH.
Do UVA Photons (369 nm; LED) Synergize Antimicrobially with SMD in Buffered Water?

· Previous studies showed that lower power SMD yields mostly O$_3$; higher power mostly N$_x$O$_y$ and H$_2$O$_2$. Both are antimicrobial at surfaces and water
  · O$_3$ in water rapidly antimicrobial but short lived
  · N$_x$O$_y$ in water less rapidly antimicrobial, long-lived (> ~ 7 days), must be acidic

Expose bacteria/water to UVA photons (via LED) before or after SMD plasma exposure: synergy observed?
Air Plasma + UVA Photons are Synergistically Antimicrobial

- Antimicrobial effect from combined UVA (LED ~ 1 W/cm²) applied to bottom of glass vial and higher power (5 mins @ 0.30 W/cm²) plasma treatment.
  - Compare separate treatments with effects added to sequential exposure
  - **UVA first, followed by plasma: no synergy**
  - **Plasma first, followed by UVA: synergy**

![Graph showing Log reductions vs UV exposure (min)]

- (O): expected additive effect; (□): UVA followed by 5 minutes of plasma treatment; (▲): UVA following 5 minutes of plasma treatment.
Adding Species to Water to Reproduce Effects: \( NO_2^- \) Important

- Plasma treatment creates \(~ 5 \text{ mM } NO_2^-\) (nitrite) and \( NO_3^-\) (nitrate); \(~ 100 \ \mu\text{M } H_2O_2\)
- Add these species to buffered water in various combinations, add UVA exposure, and compare to plasma/UVA treatments
- Identify key species created by plasma: can we reproduce plasma effects using ‘artificial plasma-treated water’?
Combining Species in Water to Reproduce Effects:

**NO$_2^-$ + H$_2$O$_2$ Key**

- Combining 5 mM NO$_2^-$ and 100 µM H$_2$O$_2$ appears to reproduce plasma activated water
- Adding 5 mM nitrate not necessary to reproduce effects of plasma treated water and UVA
Adding Ascorbate Eliminates Synergy From Plasma + UVA

- Ascorbate (vitamin C) is known to scavenge OH radical
- If adding ascorbate eliminates antimicrobial effects of plasma + UVA and/or added solutions, OH is probably key antimicrobial specie
- Ascorbate eliminates most of plasma + UVA synergy so OH is probably key specie
Proposed Mechanism for Plasma-UVA Synergy

1. NO$_2^-$ forms in water from NO, NO$_2$;
2. NO$_2^-$ photolysis to form NO, OH, OH$^-$;
3. OH can recombine to water; or
4. kills bacteria; or
5. is scavenged by ascorbate;
6. NO combines with H$_2$O$_2$ to form reactive nitrogen species (e.g. ONOO$^-$ proposed)
Concluding Remarks

- SMD modeling is challenging due to range of length and time scales; found ‘weak coupling’ model optimal
- Multiphase plasma interactions introduce additional complexities
- UVA photolysis of NO$_2^-$ creates NO & OH in plasma-water chemistry: plasma creates precursor & photons activate them: plasma-photo therapy possible?
- Sets stage for plasma-biomolecule-biological system coupling in the future