Dielectric Barrier Discharge, Ozone Generation, and their Applications

Complex Plasmas Summer Institute 2008

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Thermal vs. Non-Thermal Plasmas

The plasma components (electrons, ions, neutrals) are characterized by energy distribution functions or alternatively by an “average” energy or temperature \((T_e, T_i, T_n)\) – not quite correct, only true for Maxwell-Boltzmann distributions !!!

Electrons in general have more complicated energy distributions !!!

**Thermal Plasma:** \(T_e \approx T_i \approx T_n\) (a few thousand Kelvin for e.g. torches to \(>10^6\) Kelvin for e.g. fusion plasmas)

**Non-Thermal Plasma:** \(T_e \gg T_i, T_n\) with \(T_i \approx T_n\)
  - high electron temperature \((10,000 – 50,000 \text{ K})\)
  - low gas temperatures \((300 – 1,500 \text{ K})\)
  - “high-temperature chemistry” at low ambient temperatures (through dissociation and ionization & vibrational non-equilibrium)
Low-Temperature (“Cold”) Plasmas
[Non-Equilibrium, Non-Thermal]

\[ T_e >> T_i, \, T_n \text{ with } T_i \approx T_n \]

- High “electron temperature” (10,000 – 100,000 K)
  - \( T_e \) from 0.5 eV to 10 eV
  - Often highly non-Maxwellian EEDF; “bulk” and “beam” electrons

- Low gas temperature (350 – 2,500 K)

- “High-temperature chemistry” at low ambient temperatures
  - Electron-driven ionization and dissociation (in molecular plasmas) create reactive radicals
  - Electron interactions (in molecular plasmas) create a vibrational non-equilibrium
The Low-Pressure Glow Discharge
(Textbook !)

I-V Characteristic

Avoid !!!
The Paschen Breakdown Curve

Breakdown Voltage

Pressure x Electrode Separation
(or pressure for a fixed electrode separation)

1 kV

200 V

(mTorr – Torr)

atmospheric pressure

High Breakdown Voltage
High Current Density
Instabilities, Arcing
The Low-Pressure Glow Discharge Plasma – Well Understood
Where do we go from here? Where do we find ‘New Physics’?

- **Higher Pressures** (up to & > atmospheric pressure)
  - Highly susceptible to instabilities
  - Glow-to-arc transition
  - Collective phenomena become important
  - High collision frequencies, short mean free paths
  - Excited species, 3-body reactions, step-wise processes

- **Smaller Dimensions** (down to & < 100 µm)
  - Various regions of the plasma shrink and overlap
  - Very high field and potential gradients
  - Limits of scaling laws; Debye length \( \approx \) plasma dimension
  - Wall effects become prominent
  - Boundary-dominated discharges/plasmas
Some Atmospheric-Pressure μ-Plasma Concepts

Dielectric barrier discharge configurations

```
metal
```
```
dielectric
```
dc, ac, or rf voltage

Microhollow cathode discharge configuration

```
dielectric
```
```
metal
```
dc, ac, or rf voltage

Capillary plasma electrode discharge configuration

```
metal
```
```
dielectric
```
dc, ac, or rf voltage
Faraday’s Dielectric Capacitors

Michael Faraday (1781 – 1867)

Faraday's Dielectric Capacitor (circa 1837)

Capacitance INCREASED!
Historical Ozone Tube of W. Siemens (1857)

Werner v. Siemens
Poggendorf’s Annalen der Chemie und Physik 102, 66 (1857)
“Ozone Production in an Atmospheric-Pressure Dielectric Barrier Discharge”
Dielectric Barrier Discharge

Typical operational conditions of barrier discharges

Electric field strength $E$ of first breakdown $\approx 150$ Td ($p = 1$ bar, $T=300$ K)

Voltage $V_{pp}$ $3–20$ kV

Repetition frequency $f$ $50$ Hz–$10$ kHz

Pressure $p$ $1–3$ bar

Gap distance $g$ $0.2–5$ mm

Dielectric material thickness $d$ $0.5–2$ mm

Relative dielectric permittivity $\varepsilon_r$ $5–10$ (glass)

Single and double DBD

Single dielectric

Double dielectric
Role of the Dielectric

The dielectric is the key for the proper functioning of the discharge.

Serves two functions:

1. Limits the amount of charge transported by a single microdischarge (microplasma)
2. Distributes the microdischarges over the entire electrode surface area
EQUIVALENT CIRCUIT OF A MICRODISCHARGE

50 Hz - 10 MHz

CHANNEL

DIELECTRIC

SURFACE DISCHARGE

\[ C_D \]

\[ C_g \]

\[ R_p(t) \]
Microdischarge Activity and U-Q Lissajous Figure

Fundamental Operation of the Dielectric Barrier Discharge

- Many of relevant plasma processes that are of importance to achieving our goal occur on time scales that allow us to study them.

- Optical emission spectroscopic studies will allow us to determine the temporal and spatial development of important plasma species such as radicals (OH, NO, various oxygen radicals) with high time resolution (less than 10 ns) and a spatial resolution on the scale of mm in the plasma volume following pulsed plasma excitation.

Fundamental Operation of the DBD

Electron Density

Outer Contour Line
\( n_e = 10^{10} \text{ cm}^{-3} \)

Inner Contour Line
\( n_e = 10^{14} \text{ cm}^{-3} \)

Streamer Propagation in 1 bar Air
Numerical Results of Microdischarge Formation in Dielectric-Barrier Discharges

Starting Phase of a Microdischarge (1 bar: 20% CO₂ / 80% H₂)

An electron avalanche propagates towards the anode

Reverse propagation towards the cathode
Numerical Results of Microdischarge Formation in Dielectric-Barrier Discharges

Cathode Layer Formation

Just before the peak of the total current

Peak current
Numerical Results of Microdischarge Formation in Dielectric-Barrier Discharges

Local Field Collapse in Area Defined by Surface Discharge

\[ n_e = 10^9 \text{cm}^{-3} \]
\[ n_e = 10^{14} \text{cm}^{-3} \]

Cathode

Anode

1 mm
2 mm
6 mm

100.00 ns
Principals of DBD Microdischarges
Dielectric Barrier Discharge

Four Different Gap Widths

Dielectric-Barrier Discharges

Plasma Chemistry

- Electric Field
  - Breakdown
  - Electrons & Ions
  - Excited Species
  - Chemical Reactions

Discharge Physics

- Ozone Generation
- Surface Treatment
- Pollution Control
- Excimer Formation
- CO₂ Lasers
- Hydrogenation of CO₂

- Excimer Lamps
- Plasma Displays
Plasma Display Televisions
AC Plasma Display Configuration

- Front Glass Plate
- Transparent Display Electrodes
- Rear Glass Plate
- Dielectric Barrier
- MgO Layer
- Phosphor Coating
- Address Electrodes
- Separator Ribs
Generation of Ozone

Dielectric Barrier Discharge

3 O₂ ⇌ 2 O₃

1. Power source
2. High voltage electrode
3. Glass, Ceramic or Enamel Dielectric
4. Discharge gap
5. Grounded electrode
Properties of Ozone (O$_3$)

- Tri-atomic form of oxygen. \[ \text{O}_3 \]
- Most powerful commercial oxidizing agent
- Unstable - must be generated and used onsite
- Limited solubility in water, but more so than oxygen
- Leaves a dissolved residual which ultimately converts back to oxygen
Discharge Tubes in Ozone Generators
Traditional Ozone Generator with Glass Tubes
Generation of Ozone
Ozonia Advanced Technology
Ozone Generator
Generation of Ozone

Advantages of Enamel Dielectrics

Proven, Patented Design

• Simplicity

• Single Dielectric Component
  – Reduced number of Dielectrics

• Safety
  – Lower operating voltage
    \(< 4000 \text{ V}\)

• Reliability
  – Fused Dielectrics ensure continuous production

• \textit{Lowest Power Consumption}
  – \textit{Operational Savings}!
Modern Ozone Generator

Generating Ozone (cont')

- Feed Gas Inlet
- Cooling Water Outlet
- Ground
- Cooling Water Inlet
- Ozone Outlet
Generation of Ozone
Generation of Ozone

Power Supply Unit
Ozone Water Treatment

Ozone Contacting Systems

Bubble Diffusion

- Easy to use
- Low energy usage
- Mass transfer efficiencies to > 90%
Ozone Process Flow Diagram

- LOX Tank
- Vaporizers
- Ozone Generators
- Ozone Contact Chamber
- Off-Gas Blower
- Ozone Destruct Unit
- Vent to Atmosphere
- Oxygen
- 10-12% O₃
- O₃/O₂
## Municipal Ozone Installations

### Key Ozonia Installations (Partial List)

<table>
<thead>
<tr>
<th>Ozonia Installations</th>
<th>Ozone Plant Size [lb/day]</th>
<th>Start-Up Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Los Angeles, CA</td>
<td>10,000</td>
<td>1986</td>
</tr>
<tr>
<td>Fairfax, VA – Corbalis</td>
<td>9,000</td>
<td>2003</td>
</tr>
<tr>
<td>MWD, CA – Mills</td>
<td>9,000</td>
<td>2003</td>
</tr>
<tr>
<td>Fairfax Co., VA – Griffith</td>
<td>9,000</td>
<td>2004</td>
</tr>
<tr>
<td>MWD, CA – Jensen</td>
<td>18,750</td>
<td>2005</td>
</tr>
<tr>
<td><strong>Indianapolis, IN – Belmont AWT</strong></td>
<td><strong>12,000</strong></td>
<td><strong>2007</strong></td>
</tr>
<tr>
<td><strong>Indianapolis, IN – Southport AWT</strong></td>
<td><strong>12,000</strong></td>
<td><strong>2007</strong></td>
</tr>
<tr>
<td>MWD, CA – Diemer</td>
<td>13,400</td>
<td>2008</td>
</tr>
<tr>
<td>MWD, CA – Weymouth</td>
<td>13,400</td>
<td>2009</td>
</tr>
</tbody>
</table>

### Ozonia North America - Potable Water Summary

- **Total Number of Installations:** 90
- **Total Installed Production:** > 265,000 lbs/day
Ozone Water Treatment
MWD Mills WTP - California

3 x 3,000 lbs/day of ozone
Ozone Generators at Rostock Water Works (Ozonia)
Ozone Water Treatment

Ozone - How it works:

**Oxidant:**
- Breaks double carbon bonds
- Creates \( \text{OH}^- \) radicals which break higher carbon bonds
- Increased temp. and pH accelerates \( \text{O}_3 \) decomposition to \( \text{OH}^- \)

**Disinfectant:**
- Kills by cell lysing or causing the cell wall to rupture
- Attacks all bacteria virus, cysts and spores in varying degrees
Micro-organism / DNA

Adenine
Thymine
Cytosine
Guanine
Microbial Growth at Various Ozone Concentrations

- **Growth likely**
- **Growth possible**
- **NO GROWTH**

Ozone concentration (mg/l)

0.004  0.008  0.012  0.016  0.020
# Typical Water Treatment Usage

<table>
<thead>
<tr>
<th>Application</th>
<th>O₃ mg/l</th>
<th>Contact time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra Pure Water</td>
<td>0.05 - 0.25</td>
<td>sec. – min.</td>
</tr>
<tr>
<td>Water bottling</td>
<td>0.4 – 1.0</td>
<td>5 – 10 min.</td>
</tr>
<tr>
<td>Swimming pools &amp; spas</td>
<td>0.1 – 0.75</td>
<td>4 minutes</td>
</tr>
<tr>
<td>Potable, taste &amp; odor disinfection</td>
<td>1.5 – 5.0</td>
<td>5 – 10 min.</td>
</tr>
<tr>
<td>Microfloculation</td>
<td>1.0 – 3.0</td>
<td>5 – 10 min.</td>
</tr>
<tr>
<td>Lignin &amp; tammin removal</td>
<td>3.0 – 10.0</td>
<td>10 – 30 min.</td>
</tr>
<tr>
<td>Municipal wastewater</td>
<td>5.0 – 15.0+</td>
<td>15 – 30 min.</td>
</tr>
</tbody>
</table>
Ozone Water Treatment

Ozone – Municipal Applications

- Taste and Odor
- Color Removal
- Disinfection Without THM’s
- Improved Filtration Efficiency and Flocculation
- Cryptosporidium Deactivation
- Giardia & Virus Inactivation
- Oxidation - Organics, Fe & Mn
- Wastewater disinfection
- BOD, COD and TOC reduction
Applications of Ozone

Wastewater Treatment

- Disinfection of Secondary and Tertiary Effluents
- Color Reduction
- TOC Oxidation (Industrial)
- Oxidation of Odor Causing Compounds
- Oxidation of Endocrine Disruptors (EDC’s) and Pharmaceutically Active Compounds (PAC’s)
What are Endocrine Disruptors (EDC’s) and Pharmaceutically Active Compounds (PAC’s)?

- EDC’s and PAC’s are Naturally and Synthetic compounds that may affect the balance or normal functions in animals and humans.

What can EDC’s and PAC’s do?

- Even in very small concentrations these compounds can disrupt normal bodily functions.
- Man-made chemicals can trick the bodies endocrine system.
Applications of Ozone

Examples of Endocrine Disruptors

1000’s of compounds that may be investigated as EDCs – Some examples are:

- Synthetic Hormones
- Naturally Occurring Estrogens
- Health and Beauty Aids
- Solvents
- Pesticides
- Surfactants
- Plastics
- Fungicides
Ozone Water Treatment

Ozone - Industrial Applications

- Ultrapure Water for Pharmaceutical Applications
- Wastewater disinfection / color removal
- Soil and Groundwater Remediation
- Cooling Tower Water Treatment
- Food Processing
- Aquaculture / Aquariums
- Beverage Applications
- Pulp & Paper Bleaching
High Purity Ozonation

Microchip manufacturing
What are the current issues in large-scale ozone generation?
Experimental Setup

*Front view of the two units after the redesign and reworking of the gas, water and instruments connections.*
Experimental Setup

Top view of the two experimental units. Spectroscope (not shown) is to the left of the DBD. The units were different with respect to their electrodes: one had only the electrode coated with the dielectric ("single-coated"), the other one had the electrode and the anode coated with the dielectric ("double-coated").
Generation of Ozone

**Generation of Ozone**

- **Discharge**
  - $e + O_2 \rightarrow O_2^+ + 2e$
  - $e + O_2 \rightarrow e + O + O$

- **Electrons**
  - $O + O_2 + M \rightarrow O_3 + M$

- **O - Atoms**

- **O$_3$ - Molecules**

**Competing Reactions**

- $e + O_3 \rightarrow e + O_2 + O$
- $O + O + M \rightarrow O_2 + M$
- $O + O_3 \rightarrow 2O_2$
- $O_3 + O_2 \rightarrow 2O_2 + O$
Spectroscopy

Source of Continuous Spectrum

white light

PRISM

Plasma

Absorption Spectrum

Continuous Spectrum

PRISM

Emission Spectrum

Brightness (B)

wavelength \( \lambda \)

Brightness (B)

wavelength \( \lambda \)
Plasma Absorption Spectroscopy
IR spectra in pure oxygen (black curve) and at approximately 10wt% N₂ admixture (red line). N₂O₅ peaks appear at 1245 cm⁻¹ and at 1725 cm⁻¹.
Infrared Absorption Spectroscopy

IR spectra of several methane variations. The green curve envelopes all of the methane peaks at 1325 cm⁻¹, recorded at smaller methane admixtures. Simultaneously, the N₂O₅ peaks disappear as the methane peaks appear.
N$_2$O$_5$ Formation

Amount of formed N$_2$O$_5$ and N$_2$O as a function of ozone concentration at 3 wt% of nitrogen admixture and for various electrode arrangements.

$p=2$ bara, cwt=20°C, $q=3.5$ kW/m$^2$, $f=1450$ Hz
Plasma Emission Spectroscopy
Relative Emissions of the Ozonizer plasma

Region 300-850 nm from individual (calibrated) regions (smoothed by PeakFit). Single-coated ozone generator. Inlet side.
Absolute Emission of the DBD Plasma

Intensities in (O₂+3 wt%N₂) plasma

![Graph showing emission intensities in (O₂+3 wt%N₂) plasma.]

O*(777)
Plasma emission diagnostics: role of $\text{N}_2$

Modeling of plasma chemistry incl. the $N_xO_y$ chemistry up to $N_2O_5$, for different Oxygen Nitrogen mixtures, varying power deposition scenarios and initial ozone background concentrations (up to 15%) previously done.

With $\text{N}_2$ present – less oxygen atoms are formed. However, the difference in intensity is very small.
The Role of nitrogen ($N_2$) in ozone generation

The role of $N_2$ must be related to its by-products reacting on the surface of the electrode.

The following facts, which were verified on various oxygen-fed ozone generator vessels (utilized with and without pickling and passivation) were established.

Above 8wt% of $O_3$:

1. **Deterioration of the generator performance without $N_2$ admixture**, even with p&p; (removal of the p&p oxide layer during aggressive cleaning of surfaces is equivalent to the case without p&p).

2. The experiments performed by Pontiga et al. in 2004 confirm the above conclusion. The by-products seem to just conserve the properties of a surface; it will deteriorate without them. A deterioration of the surface is due to oxidation, which extends the thickness of the oxide layer. $N_2O_5$ is found to deposit as crystalline substance on surfaces, which are slightly cooler than the $N_2O_5$-carrying gas. An $N_2O_5$ layer seems to inhibit the advanced oxidation of the stainless steel surface.
The Role of nitrogen (N₂) in ozone generation

Three possibilities have to be considered for the oxygen-fed ozone generator:

- Excited N₂ molecules lead to an increased O₂ dissociation; in such case, an increased efficiency is correlated to the N₂ admixture

- The by-products perform a chemical/physical process on the electrodes, which turns out to be beneficial

- The UV emission from O₂ dissociation that leads to photon or light splitting of O₃ is suppressed by N₂
Effect of methane on ozone efficiency and specific power
Effects of $\text{N}_2$ and $\text{CH}_4$

Picture of an amorphous-crystalline $\text{N}_2\text{O}_5$ structure captured at the Orlando Skylake water plant in 2006.
Plasma Chemistry with CH$_4$ Impurities
Effect of methane on electrode surface

- Electrode of the ozone generator after:
  * Several hours in CH₈/O₂ and up to 2 wt% of methane (a, b, c)
  * Three hours in CH₈/O₂ + traces of N₂ and up to 1 wt% of methane (d)
- Visible change of discharge character at about 1/3 length of electrode (a, d)
Kinetics of CH_x Conversion *without* N_2

\[ \text{O}_2 + \text{CH}_x \rightarrow 12\text{wt}\% \text{O}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

- conversion by collisions
- deposition
- vaporization by sputtering

Reversible process below 1000ppm CH_4
Effect of water on electrode surface with $N_2$
Effect of water on electrode surface

- Long term effect (800 hrs) of $H_2O/O_2/N_2$
Kinetics of CH\textsubscript{x} Conversion with N\textsubscript{2}

conversion by collisions
HNO\textsubscript{3} formation

O\textsubscript{2} + N\textsubscript{2} + CH\textsubscript{x}

12wt%O\textsubscript{2} + CO\textsubscript{2} + H\textsubscript{2}O + HNO\textsubscript{3}

H\textsubscript{2}O + HNO\textsubscript{3}

deposition
vaporization by sputtering

irreversible process above a N\textsubscript{2} threshold (??) \ll 1000ppm N\textsubscript{2}
@ any CH\textsubscript{4} concentration (60ppm??)
Plasma Chemistry with CH₄ Impurities

- Formation of NO and NO₂ depends on O₃, N₂ and gas temperature.

**Conclusion:** N₂ admixture is the key factor!
Summary

The mechanisms of formed NO$_x$ by-products follow the same principles as the air fed ozone generators; the amount of formed N$_2$O$_5$ is found to depend on just three parameters:

- ozone concentration
- nitrogen admixture
- cooling water temperature ( = gas temperature)

The conversion of methane to OH and H$_2$O is found to depend on:

- dissociation by electron impact (→ microdischarge)
- energy distribution of electrons in the microdischarges (→ discharge gap)
How to you optimize an ozone generator?
Theoretical

\[ P = \alpha \cdot 4f \sum_{i=1}^{n} C_{D,i} \frac{1}{1+\beta_i} U_{\text{min},i} \left( U_{\text{peak}} - U_{\text{min},i} \right) \quad \text{[kW]} \]

where

- \( i \) : \( i^{\text{th}} \) slice
- \( n \) : amount of slices per cylinder []
- \( U_{\text{peak}} \) : peak voltage [V]
- \( U_{\text{min},i} \) : minimum voltage of \( i^{\text{th}} \) slice [V]
- \( f \) : frequency [Hz]
- \( C_{D,i} \) : capacitance of dielectrics of \( i^{\text{th}} \) slice [F]
- \( \alpha \) : adjustable parameter \([0, \infty]\)
- \( \beta_i \) : \( C_{G,i}/C_{D,i} \) []

Scientific Approach

Experimental

\[
\begin{align*}
\text{ozone concentration} & \quad [\text{wt\%}] \\
\text{power density} & \quad [\text{kW/m}^2] \\
\text{efficiency} & \quad [%] \\
\end{align*}
\]
Impact of Power Induction

- Arr. B: unstable
- Arr. C: -2%
- Arr. D: +0%
- Arr. E: +4.5%
- Arr. F: +7%
- Arr. G: +3%

Position (1: inlet, 4: outlet)
Experimental Test Rig
Experimental Test Rig

Outer grounded electrode (left picture) and the dielectric covered inner electrodes (right).
Reference Arrangement

Inlet

Gas flow direction

Outlet
Optimized Arrangement

Gas flow direction

Inlet  Outlet
Intelligent Gap System (IGS)

Molecular Oxygen ($O_2$)

Ozone ($O_3$)
Particle Size Synthesis: 
By-Products Cluster Formation

- **high diffusion and deposition to surfaces**
- **low diffusion rate, good transport**
- **high sedimentation on the structure**
Conclusions

Fundamentals of ozone synthesis in a DBD plasma:

– Highly filamented DBD discharges are best-suited for the production of ozone concentrations in the range of 6 to 14 wt%.

– The preferred characteristic of the microdischarges are Townsend-like, at reduced electric fields $E/n$ around 190 Townsend.

– Detrimental side-effects, induced by by-products, can be avoided by a proper design of the electrode arrangement. The phenomenon is related to the diffusion rates of formed by-product clusters.
Conclusions

Benefits from DBD Plasma Tailoring:

– Reduced power consumption of up to 10% improvement

– Increased ozone concentrations of up to 14% now achievable

– Improved neutralization and conditioning of detrimental by-products

– Reduced system capital and operational cost!!!
Homogeneous Dielectric Barrier Discharge

A picture of the HV fast-switch DBD plasmas taken at high pressure.
Experimental Setup

The Dielectric Barrier Discharge (DBD) cell.

A typical plasma in pure nitrogen environment.

Side view of the DBD cell experiment with the fast high voltage transistor switch connected to the bottom electrode.
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Questions???
Thank You!

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