Plasma-enhanced Ammonia Combustion

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NH_3 Fuel: The Key to US Energy Independence
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Gas Discharge Plasma

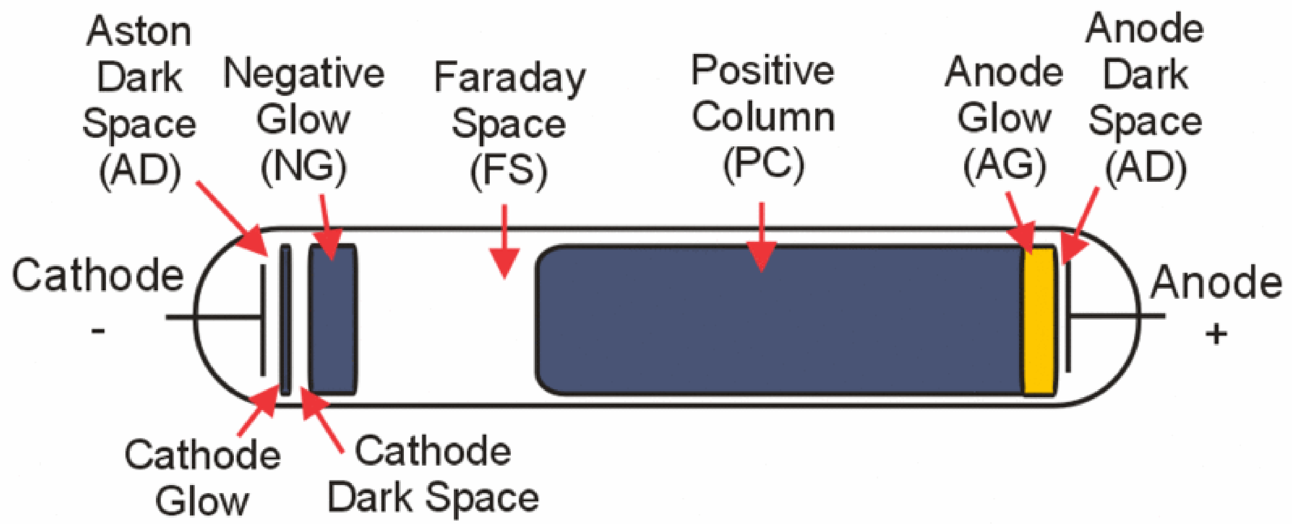
A Gas Discharge Plasma (GDP) occurs when electrons flow from anode (-) to cathode (+) through a gas.

Gas Discharge Plasma

An important note: Gases would be near-perfect insulators, if not for the background ionization by cosmic rays.

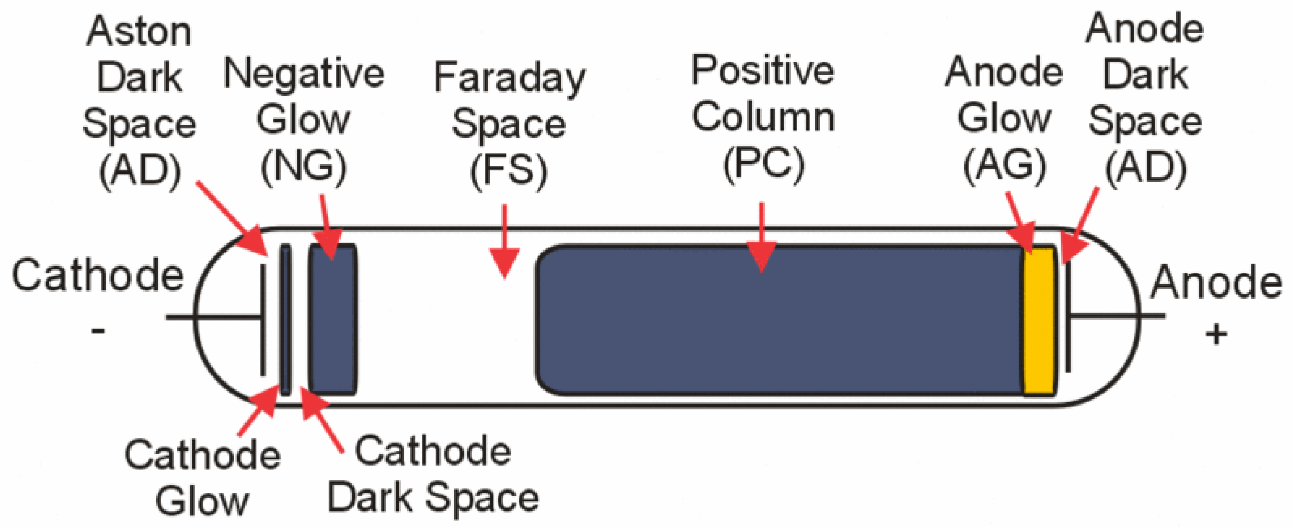
This background ionization allows plasma ignition with hundreds of volts, rather than tens of thousands of volts.

Regions in the GDP



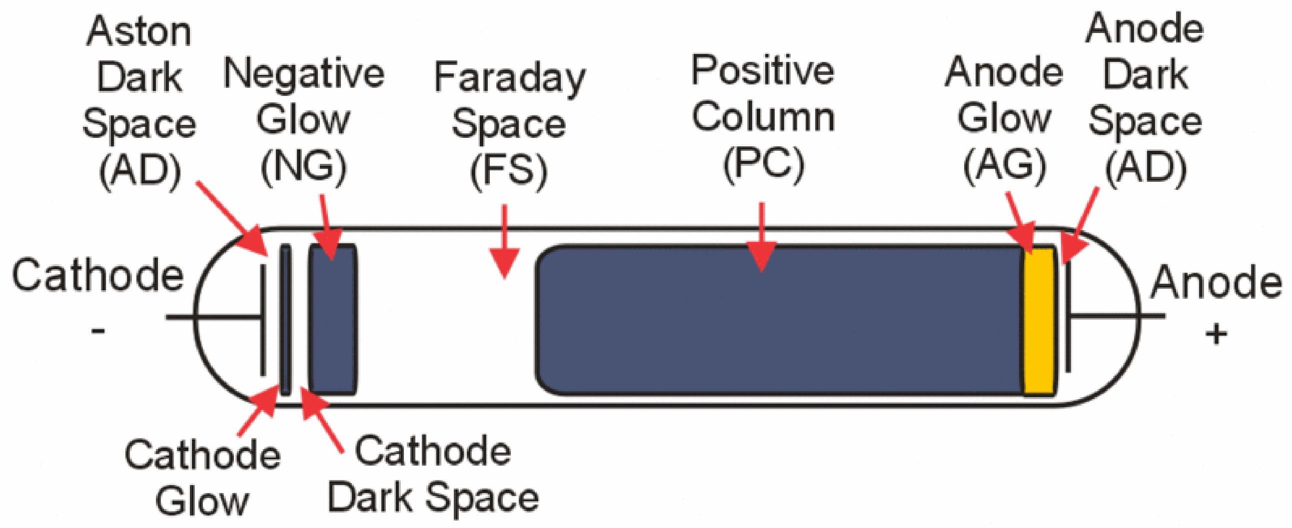
- **Electrons accelerate away from the cathode after they enter the plasma.**
- **As they get farther away from the cathode, they go faster and have more energy.**
- **Close to the cathode, the electrons are still slow, with insufficient energy to cause excitiation– this is the "Aston Dark Space."**

Regions in the GDP



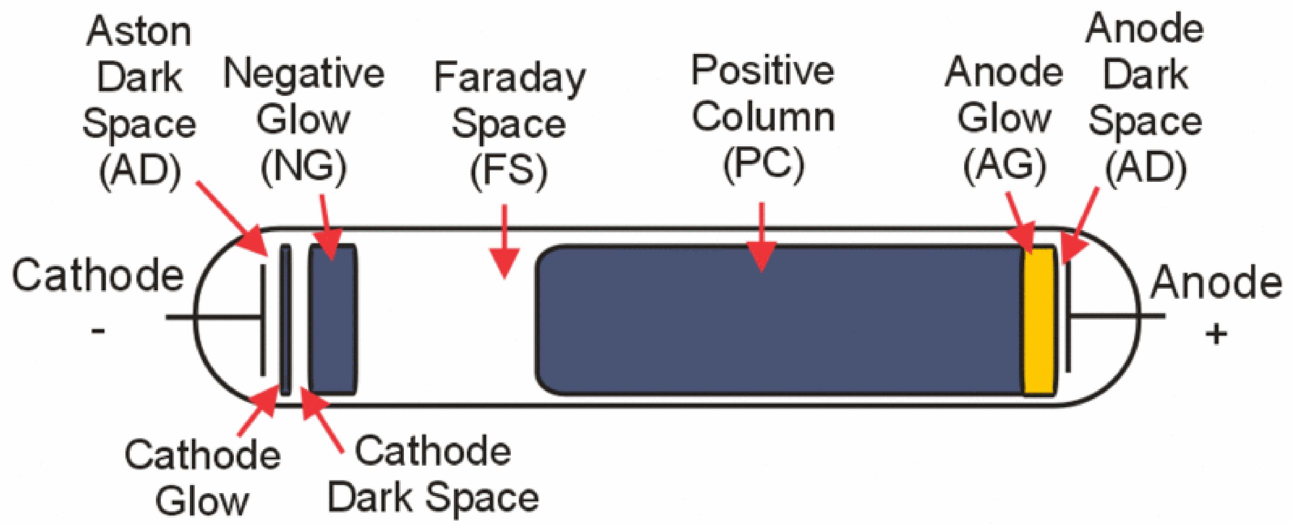
- **The Aston Dark Space extends only around 1 mm, even at low pressures.**
- **A bit further away, the electrons have gained enough energy to exite gas atoms' electrons to new quantum states – after which they relax and emit light. This is the "Cathode Glow" region.**

Regions in the GDP



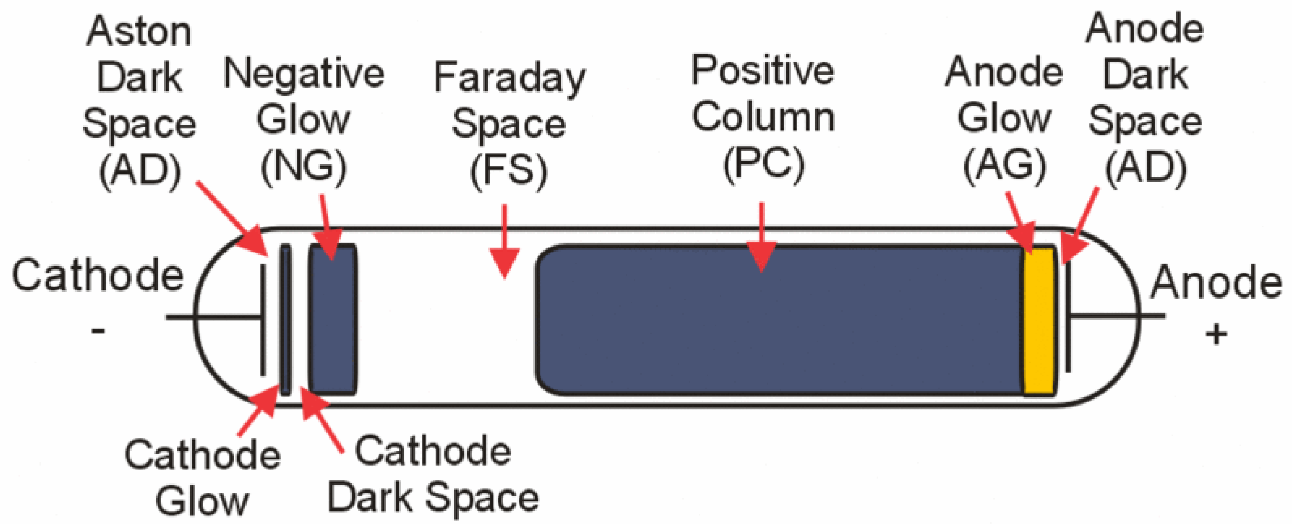
- **Very little other than light emission is accomplished in the Cathode Glow.**
- **Further away, the electrons have gained enough energy to completely dislodge electrons from the gas atoms, generating positive ions which drift towards the cathode. No light is emitted: no relaxation!**

Regions in the GDP



- Positively-charged ions created in this so-called Cathode Dark Space move slowly at first, then accelerate and collide with a vengeance into the cathode, generating new electrons which enter the plasma.
- Electrons slow after CDS collisions, yet excite atoms in the Negative Glow region.

Regions in the GDP



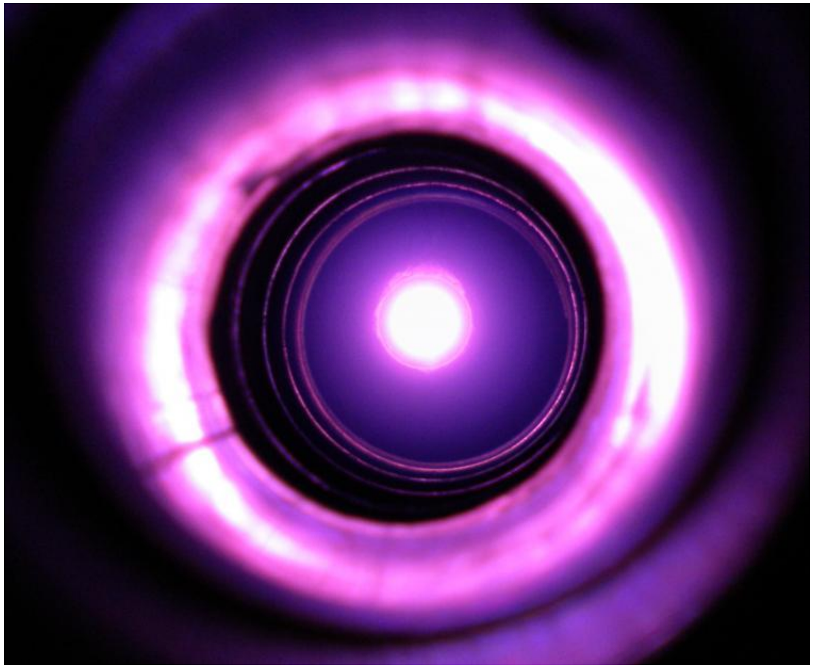
- **The Negative Glow region marks the outer boundary of the "Cathode Fall Region."**
- **Chemically, this is where the plasma energy is put to its greatest use – ions bombard the cathode to sustain the plasma, and chemical bonds are broken during ionization in the CDS.**

Standard Electrode Configuration

- **Shown here is the standard electrode set for a tubular glow discharge.**
  - Two electrodes of comparable size
  - Electrodes face one another, and are planar
- **The path of the electrons shows the inherent inefficiencies of this configuration**
  - Very little of the total length is the chemically useful Cathode Fall Region
  - Electrons have only one chance at attaining the proper energy to create ions in the CDS

Hollow Cathode Configuration

- **Creation of a radial, or hollow, cathode**
  - This cavity folds the cathode fall region within
  - Electrons accelerate or decelerate as they depart or approach opposing cathode surfaces, resp.
- **Electrons in plasma may spawn multiple ions while rebounding**
- **Lasers, ion thrusters, light sources, gas rxtrs**



Helium HCD
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Efficiency Through Geometry

- **The main goal is to contain the entire cathode fall region within the cavity.**
- **Pressure and distance play important roles.**
  - A pressure-distance (Pd) product is used for scaling.
  - If **P** is too great, the cathode fall region becomes too small, and any ions generated will recombine before impacting the cathode, which kills the plasma.
  - If **d** is too great, ionization occurs outside of the cathode fall region (e.g. Faraday Space), wasting the ionization energy to the surroundings.
- **Each gas type has a maximum Pd product for cathode fall region containment.**
- **Example – neon, Pd_{max} = 7.5 torr·cm**

Finally Getting to the Point

- **Break some NH_3 chemical bonds, and enhance its combustion**
  - Similar approach to cracking, but no warm-up
  - Similar to using a strong spark in SI
  - Ionization of NH_3 gas creates reactive intermediates, similar to those formed in a free flame
- **Known: increasing gas energy content leads to better combustion**
  - Flammability limits widen with temperature – heat increases molecular vibration & eases bond breaking
  - Overall effect is a reduction of the reaction barrier towards forming products: kinetic enhancement
  - Energy put into gas “stays there,” harvested later

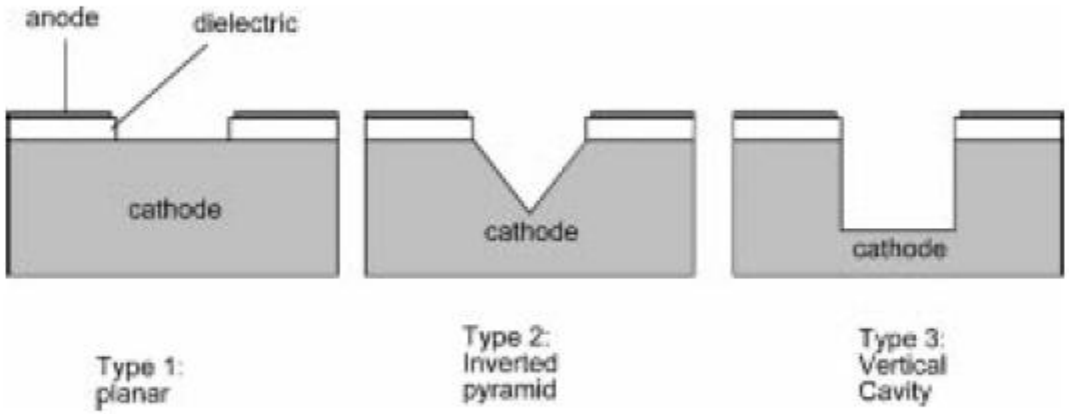
A Comparison

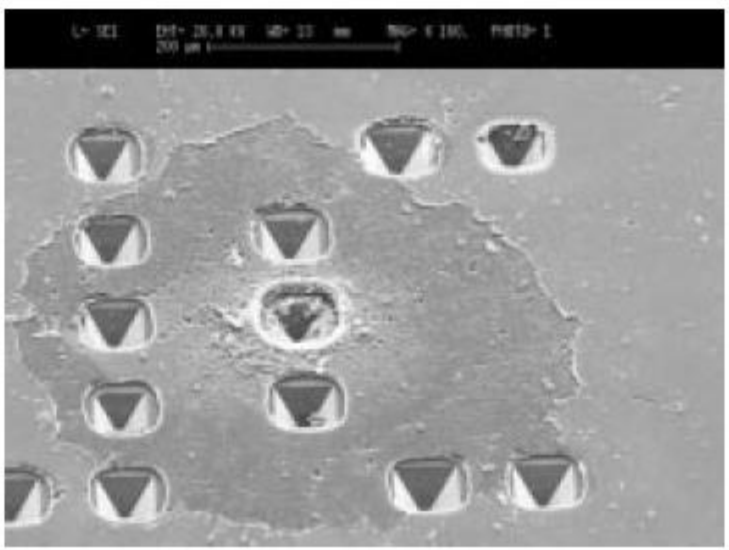
- **Imagine you have an experimental diesel engine with a stoichiometric NH_3/air mix.**
  - Compression ratio is 40:1
  - Air to ammonia ratio is 3.57:1
  - Heat capacity ratio is 1.38
  - If compression is adiabatic, final temp > 900°C
- **Gas mix should autoignite (T > 651°C)**
- **What energy did you add to the ammonia to get this nice result?**
  - $\Delta(PV)$ = 7.6 kJ/mol
  - N-H bond energy: 393 kJ/mol
  - Break 2% of the N-H bonds, and get the same effect

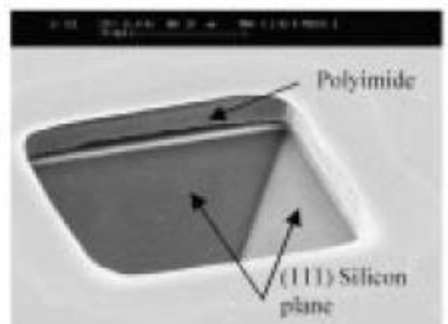
Plasma Ionization of NH_3 via HCD

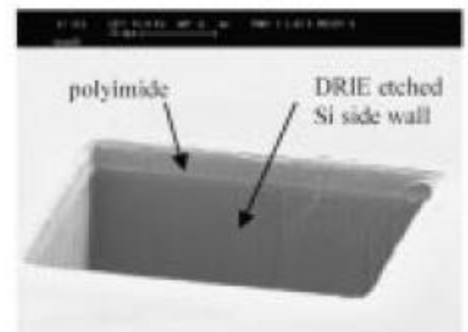
- **Each gas has its own Pd_{max}... must be determined by experiment**
- **Pressure in a pre-combustion processor will be high (~ atmospheric)**
  - Distances of HC must therefore be very small
  - Small distance = small volume
  - High gas flows will require many HC spaces
- **HC spaces must be made precisely, repeatedly, reliably**
  - Micromachining involves wear and tear of tools
  - Laser ablation is often irregular, damages substrate
  - Very good option: silicon etching

Examples of Silicon HC









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Why Should This Work?

Average Bond Dissociation Energies

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
H - H	436	N - N	160
C - H	413	N = O	631
N - H	393	N triple N	941
P - H	297	N - O	201
C - C	347	N - P	297
C - O	358	O - H	464
C - N	305	O - S	265
C - Cl	397	O - Cl	269
C = C	607	O - O	204
C = O	805	C - F	552
O = O	498	C - S	259

But Will It Work?

- **I don’t know, I haven’t tried it yet.**
- **To be determined: is the electrical energy required to partially ionize/dissociate ammonia is still to great to achieve via gas discharge at atmospheric pressure.**
- **If any plasma gas discharge going to work, this is the way to do it because…**
  - **It can be done at high pressure (unlike standard glow discharges)**
  - **It is much more efficient than gliding arc discharges, which are stable at higher pressures but waste energy as heat.**