DIELECTRIC BARRIER DISCHARGES IN HUMID AIR*

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AGENDA

• Atmospheric Pressure Dielectric Barrier Discharges
• Model
• Base Case
• Effect of Flow Rate on ROS/RNS
• Effect of Humidity on ROS/RNS
• Conclusions
ATMOSPHERIC PLASMAS

- Plasma-Medicine
  - Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are produced in plasma discharges
  - ROS/RNS signal cells, optimal dose is difficult to determine [1]
  - Sanitize sensitive wounds without tissue damage [2]
  - Reduce the size of cancerous tumors. [3]
  - Greater certainty in the fundamental processes required before it could be used on humans – modelling is essential

- Environmental Remediation
  - Air and surface sterilization, control of air pollutants, CO$_2$ sequestration have shown promising results. [4]
  - Air discharges used on pilot scale for the removal of NO$_x$ and SO$_2$ from incinerator exhaust. [5]
  - Many challenges with scaling up, modeling is valuable.
ATMOSPHERIC PLASMAS

- Examples of atmospheric pressure plasmas devices
- This type of DBD discharges below may be used to directly treat wounds or tumors

MG Kong [et al]

University of Michigan
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MODEL: GLOBAL-KIN

- Global model (0-D) - assumes all densities are uniform throughout plasma volume.
- Electron temperature:

\[ \frac{\partial \left( \frac{3}{2} n_e k_b T_e \right)}{\partial t} = \vec{j} \cdot \vec{E} + n_e \sum_i \Delta \varepsilon_i k_i N_i - \sum_l \frac{3}{2} n_e v_{mi} \left( \frac{2m_e}{M_i} \right) k_b (T_e - T_i) \]

- Species densities:

\[ \frac{dn_i}{dt} = \sum_j \left( a_{ij}^{(L)} a_{ij}^{(R)} \right) k_j n_{ij}^{a_{ij}^{(R)}} \]

\( a_{ij}^{(L)} \) and \( a_{ij}^{(R)} \) LHS and RHS stoichiometric coefficients
• Power deposition approximates a DBD
  • 5 ns pulse
  • 1 kHz pulse repetition freq.
• Flow gas (humid air):
  • \( \text{N}_2/\text{O}_2/\text{H}_2\text{O} = 78/21/1 \)
  • \( \text{CO}_2 \) 3.5 x 10^{-2} %
  • \( \text{CH}_4 \) 4 x 10^{-4} %
• Air flow direction, and electrode configuration need not be specified for the global model.
• Flow produces a "residence time" for gas in plasma.
BASE CASE CONDITIONS

- 500 sccm humid air
- 25% relative humidity
- 1 kHz pulse repetition rate
- Initial and inlet gas are the same composition – all species flow out.
- $T_e \approx 4.5$ eV during pulse
- $T_{\text{gas}}$ increases during pulses due to joule heating – decreases between pulses due to conduction, flow.

- $T_e$, $T_{\text{gas}}$ at 1 kHz.
REACTIVE OXYGEN SPECIES (ROS)

- Electron impact dissociation / attachment of $\text{O}_2$, $\text{H}_2\text{O}$ during pulse produces $\text{O, OH, H, O}_2^-$

- Reactions between pulses:
  - $\text{O + O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
  - $\text{H + O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$
  - $\text{OH + OH + O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$

- Gas flow (residence time, $\tau = 9.6$ ms) depletes products.

**Graph:**

- $\text{O}_3$
- $\text{O}_2^*$
- $\text{HO}_2$
- $\text{H}_2\text{O}_2$
- $\text{OH}$

**Axes:**

- Vertical axis: Density [cm$^{-3}$]
- Horizontal axis: Time [s]
REACTIVE NITROGEN SPECIES (RNS)

- Terminal RNS include nitrogen oxides ($N_xO_y$) and acids ($HNO_x$)
  
  \[
  \text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \\
  \text{O} + \text{NO} + \text{N}_2 \rightarrow \text{NO}_2 + \text{N} \\
  \text{O} + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M} \\
  \text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \\
  \text{OH} + \text{NO}_2 + \text{N}_2 \rightarrow \text{HNO}_3 + \text{N}_2
  \]

- RNS stabilize after about 0.02 s (20 pulses), which is about $2.1\tau$
EFFECT OF FLOW RATE - RNS

- Residence time $\tau$ decreases with increasing flow rate.
- RNS increase with smaller flow rate as longer $\tau$ enables more formation reactions.
- $\text{N}_2\text{O}_5$ is an exception:
  $\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$
  $\text{NO}_2^- + \text{N}_2\text{O}_5 \rightarrow \text{NO}_3^- + \text{NO}_2 + \text{NO}_2$
- $\text{N}_2\text{O}_5$ is consumed by a $\text{NO}_2^-$ at low flow, limited by $\text{NO}_3$ at high flow.
In absence of hydrocarbons, ROS are fairly stable and accumulate in discharge.

ROS do react with RNS:

\[
\text{HO}_2 + \text{NO} + \text{M} \rightarrow \text{HNO}_3 + \text{M}
\]

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

Shorter residence times produce less RNS and so less depletion of ROS.

Control of ROS/RNS by varying flow rate
HUMIDITY – RNS PRODUCTION

- Production of HNO$_2$ and HNO$_3$ increase with increasing humidity.
  
  \[
  \text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}
  \]
  
  \[
  \text{OH} + \text{NO}_2 + \text{N}_2 \rightarrow \text{HNO}_3 + \text{N}_2
  \]

- Humidity above 10% does not effect RNS generation

- Water impurities below 1 ppb do not effect RNS generation
HUMIDITY – ROS PRODUCTION

- $\text{H}_2\text{O}_2$, $\text{HO}_2$, and OH increase with humidity – origins are traced to electron impact dissociation of $\text{H}_2\text{O}$.
- Humidity above 10% does not affect ROS – likely due to finite energy deposition.
- Impurities less than 1 ppb not important
CONCLUDING REMARKS

- Increased flow rates (smaller residence times) decrease RNS densities, except for N_2O_5.
- Increasing humidity increases production of HNO_2, HNO_3, H_2O_2, HO_2, and OH – electron impact dissociation of H_2O.
- Water impurities in dry air below 1 ppb, have a negligible effect on ROS and RNS.
- Increasing humidity above 10% has a negligible effect on ROS and RNS.

Future Work:
- Expand reaction mechanism and validate by comparison to experiment.
- Improve functionality of Global_Kin to include interaction with a liquid.
- Analyze devices with a broad range of flow rates, from surface micro-discharges to DBDs and plasma jets.
REFERENCES


