Nitrogen Fixation as NOx Using Air Plasmas Coupled with Heterogeneous Catalysis

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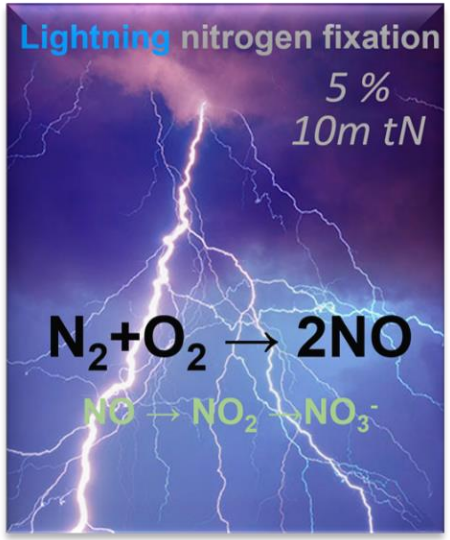
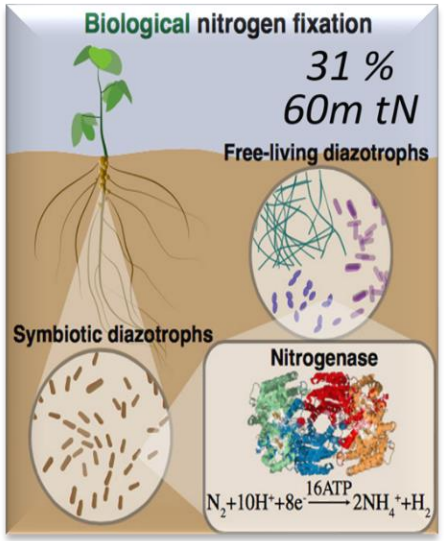
09/21/2021 @Online Low Temperature Plasma Seminar

Outline

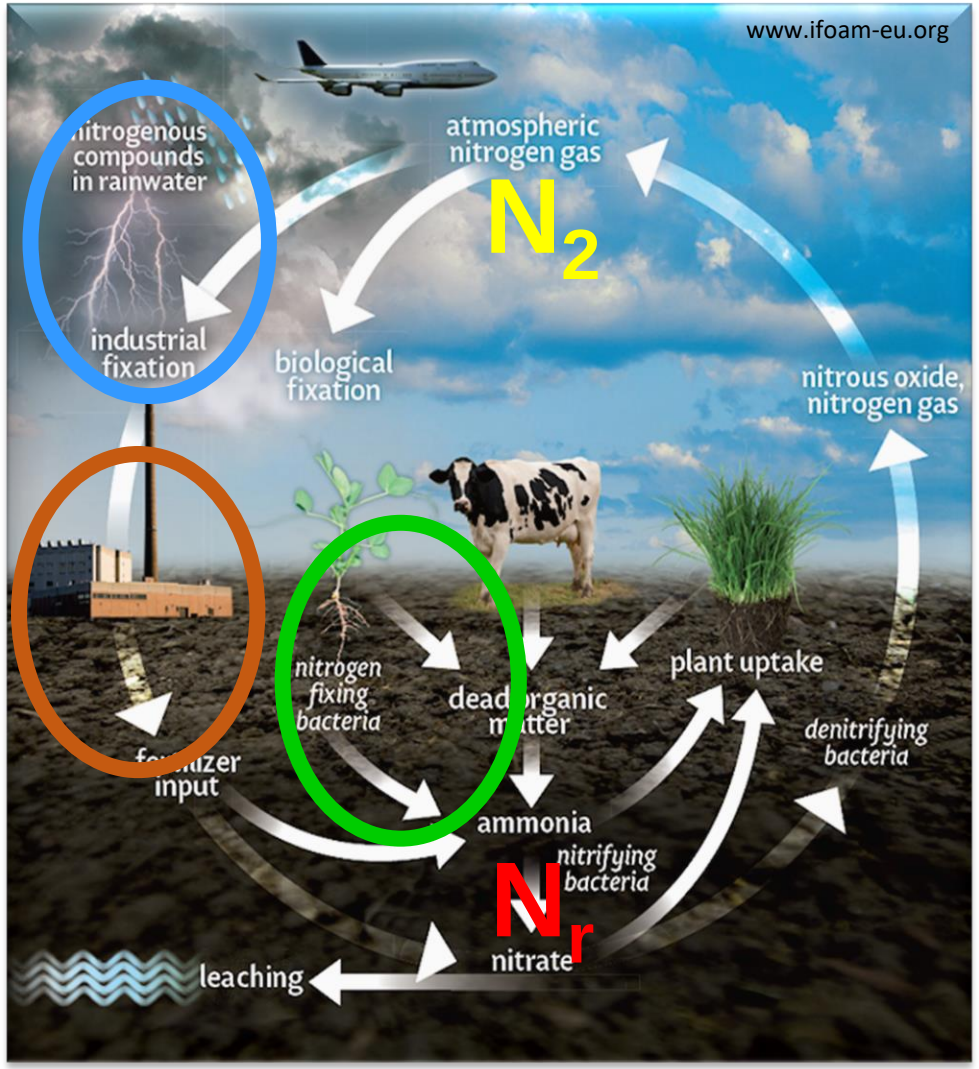
- Introduction
- Air plasma for NF: insights from reducing Energy Cost
- Air plasma coupled with heterogeneous catalysis
- Concluding remarks

Introduction: Nitrogen Fixation (NF)

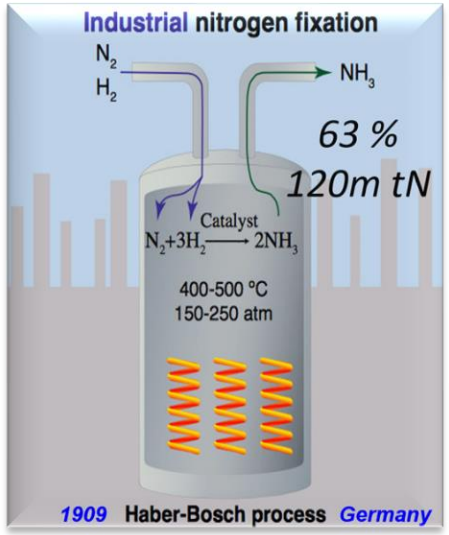


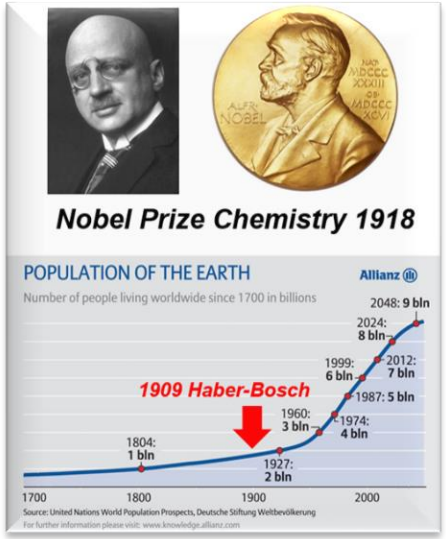


NSF workshop report #1550842



Nitrogen cycle on the earth





Erisman, J. W., et al. (2008). Nature Geoscience 1(10): 636-639.

Introduction: Challenges

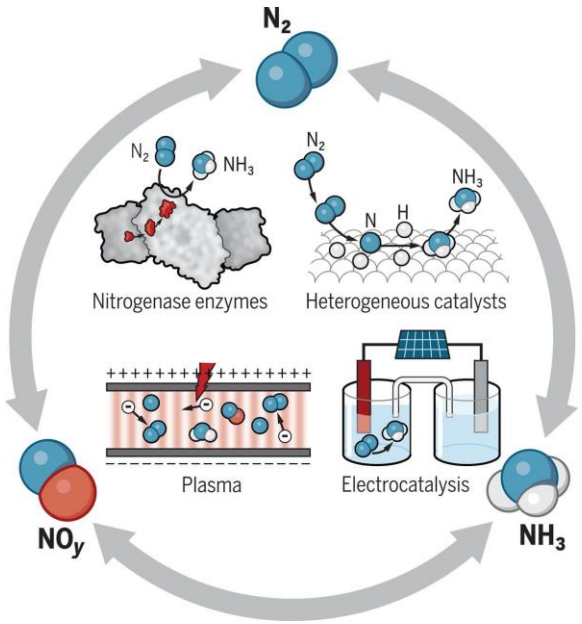
- **Energy-intensive:** Reliance on fossil fuels.
- **Huge quantity of H_2: 5%** natural gas.
- **Environmental issue:** 0.4 billion-ton CO2 /year. **$8NH_3 \rightarrow 3CO_2$**
- **Efficiency confined: 30 GJ/tN** → 24 GJ/tN.

Introduction: Solutions

REVIEW

Beyond fossil fuel–driven nitrogen transformations

Jingguang G. Chen[1,2,*], Richard M. Crooks[3,*], Lance C. Seefeldt[4,*], Kara L. Bren[5], R. Morris Bullo…
+ See all authors and affiliations



A. Nitrogenase

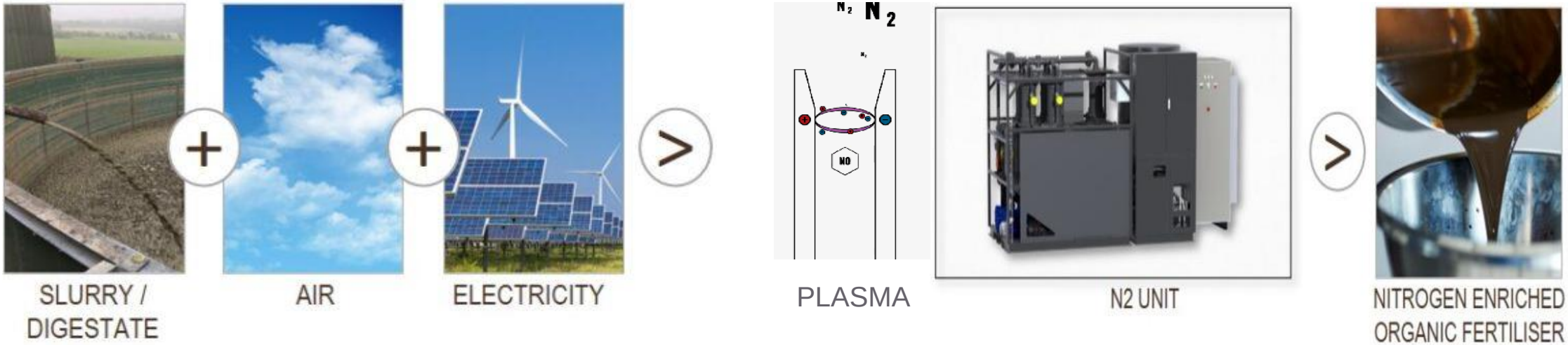
B. Catalysts

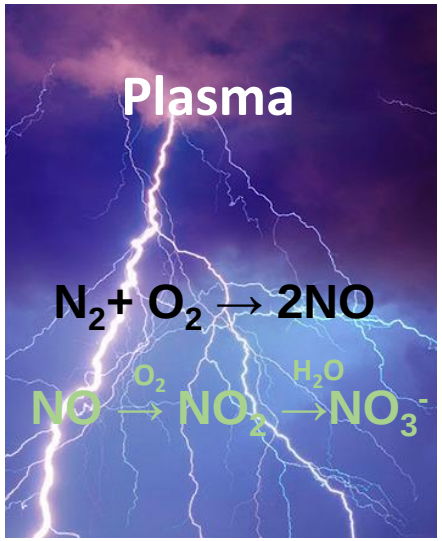
C. Plasma √

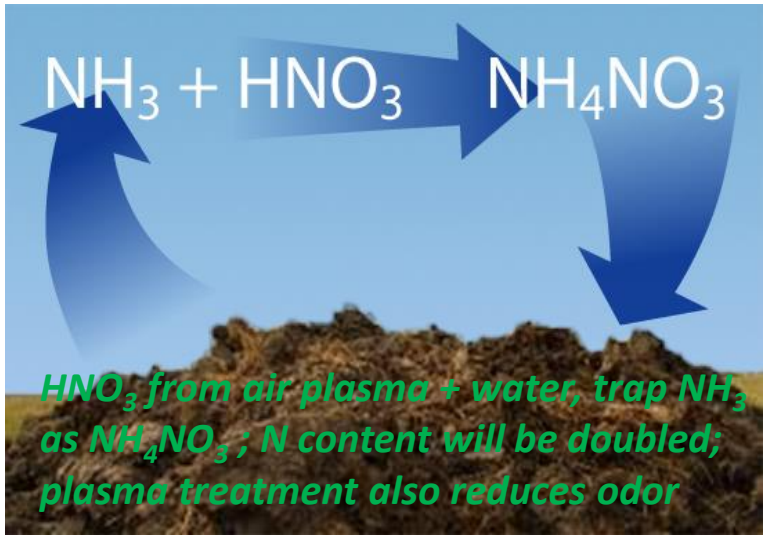
D. Electrocatalysis

Chen, J. G., et al. (2018). Science 360(6391): 873.

Introduction: N2 — Applied

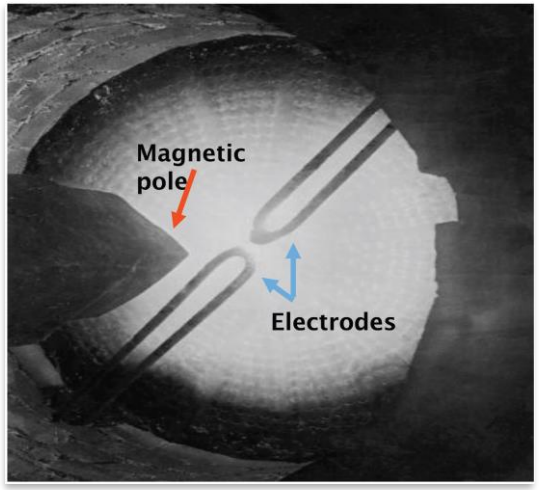




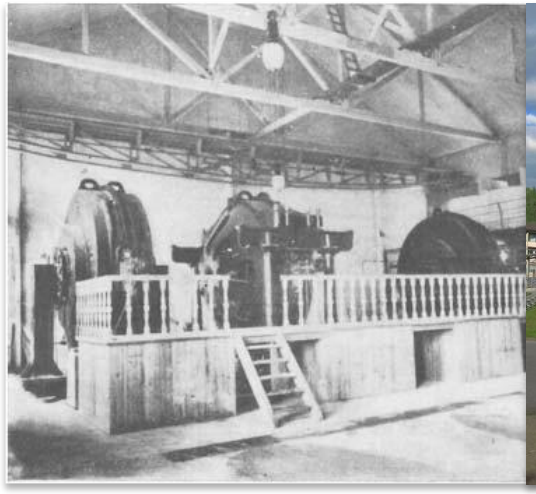


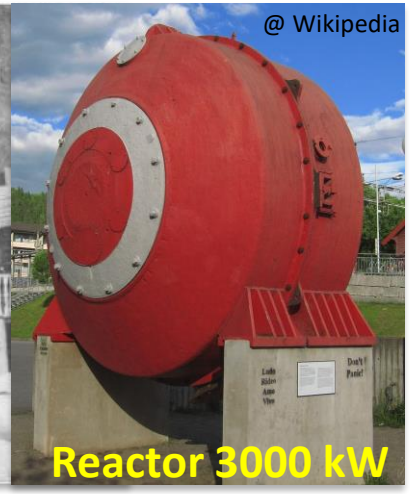
- **Renewable**
- **Air + Water** **Green**
- **Small scale**

Introduction: Birkeland-Eyde process



1903 Birkeland-Eyde process





1906 Notodden Manufactory

$N_2 + O_2 \rightarrow 2NO$ $\quad$ $NO + 1/2\ O_2 \rightarrow NO_2$

$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$

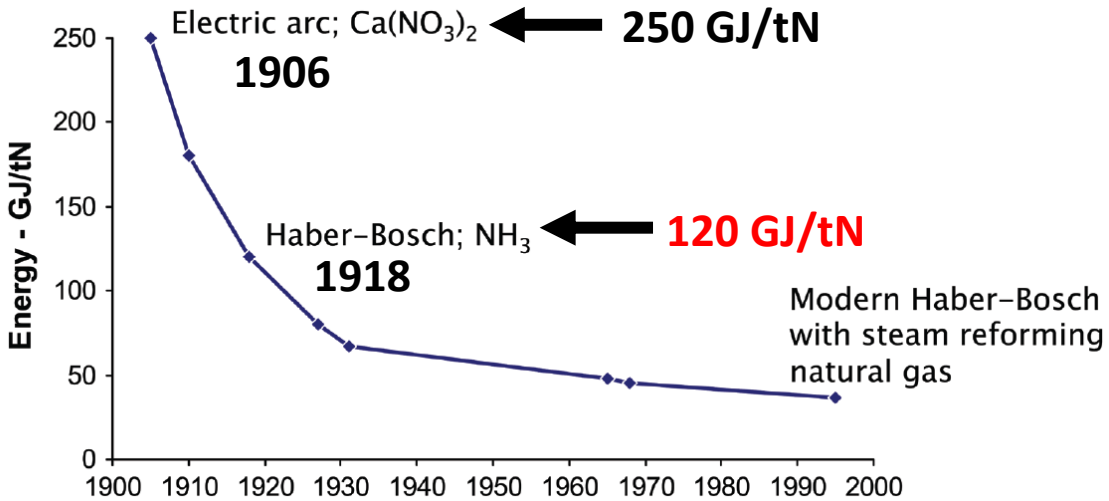
$Ca(NO_3)_2$ 'Norwegian saltpeter' N fertilizer

Kristian Birkeland
(1867-1917)

Electron → **Plasma**

1897 **1903** **1928**

J. J. Thomson **I. Langmuir**



Progress of energy cost for NF

Birkeland, K. (1906). Transactions of the Faraday Society 2(2): 0098-0119.

Introduction: Birkeland-Eyde process

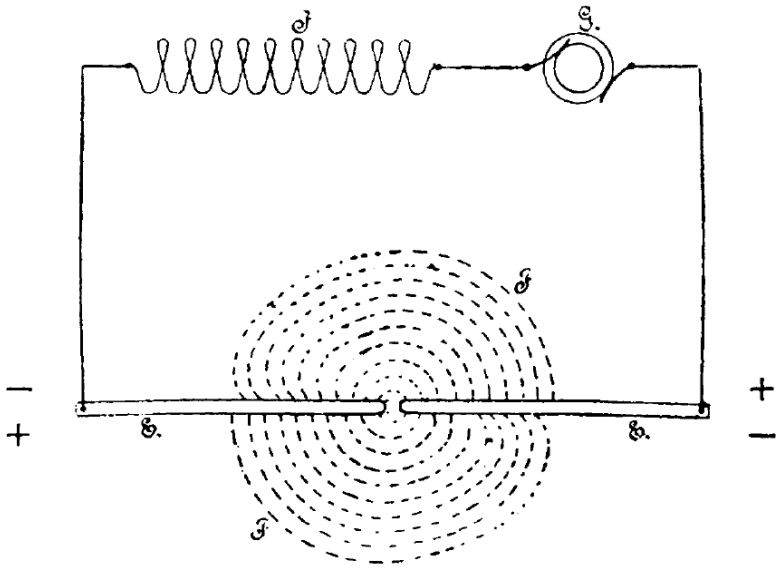
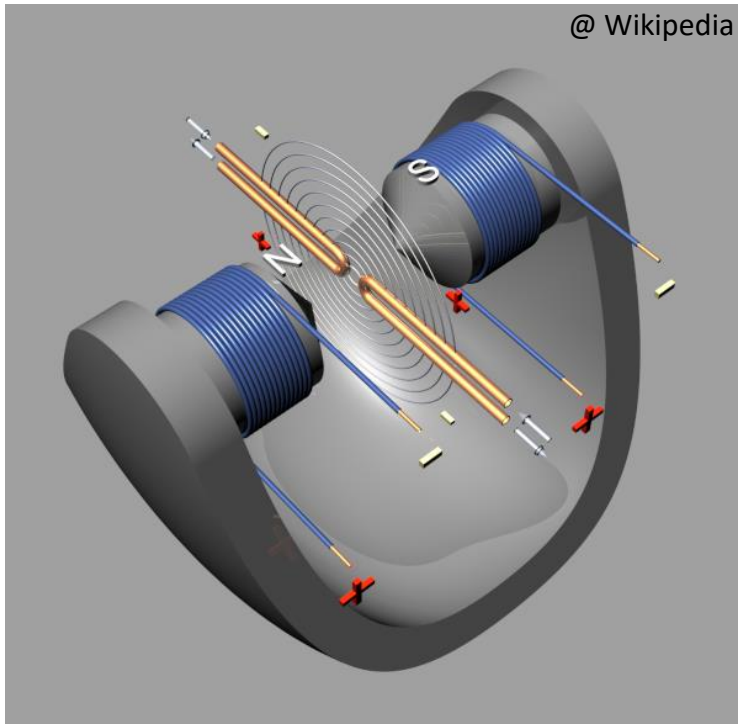
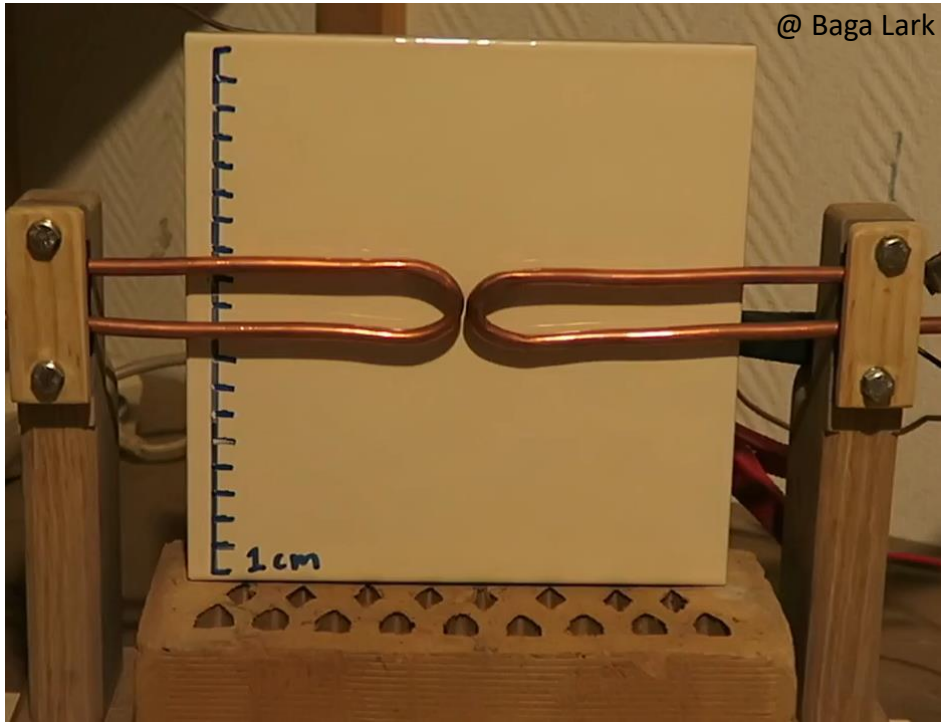


FIG. 2.



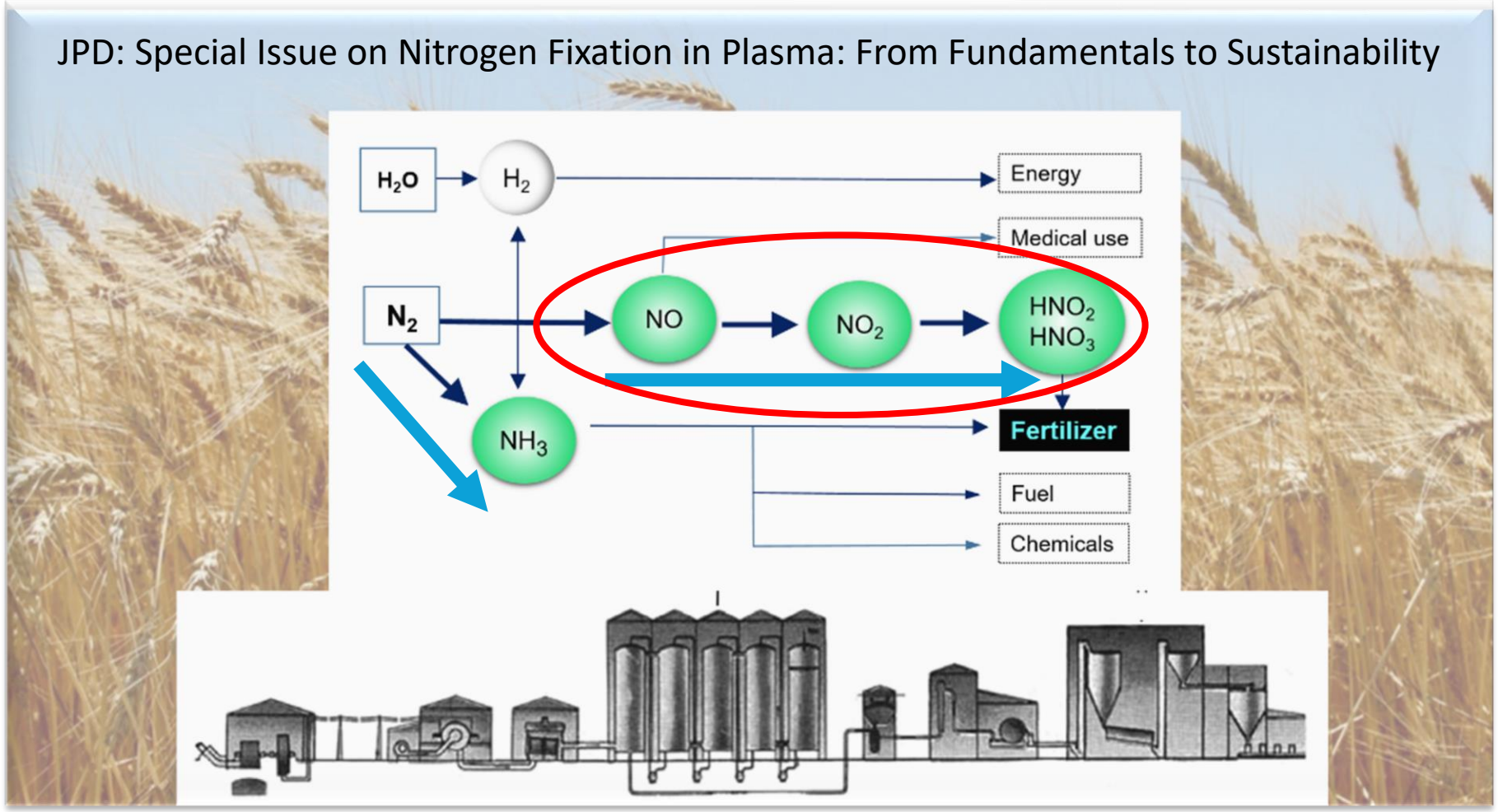


Birkeland-Eyde process video

In an alternating current (see Fig. 2), all the arcs with a positive direction of current run one way, while all with a negative direction run the opposite way, presupposing the magnetising being effected by direct currents. In this way, a complete, luminous, circular disc is presented to the eye.

Birkeland, K. (1906). Transactions of the Faraday Society 2(2): 0098-0119.

Introduction: Nitrogen Fixation in Plasma



Plasma-enabled reaction pathways and historical fertilizer plant

Guest Editors

Volker Hessel, *The University of Adelaide, Australia*

David B Graves, *University of California, Berkeley, United States of America*

Hyun-Ha Kim, *National Institute of Advanced Industrial Science and Technology (AIST), Japan*

JPD: Special Issue on Nitrogen Fixation in Plasma: From Fundamentals to Sustainability.

Introduction: Overview of NO production

- **A. Fridman**, Plasma Chemistry, 2008

6.1.1. Fundamental and Applied Aspects of NO Synthesis in Air Plasma

The synthesis of nitrogen oxides in air plasma is one of the "old timers" in plasma technology. This endothermic plasma-chemical process is usually presented simply as

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO, \quad \Delta H \approx 1\ \text{eV/mol}. \qquad (6\text{–}1)$$

Henry Cavendish and Joseph Priestly were the first scientists who investigated this process, in the eighteenth century. Industrial implementation of the plasma technology was performed in 1900 by Kristian Birkeland and Samuel Eyde. Birkeland and Eyde developed

- **Y. B. Zeldovich 1947**

$O + N_2 \rightarrow NO + N$ $\quad E_a \approx 3.27$ eV/molecule

$N + O_2 \rightarrow NO + O$ $\quad E_a \approx 0.3$ eV/molecule

$N_2 + O_2 \rightarrow 2NO$ **Combustion**

$N_2(^1\Sigma_g^+, v)$ $\qquad N_2^* = N_2(A^3\Sigma, B^3\Pi \cdots\cdots$

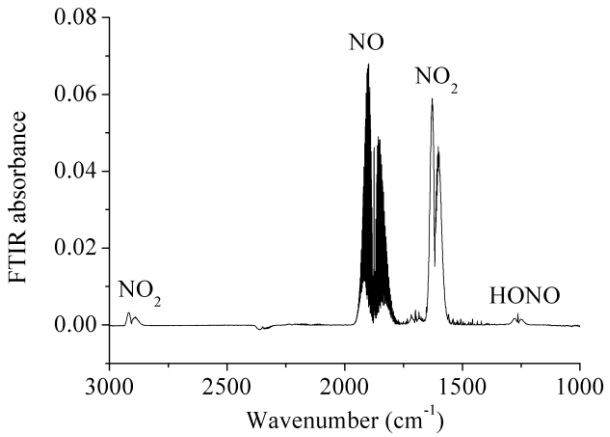
How to make the plasma process more economical ?

1 atm Air **Low Energy Cost**

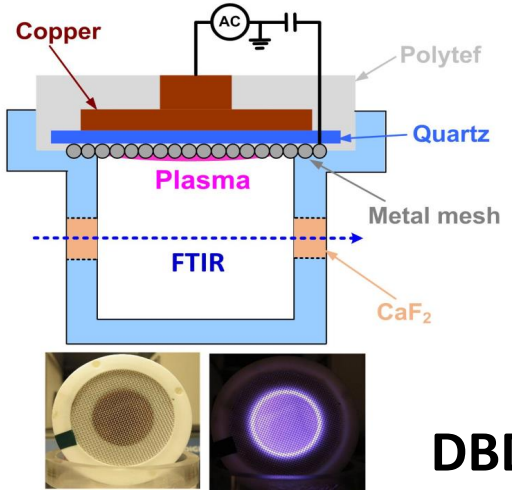
Outline

- Introduction
- **Air plasma for NF: insights from reducing Energy Cost**
- Air plasma coupled with heterogeneous catalysis
- Concluding remarks

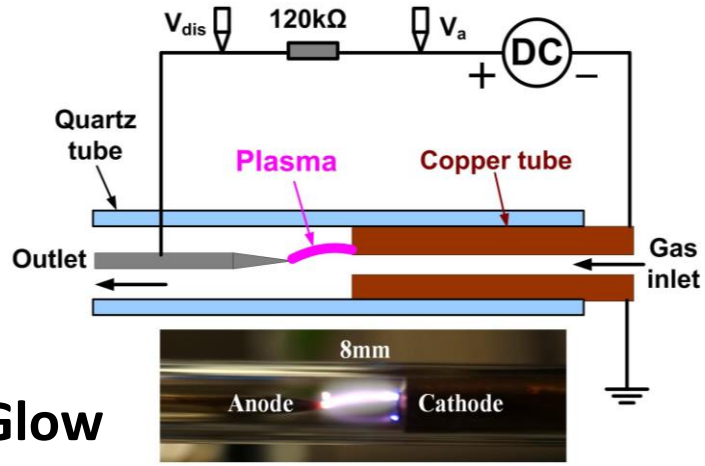
Experimental Setup



Typical FTIR spectrum

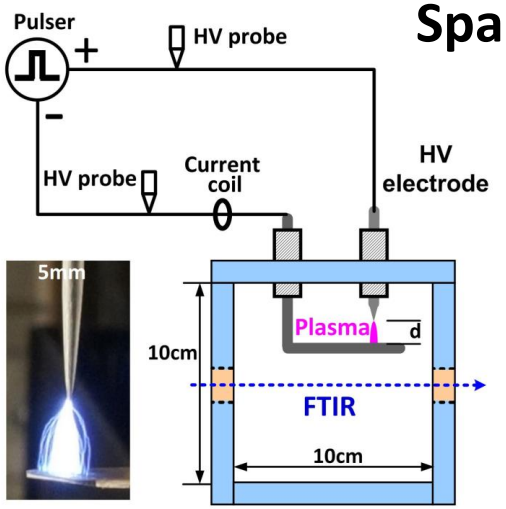


DBD

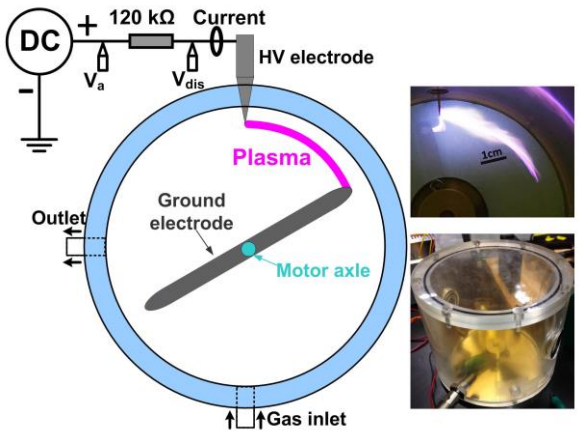


Glow

Spark



Extending Arc



Pei, X. K., et al. (2019) Chemical Engineering Journal 362: 217-228.

Specific energy cost calculation

Calculation of energy cost of plasma nitrogen fixation

$$E_{N_r} = \frac{P_{\mathrm{dis}} \times t}{\frac{V}{24\ \mathrm{L/mol}} \times c_{NO_x} \times 10^{-6} \times 14\ \mathrm{g/mol}} \times 10^{-3}$$

E_{Nr} is energy expended per unit of **reactive N_r (GJ/tN)** **MJ/mol** **kWh/kg**

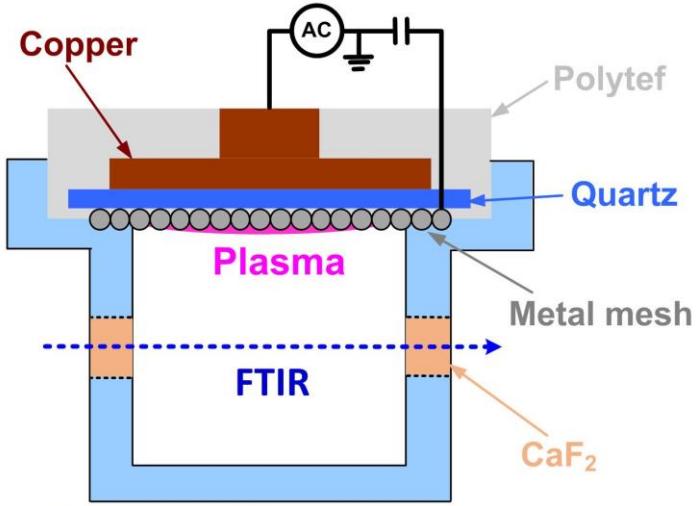
P_{dis} is the **plasma power consumption** (W) **(only for plasma)**

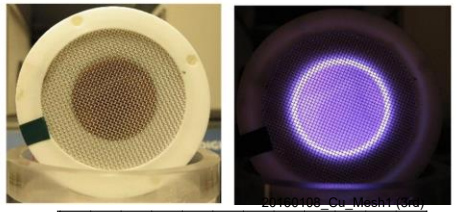
V is the volume of chamber (L) or gas flow into the chamber

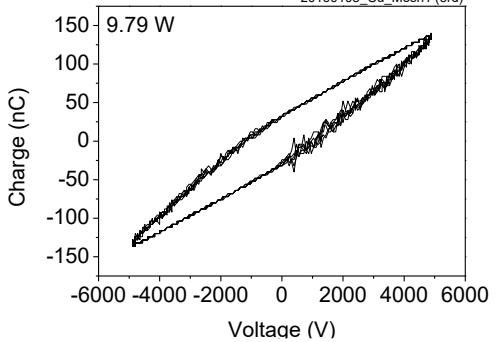
c_{NOx} is the concentration of NO_x (ppm)

Results: DBD (Surface Micro-discharge)

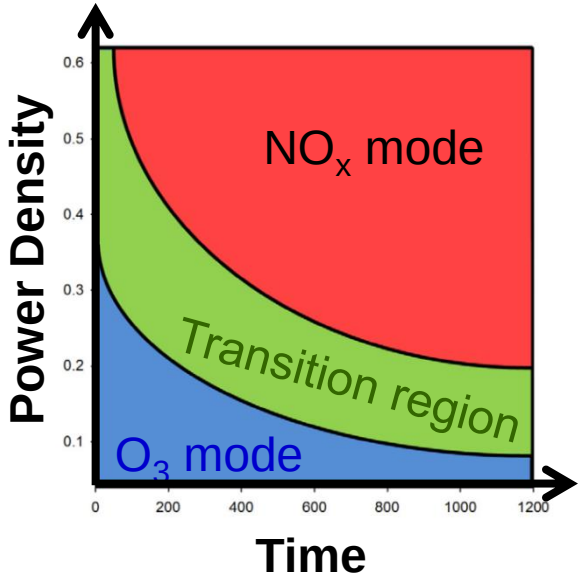
Surface Micro-discharge

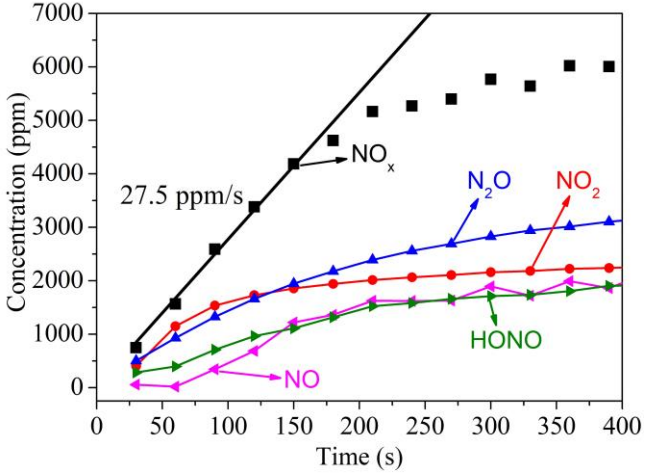






Pavlovich, M. J., et al. (2014). PSST 23 065036.

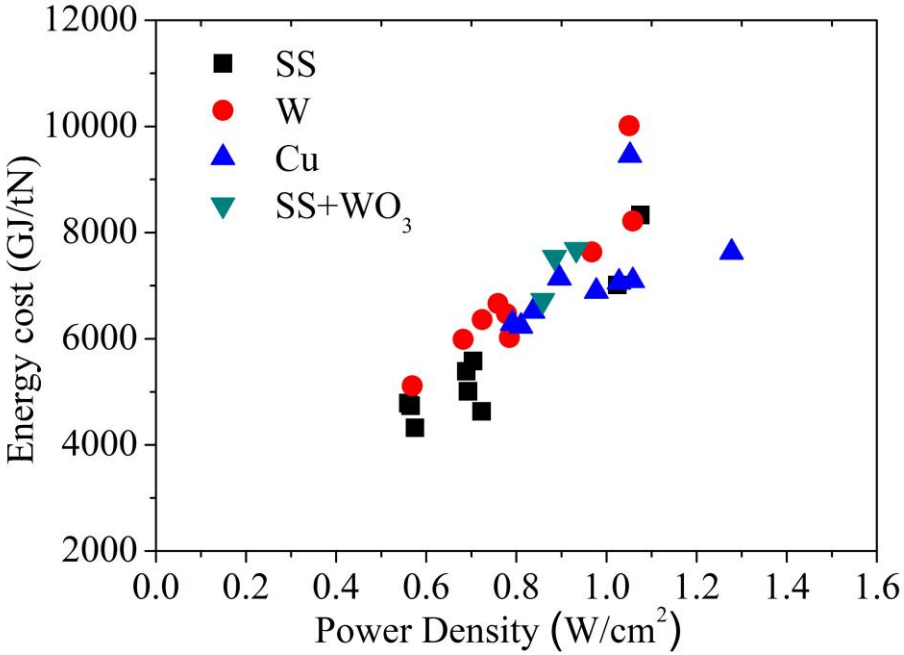




NO_x species (NO_2, NO and HONO)

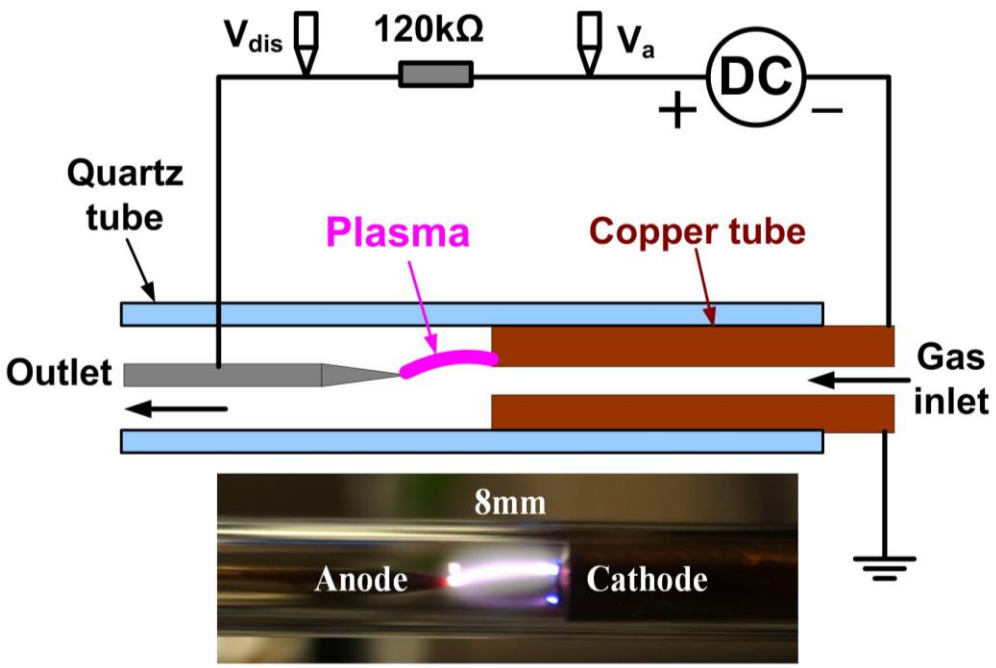
kWh/kg **GJ/tN:** MJ/mol

gigajoules cost per metric ton N produced



- No catalytic effect
- Increase with increasing power density
- 4,000 GJ/tN – 10,000 GJ/tN

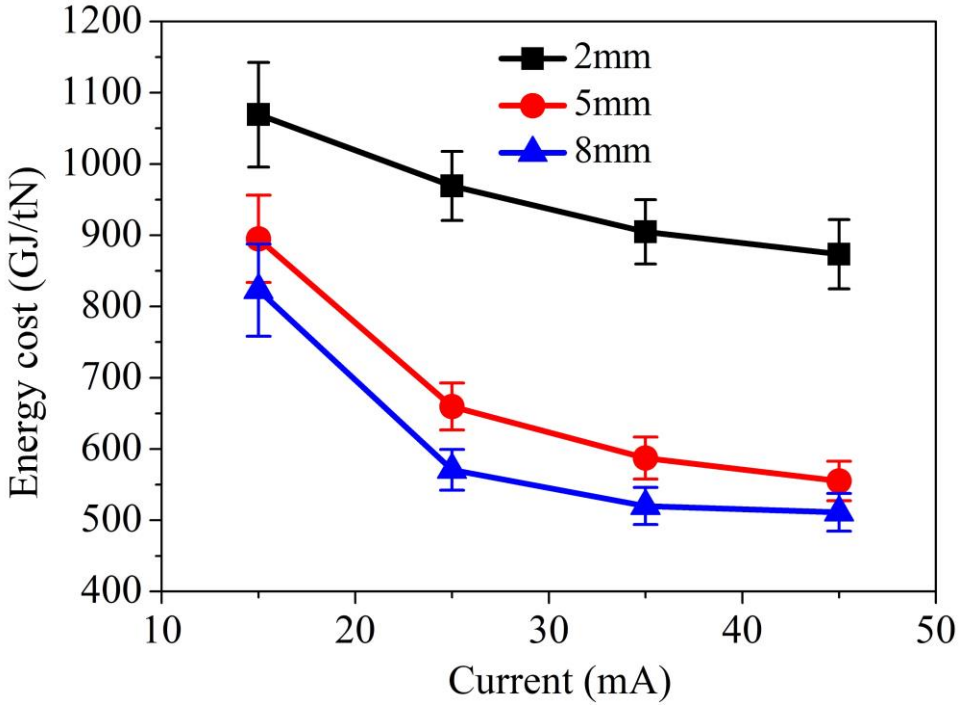
Results: DC glow discharge



DC glow discharge

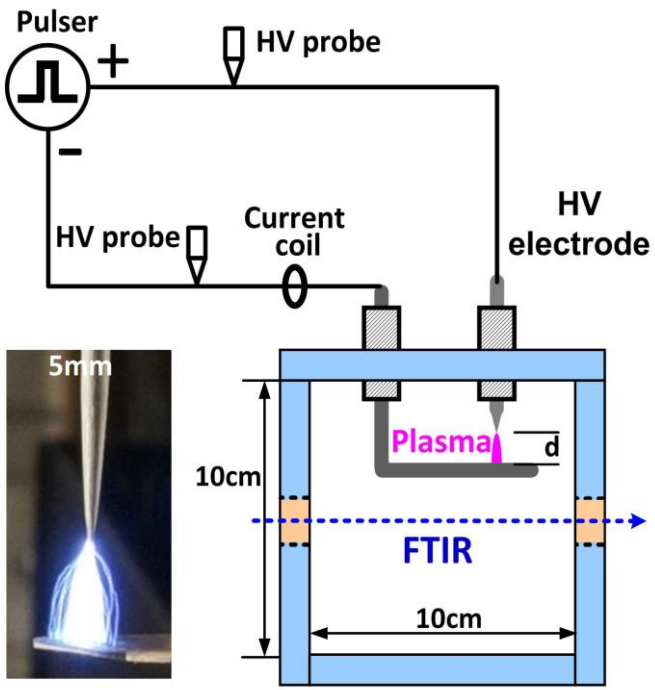
- Constant I_{dis} and V_{dis}
- High gas temperature ~1800 K

2 L/min air



- Decreases with increasing current (15-45mA)
- Lower energy cost at larger gap distance (2-8mm)

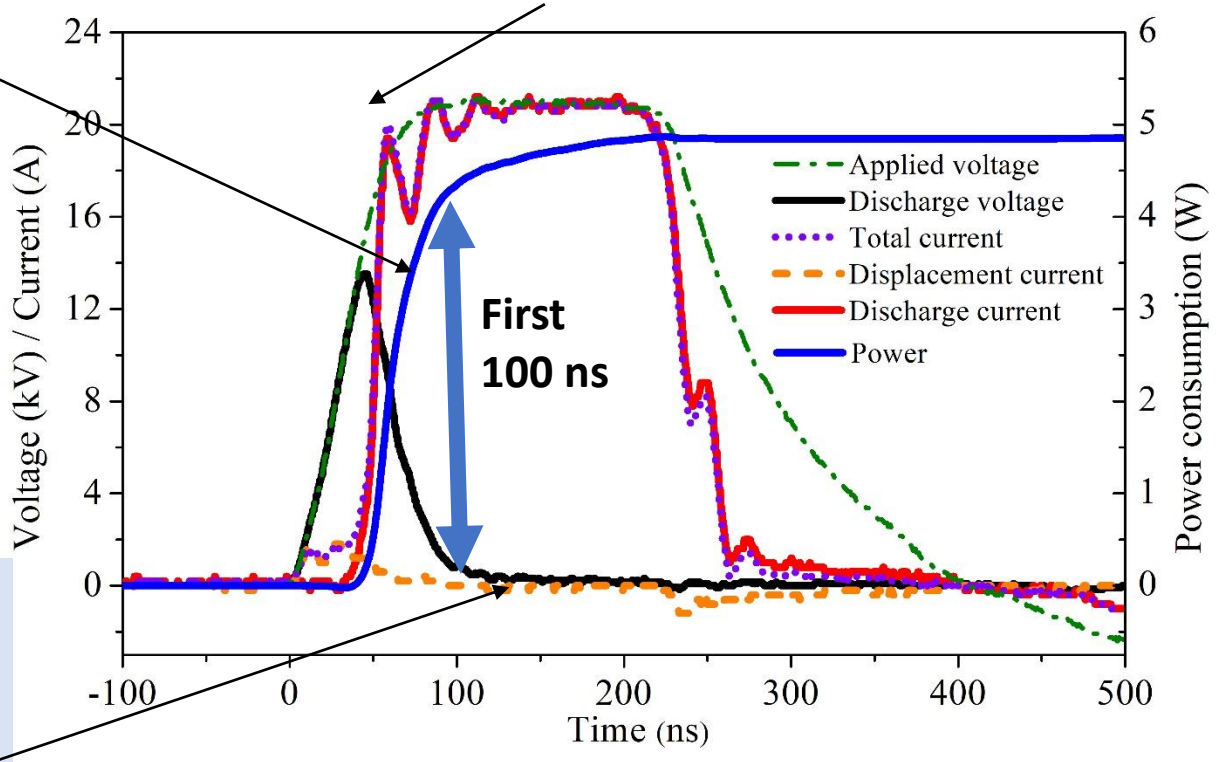
Results: ns pulse spark discharge



Eagle Harbor Technologies (EHT)

Most power dissipated during **breakdown period**

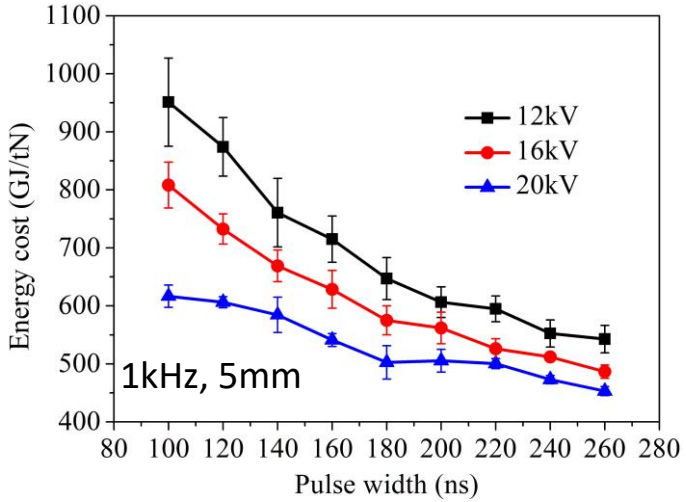
After breakdown, V_{dis} drop quickly, I_{dis} increase to a high value ~20A

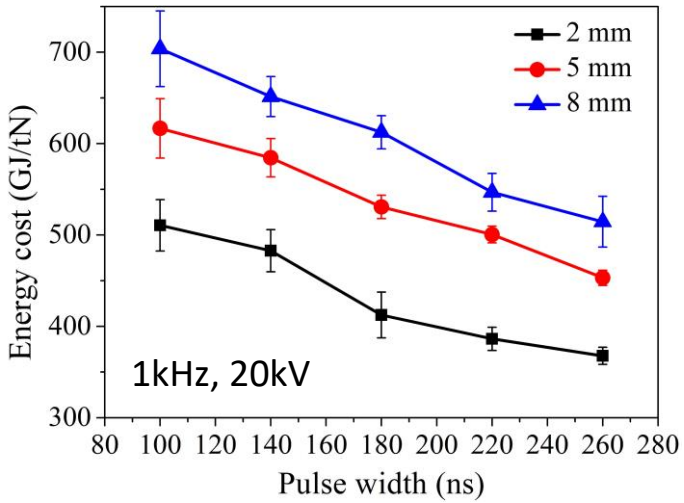


240ns, 20kv, 1khz, 5mm

When voltage across gap drops to << 1kV, power decreases, but **NO_x production continues** with high current (~ 20A)

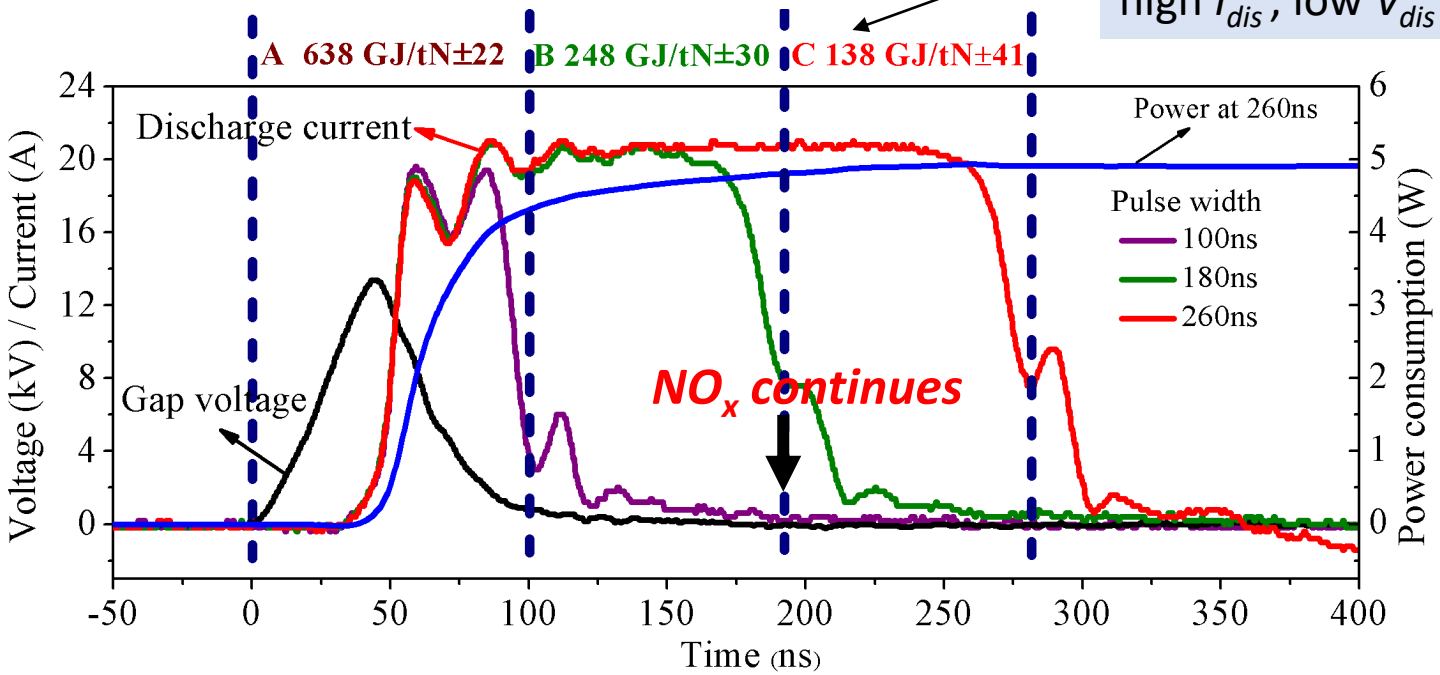
Results: ns pulse spark discharge





Pulse Width (ns)	100	180	260
Power Consumption (W)	4	4.72	4.92
NO_x production rate (ppm/s)	10.75	15.72	18.20
Energy Cost (GJ/tN)	638	514	463

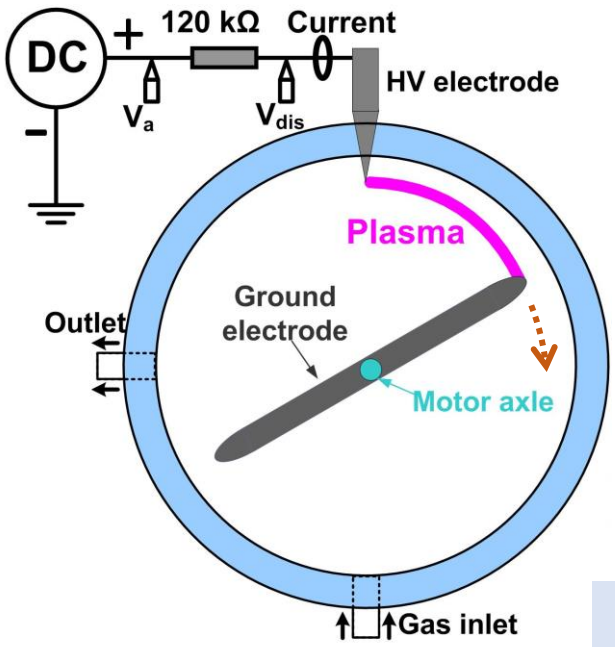
Most efficient; high I_{dis} , low V_{dis}

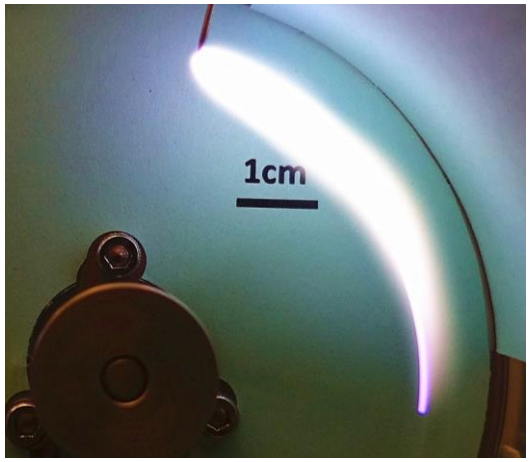


20kv, 1kHz, 5mm

Results: The Propeller Arc

Rotating cathode, driven by a motor, fixed anodes

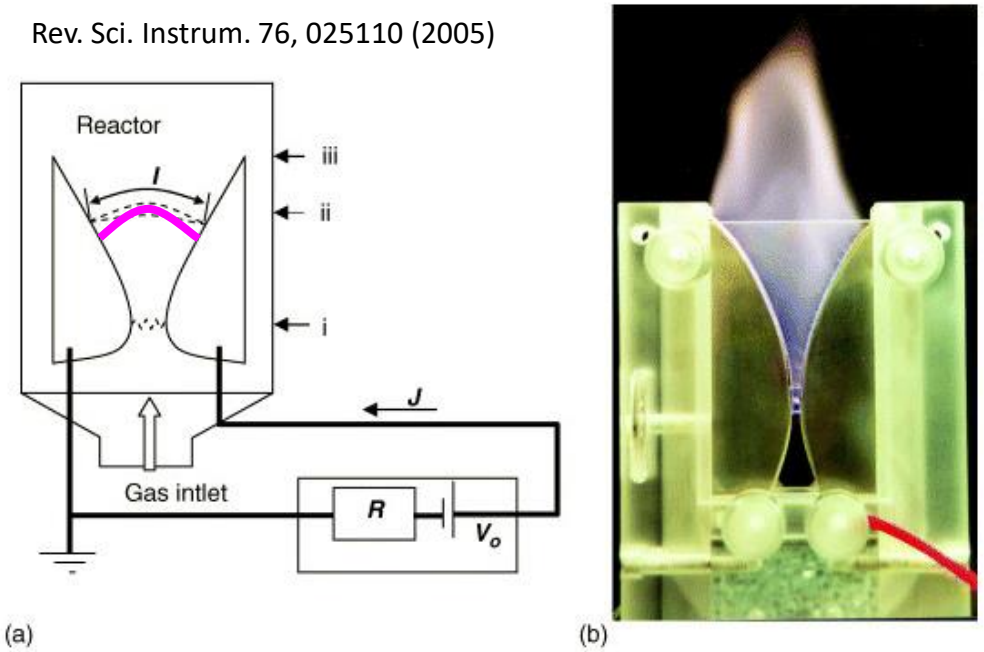




Propeller Arc (PA)

- *No need forced gas flow*
- *Low breakdown voltage*
- *Easy to control, f , L, P*
- *Simple structure, stable*

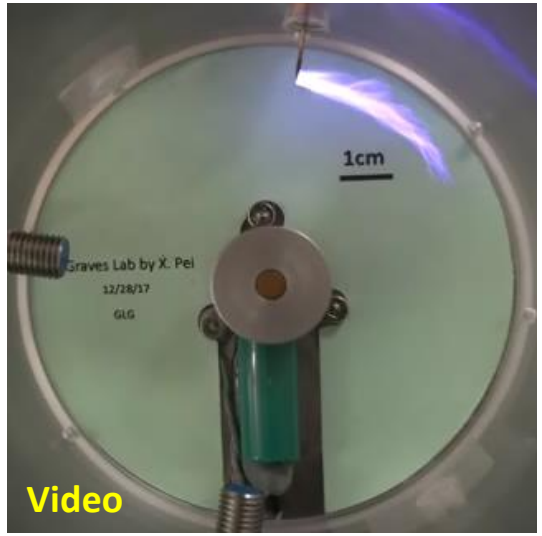
Rev. Sci. Instrum. 76, 025110 (2005)

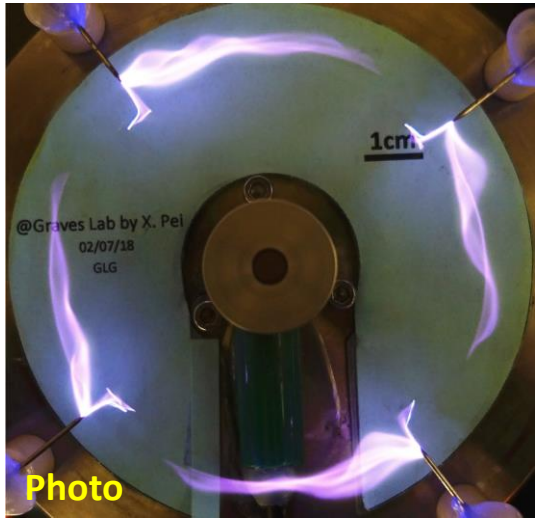


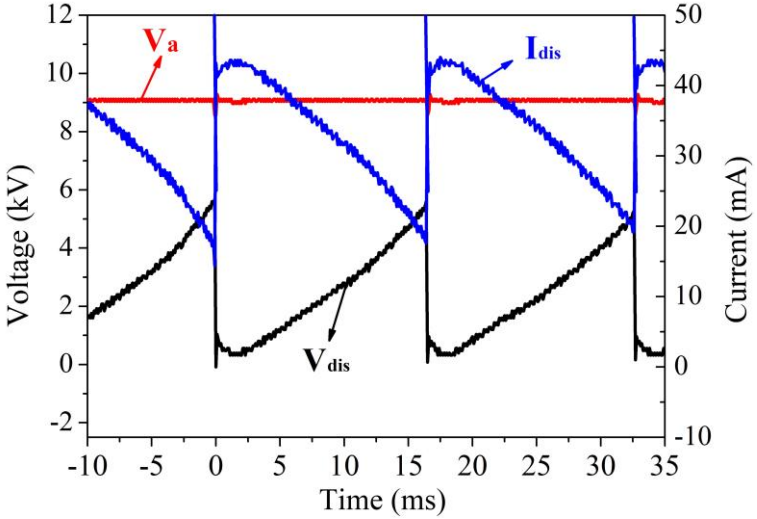
Gliding Arc

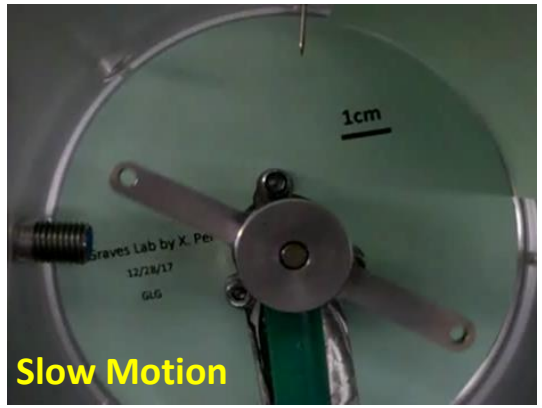
Pei, X. K., et al. (2018) Plasma Sources Sci. Technol. 27 125007

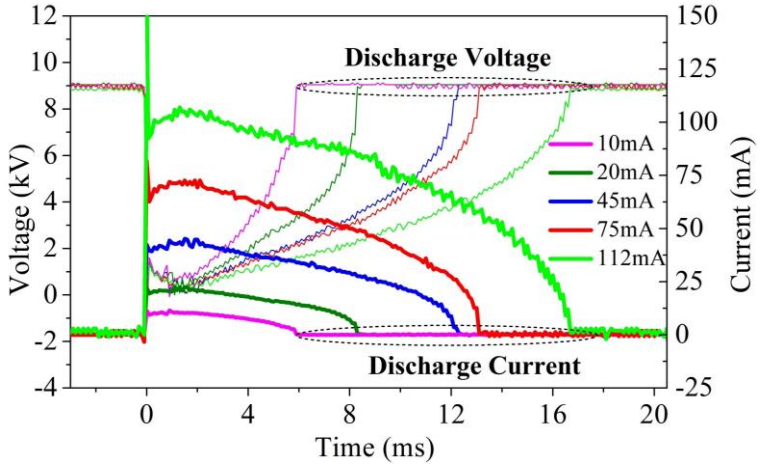
Results: The Propeller Arc







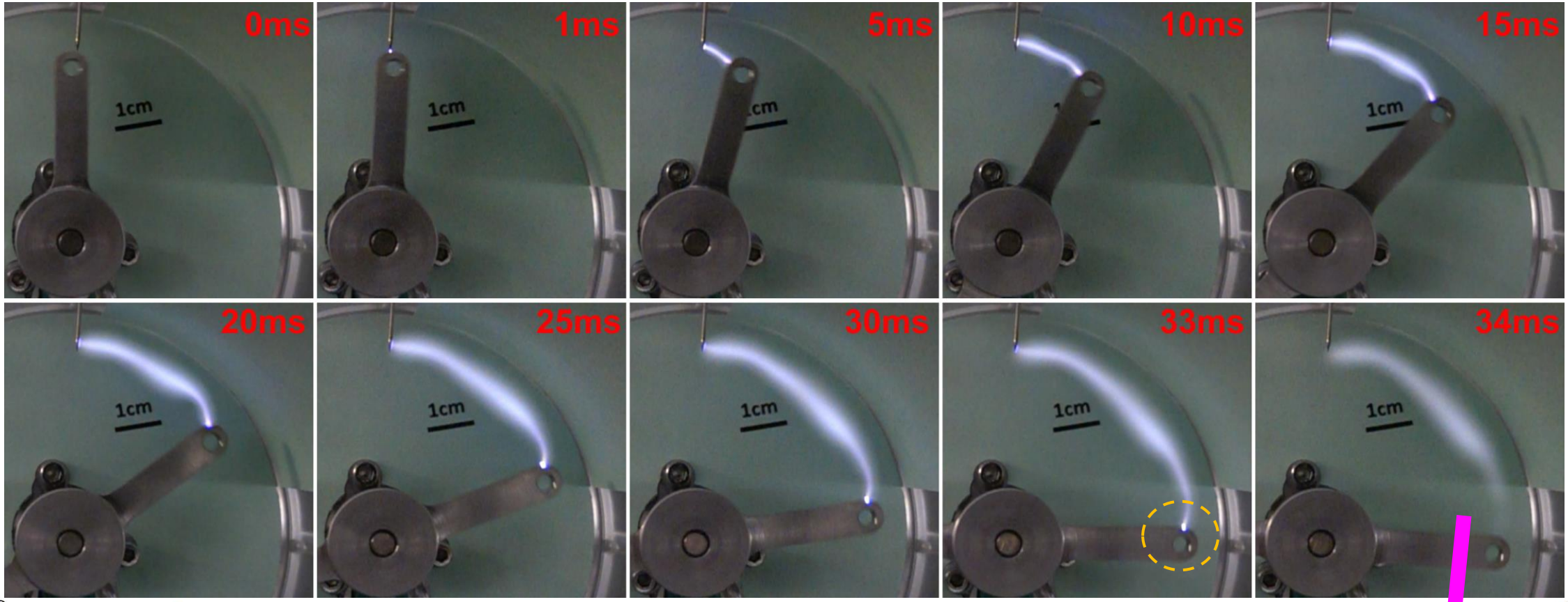


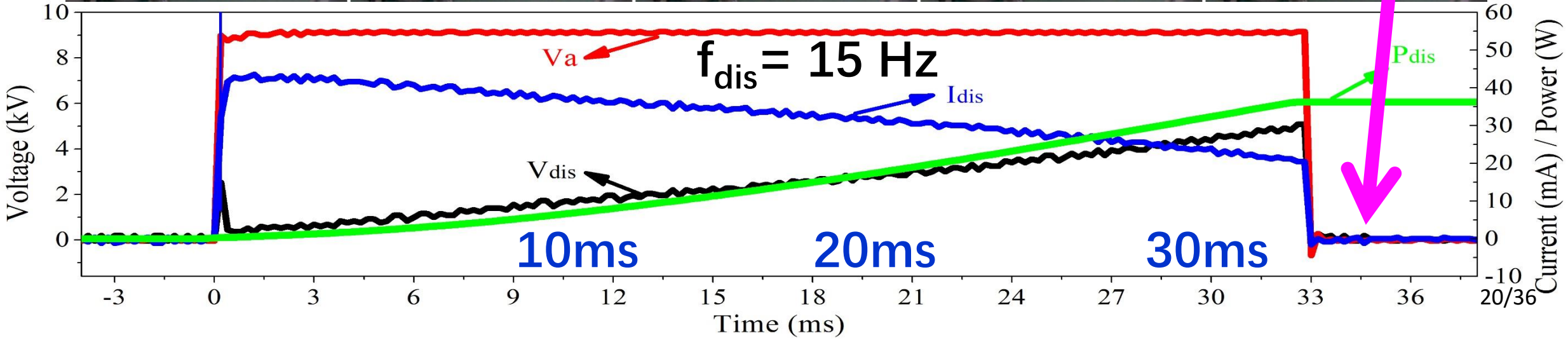


Single electrode

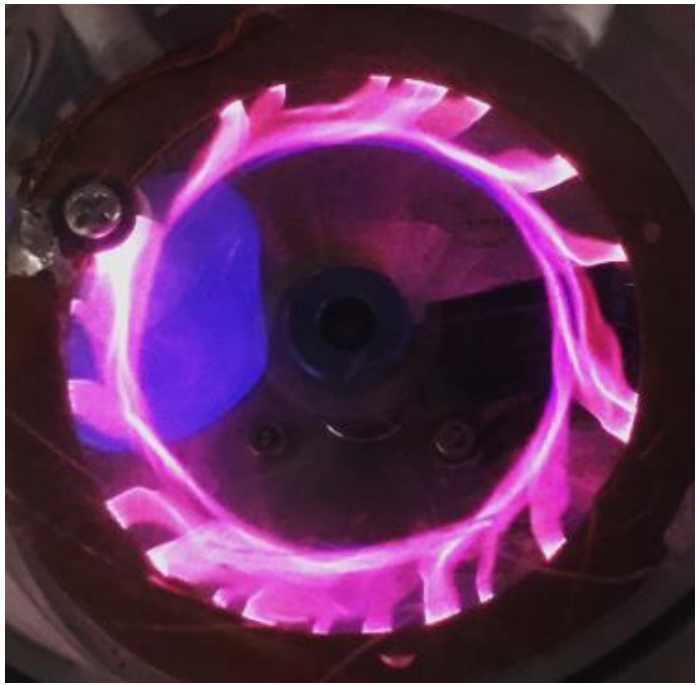
4 electrodes

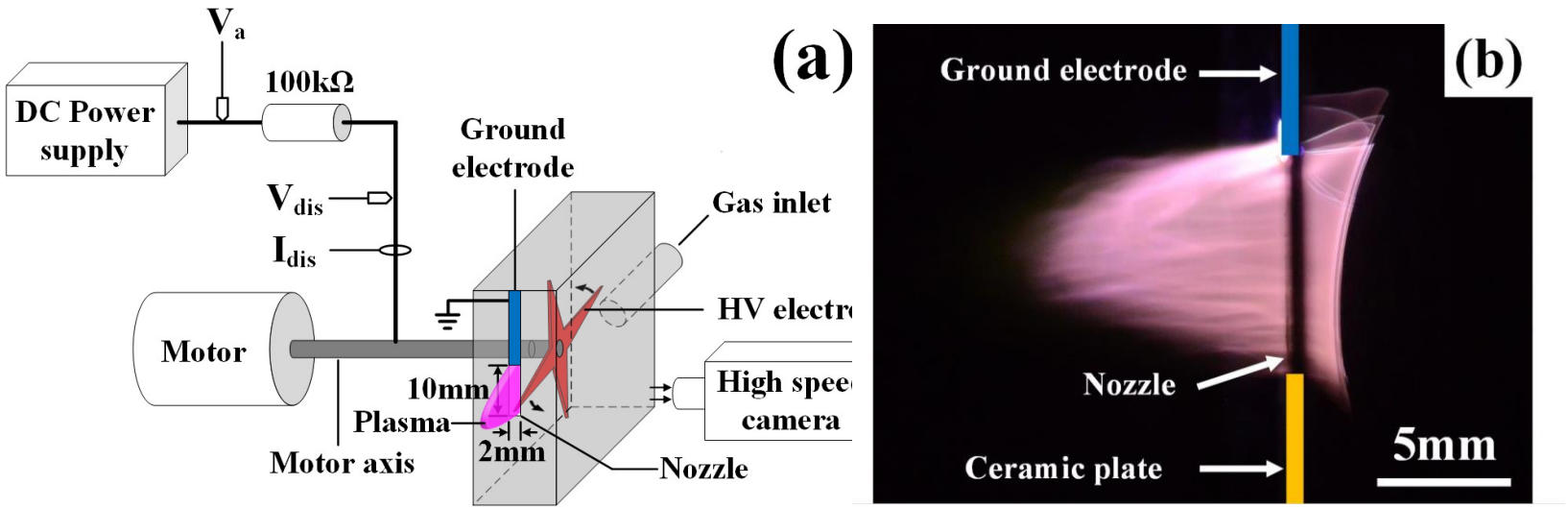
Pei, X. K., et al. (2018) Plasma Sources Sci. Technol. 27 125007


0ms
1ms
5ms
10ms
15ms
20ms
25ms
30ms
33ms
34ms
1cm


f_{dis}= 15 Hz
Va
Idis
Vdis
Pdis
10ms
20ms
30ms
Voltage (kV)
Current (mA) / Power (W)
Time (ms)

Results: The Propeller Arc

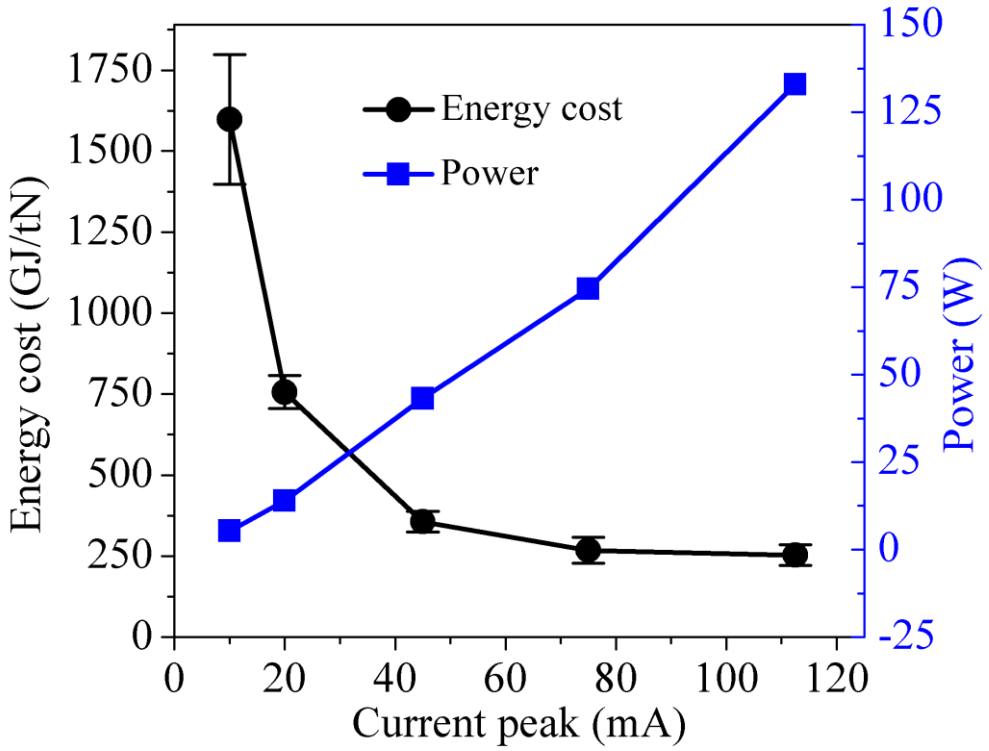


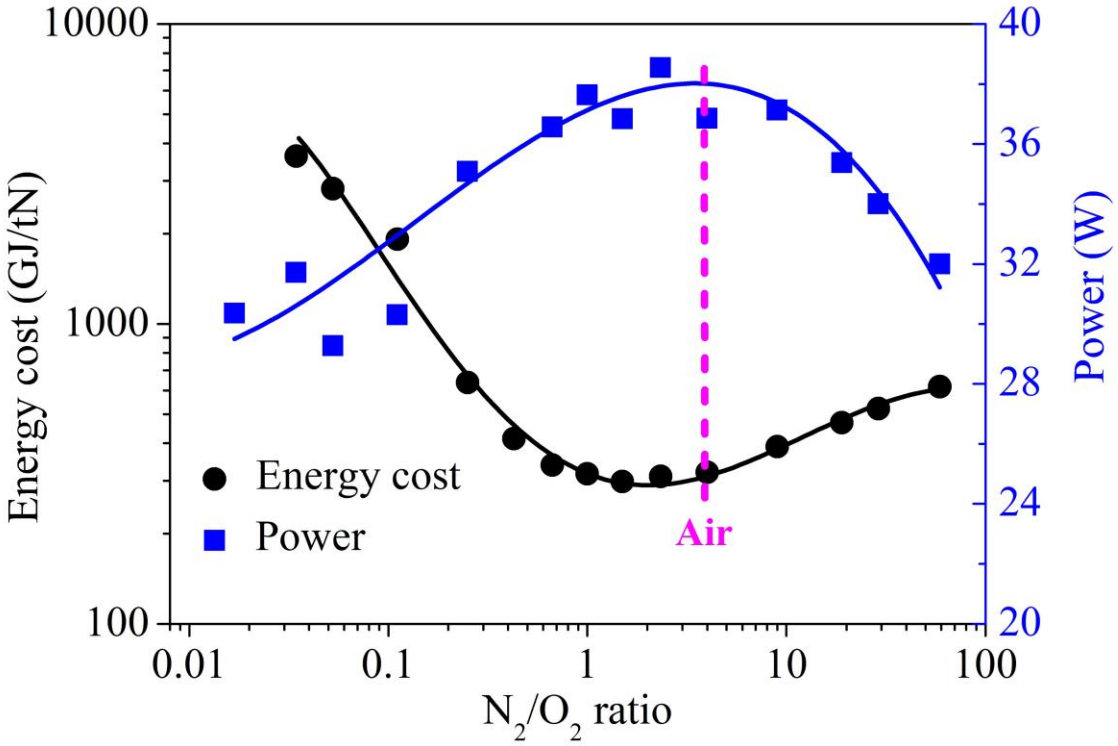


Z. Li, J. Liu, X. Lu, Plasma Sources Sci. Technol. 29, 045015

Large scale PA

Results: PA energy cost

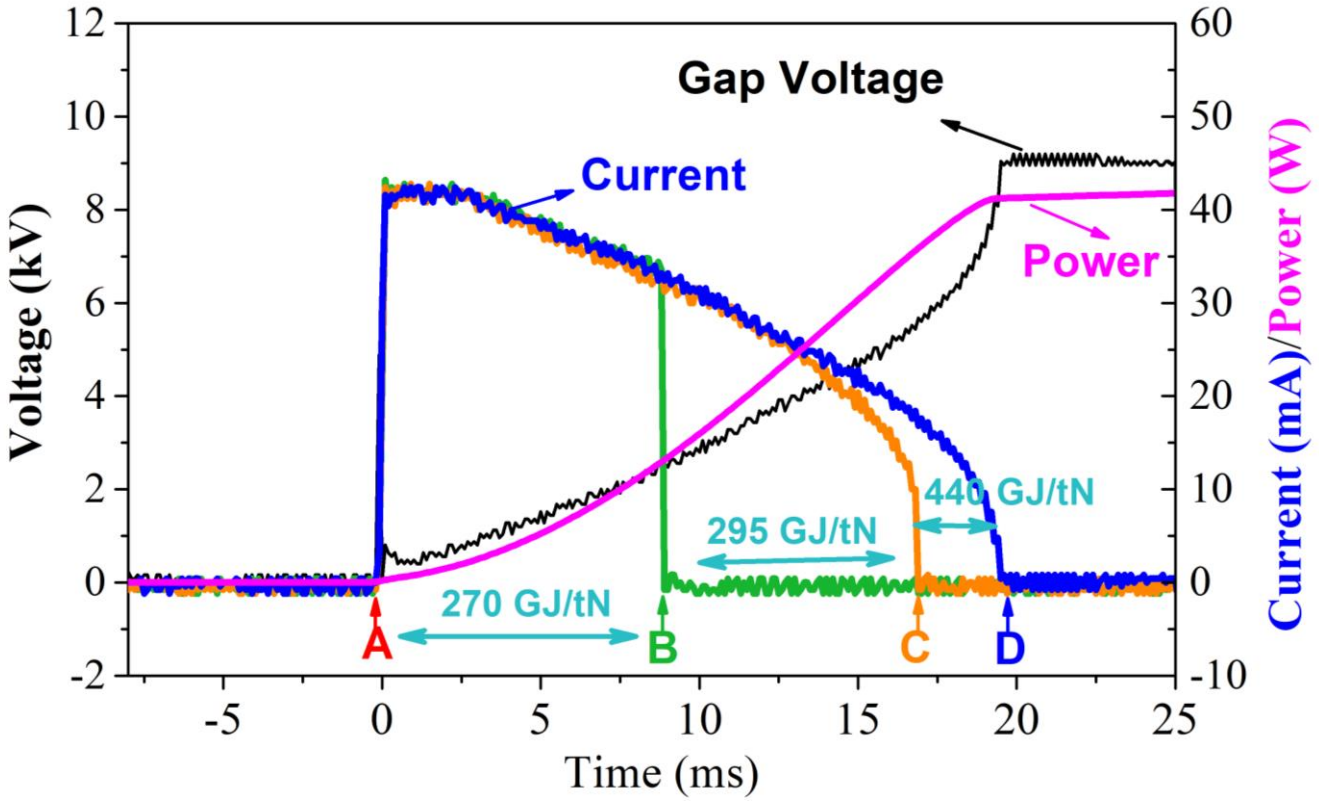


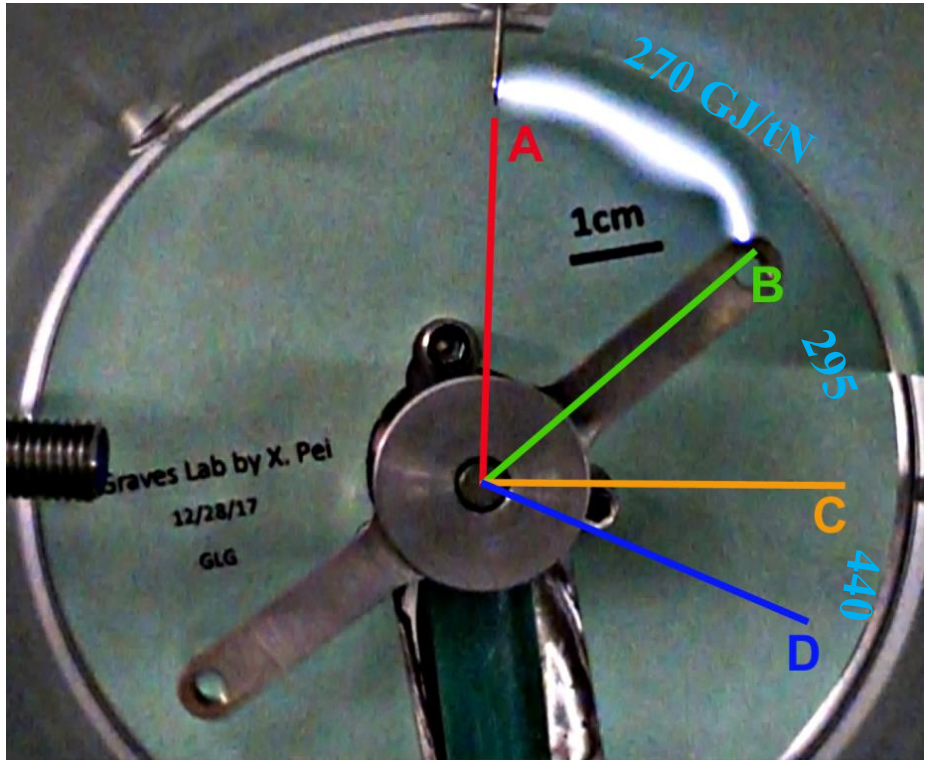


- Power increases almost linearly with I_{dis} peak
- Decreases drastically with increasing I_{dis} peak, tends to a saturation value ~250 GJ/tN

- Energy cost for air is only 13% higher than the lowest value

Results: PA energy cost





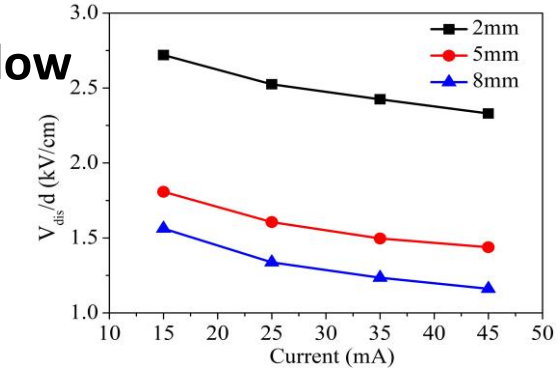
- Specific energy cost (GJ/tN) at different discharge regions

Results: Average electric fields

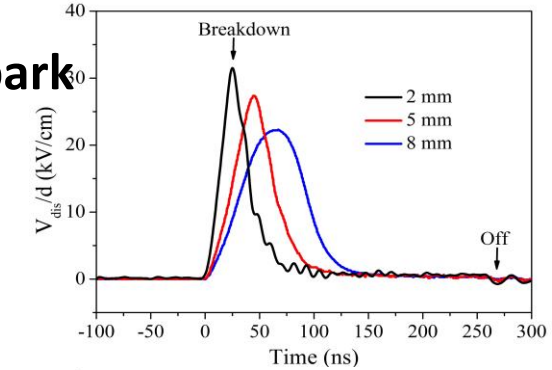
Discharge	Energy cost (GJ/tN)	Gas T (K)
DBD	4000-10000	~400
Glow	500-1000	~1800
Spark	350-900	~600
PA	250-1500	~1500

- DBD appears to not be suitable for NO_x production from the view point of energy cost.

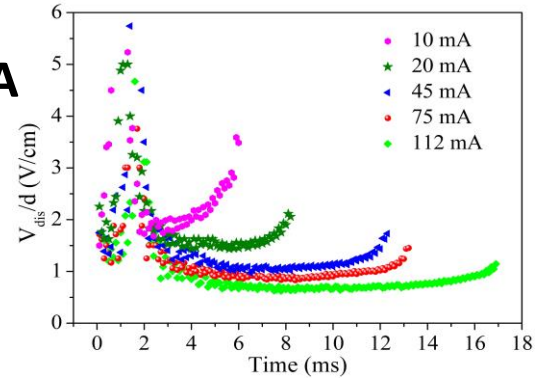
Glow



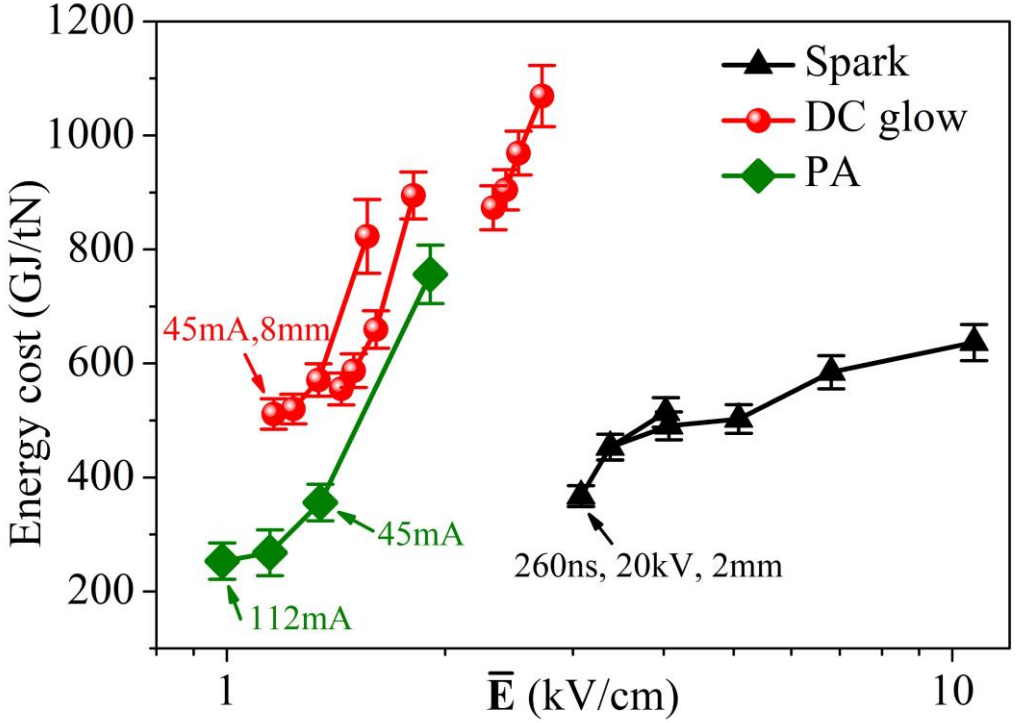
Spark



PA



$$\overline{E} = \frac{\int_{t_{bre}}^{\tau} \frac{V_{dis}(t)}{d} dt}{\tau - t_{bre}}$$



Average electric fields

Results: The χ factor

$$\chi = \frac{\bar{E} \times \bar{T}}{E_r \times T_r}$$

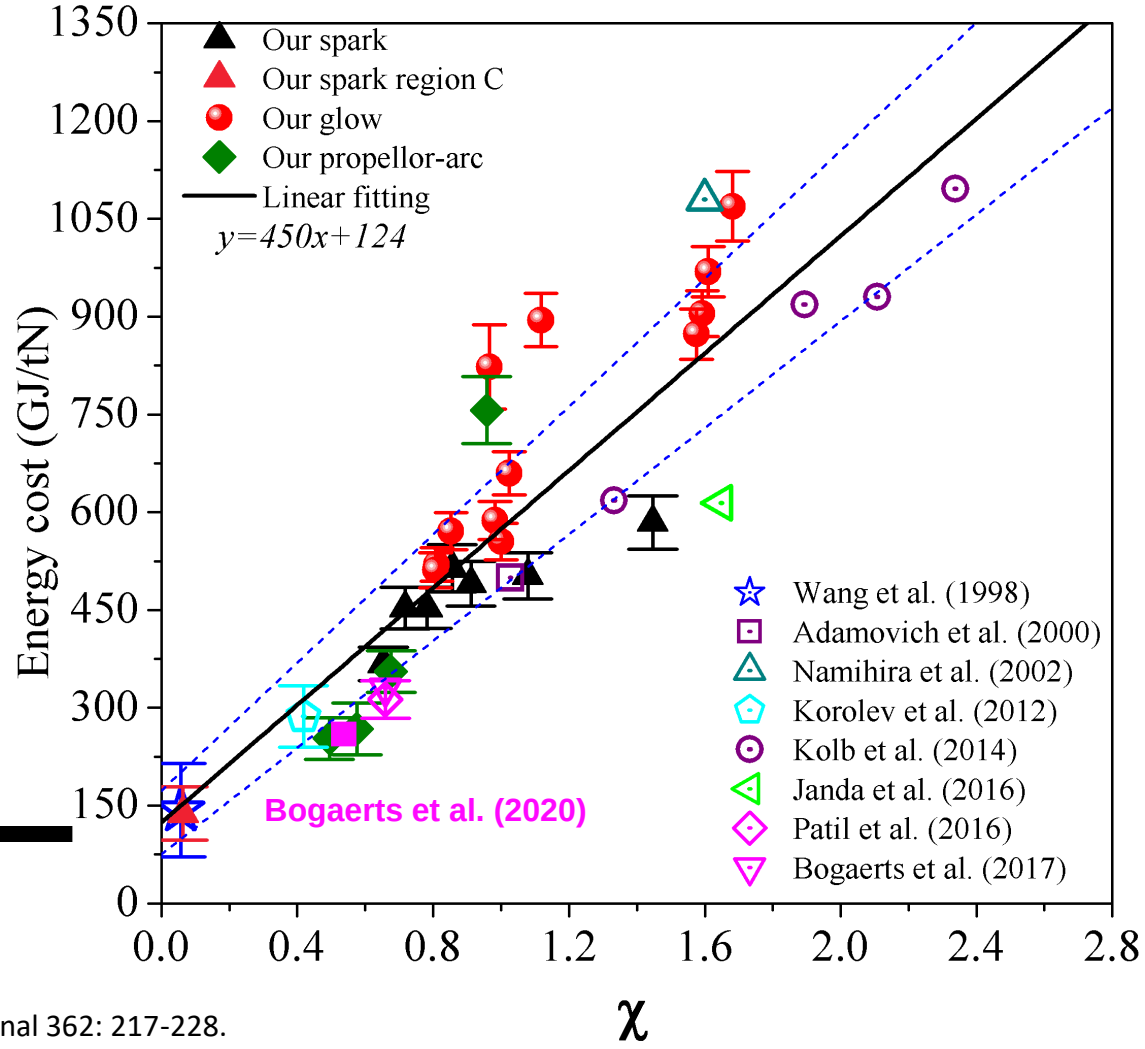
Reference condition

DC glow: 5mm, 45mA, 2slm

E_r = 1.43 kV/cm

T_r = 1800 K

124 ±49 GJ/tN



- Remarkably, there is an almost linear relationship between χ and energy cost for NO_x production.
- χ factor correlates with the energy cost for strikingly different types of discharges
- Reducing χ factor, while sustaining the discharge, can be a guiding principle for reducing the energy cost of NO_x production

Pei, X. K., et al. (2019) Chemical Engineering Journal 362: 217-228.

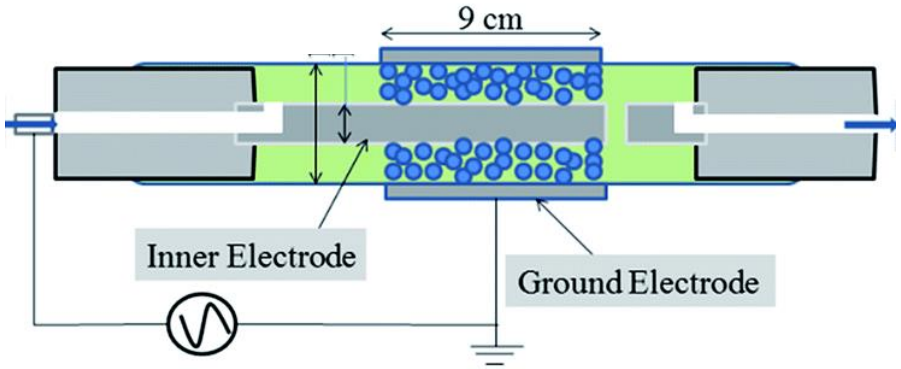
Vervloessem, E., et al. (2020) ACS Sustainable Chem. Eng 8, 9711−9720 (Gliding Arc Plasmatron)

Outline

- Introduction
- Air plasma for NF: insights from reducing Energy Cost
- **Air plasma coupled with heterogeneous catalysis**
- Concluding remarks

Reduce energy cost by coupling with heterogeneous catalysis

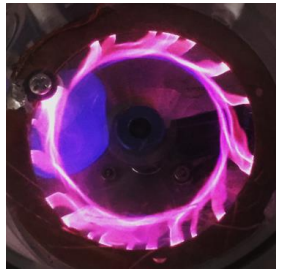
Packed DBD plasma reactor

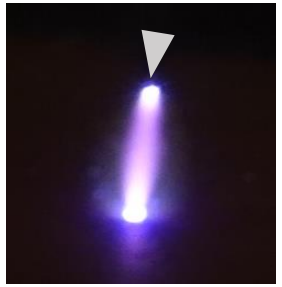


- Gas temperature is low <~1000 K
- Easy to combine with catalyst
- Wouldn't destroy catalyst

~4600 GJ/tN → DBD+catalyst → **~2200 GJ/tN**

'warm' plasma + catalyst ?



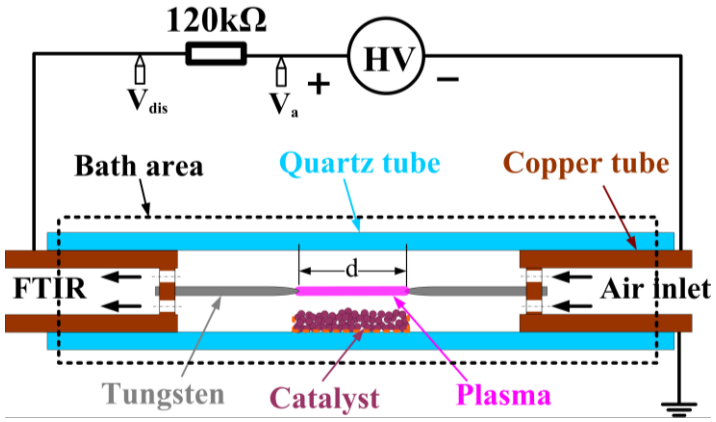


>~1500 K
~200 GJ/tN

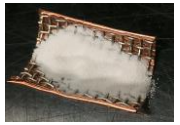
+

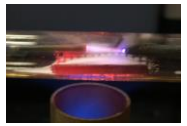
Patil, B. S., et al. (2016). Appl. Catal. B 194: 123-133.

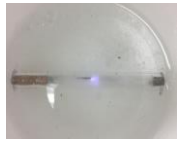
Air plasma combined catalyst for NF



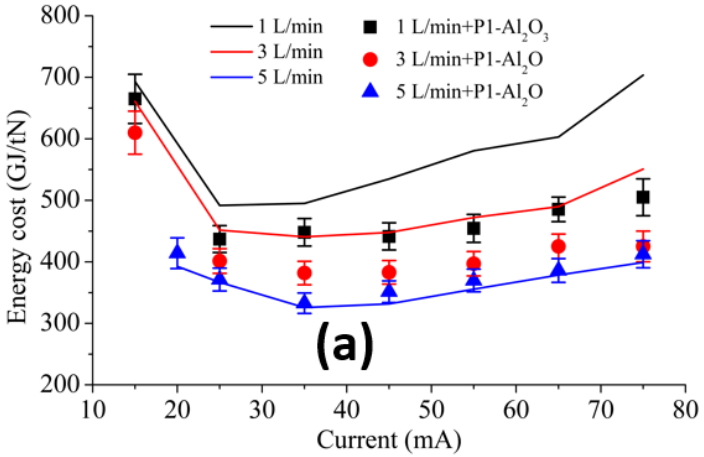
Experiment parameters

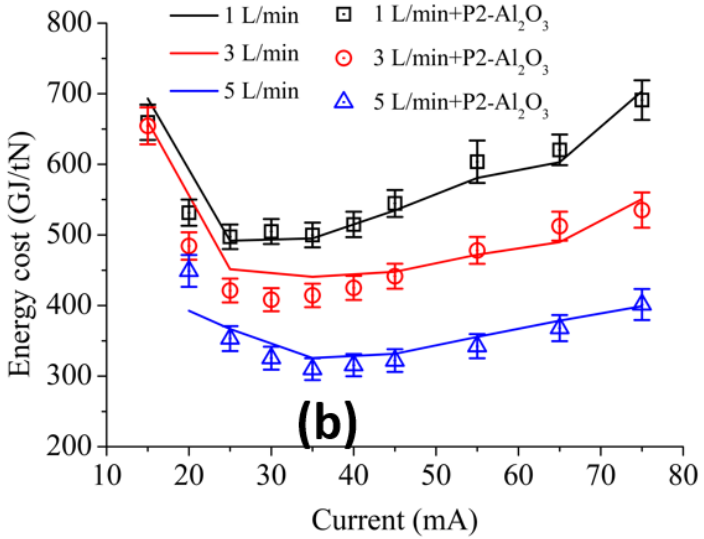


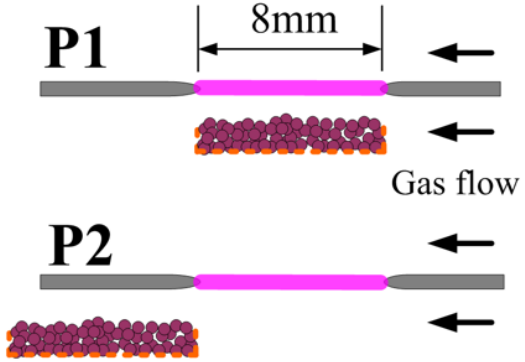


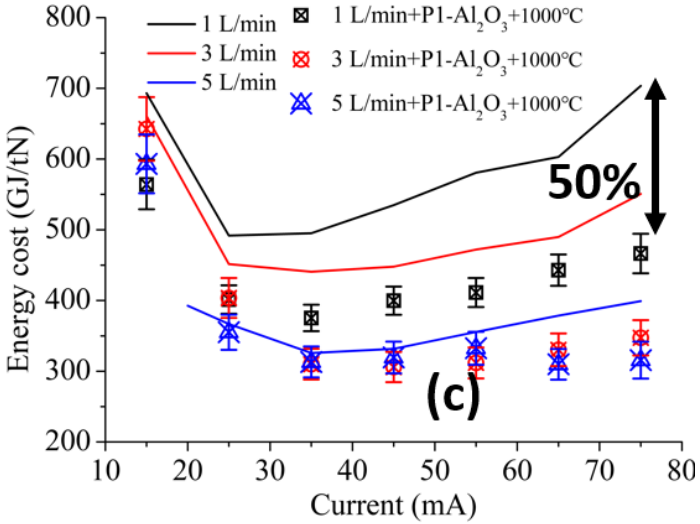


- Current: 15mA to 75mA;
- d: 2mm to 80mm;
- Flow: 1L/min to 15L/min
- Catalyst: Activated Al_2O_3
  75 microns, 0.2g



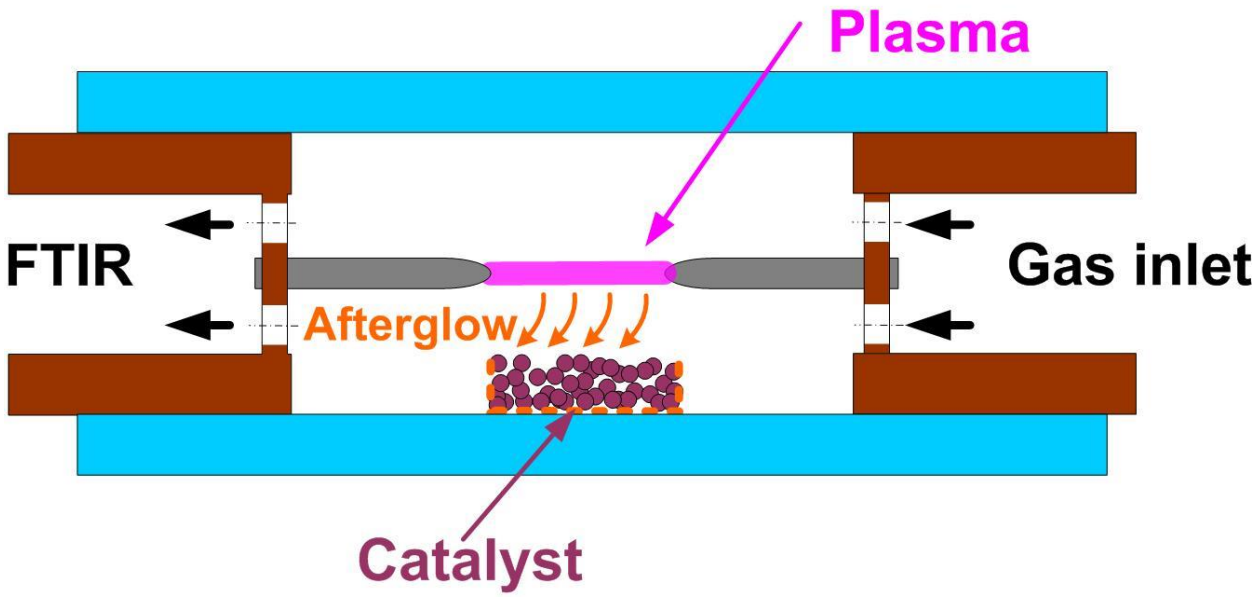


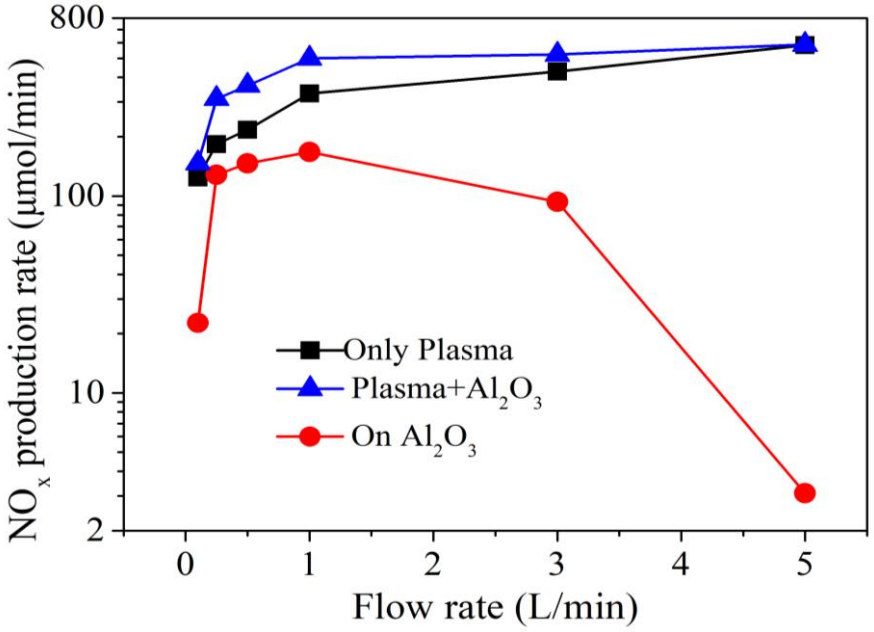




Pei X. K. et al., (2020) J. Phys. D: Appl. Phys. 53, 044002

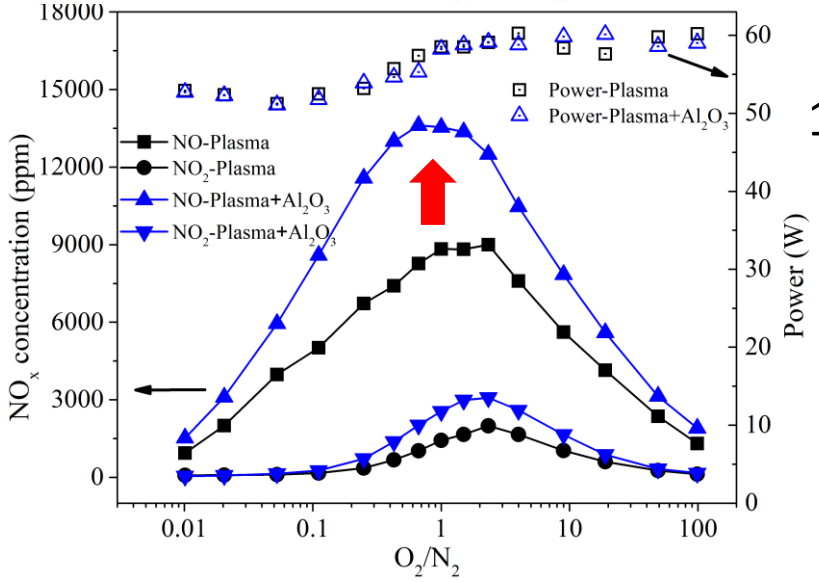
Influence of catalyst





$$O + \boxed{N_2} \rightarrow NO + N$$

$N_2(V)$ $N_2(E)$



14,000ppm

NO

9,000ppm

Influence of catalyst

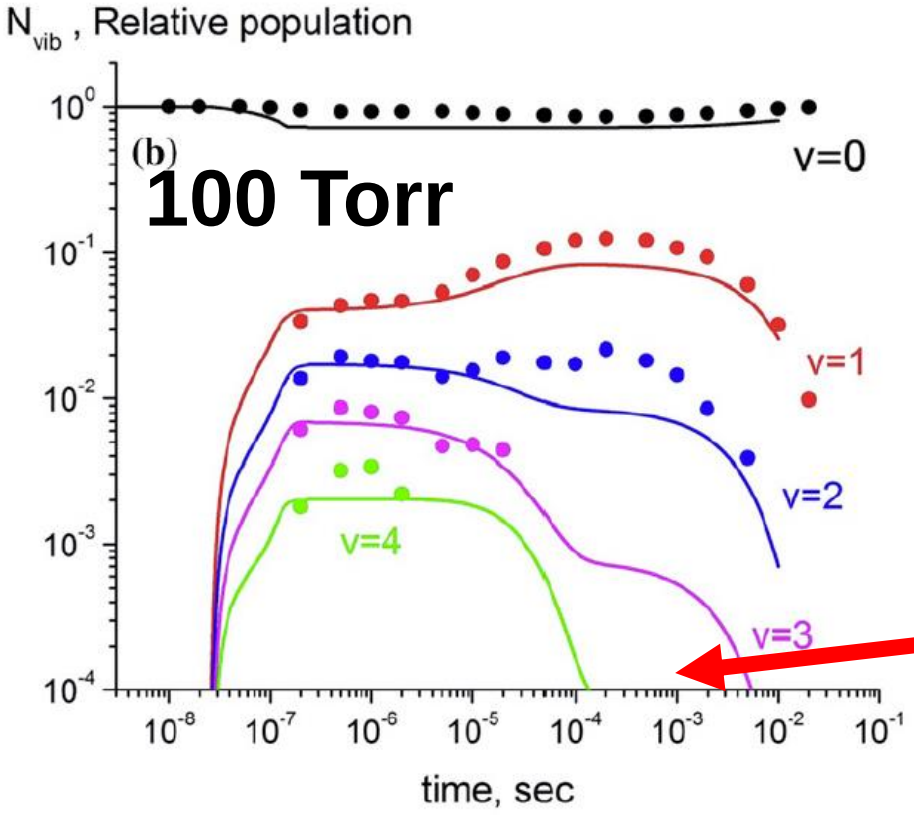
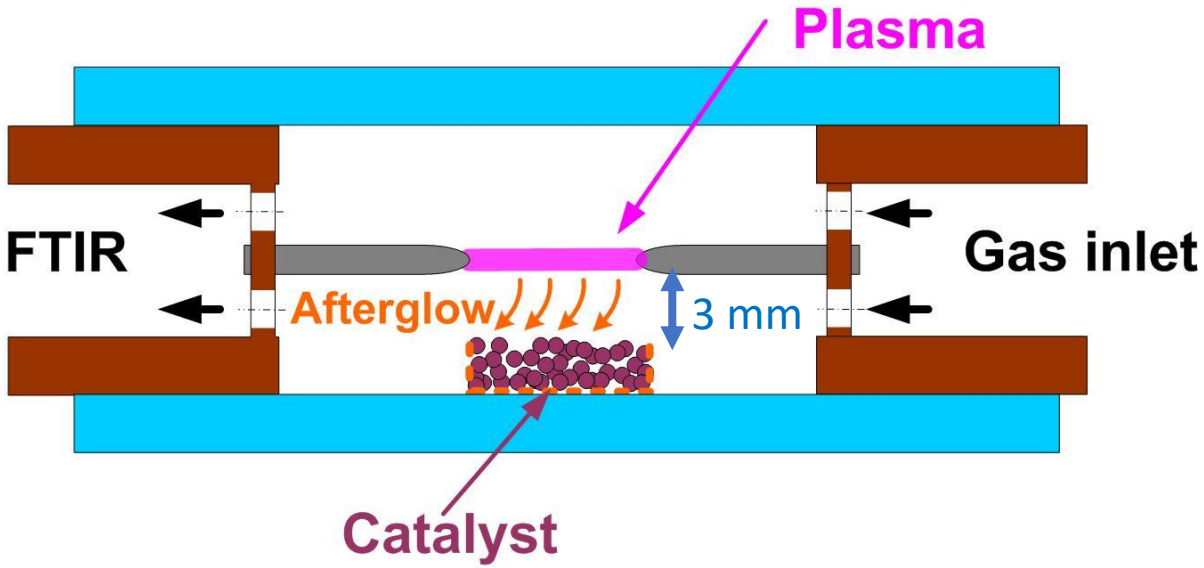


Figure 7. Experimental (symbols) and predicted (curves) N_2 vibrational level populations during the discharge pulse and in the afterglow in nitrogen (*a*) and in air (*b*).



Diffusion time > 1 ms

$N_2(v)$ $N_2(E)$?

$$N_2(E) + O \xrightarrow{\text{surface}} NO + N$$

Plasma Sources Sci. Technol. 23 (2014) 065003 I Shkurenkov

Plasma jet coupled with catalyst

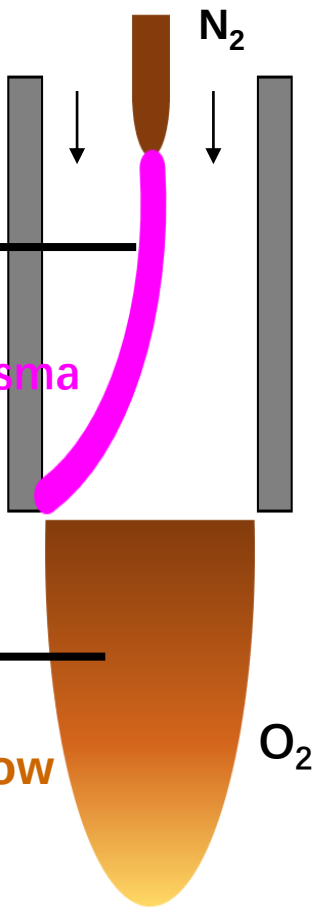
Complex process

- e^-, E, Ions …
- N_2*, N
- High T_g

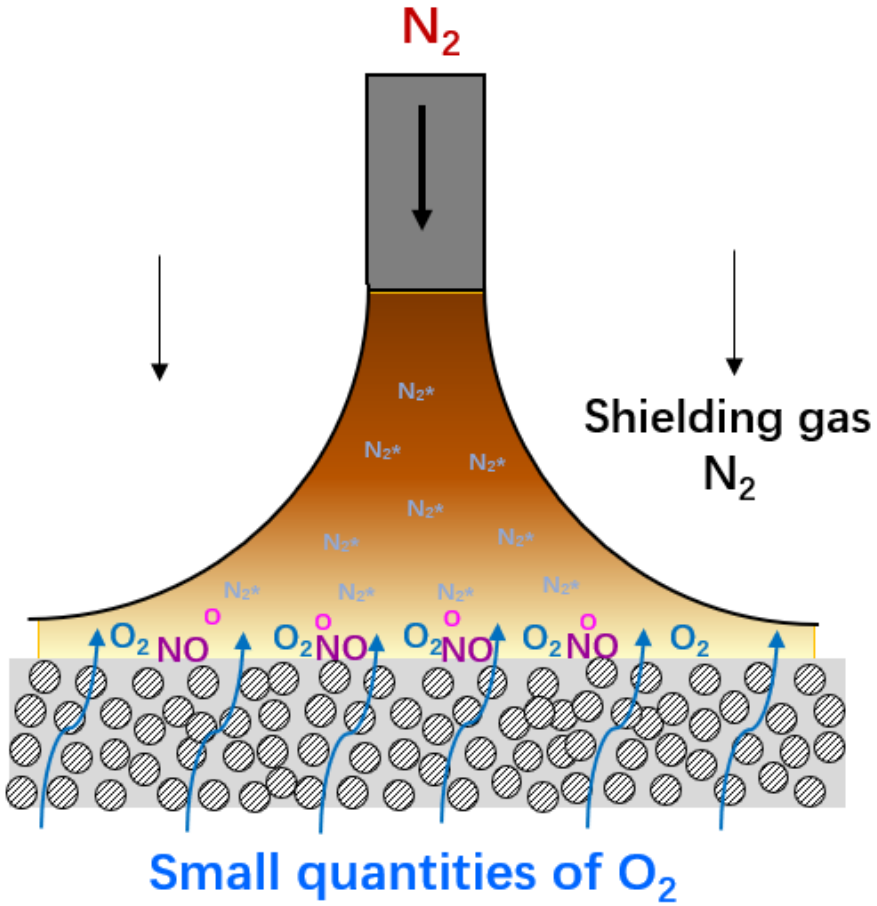
N_2*: $N_2(A)$,$N_2(B)$…

Neutral species

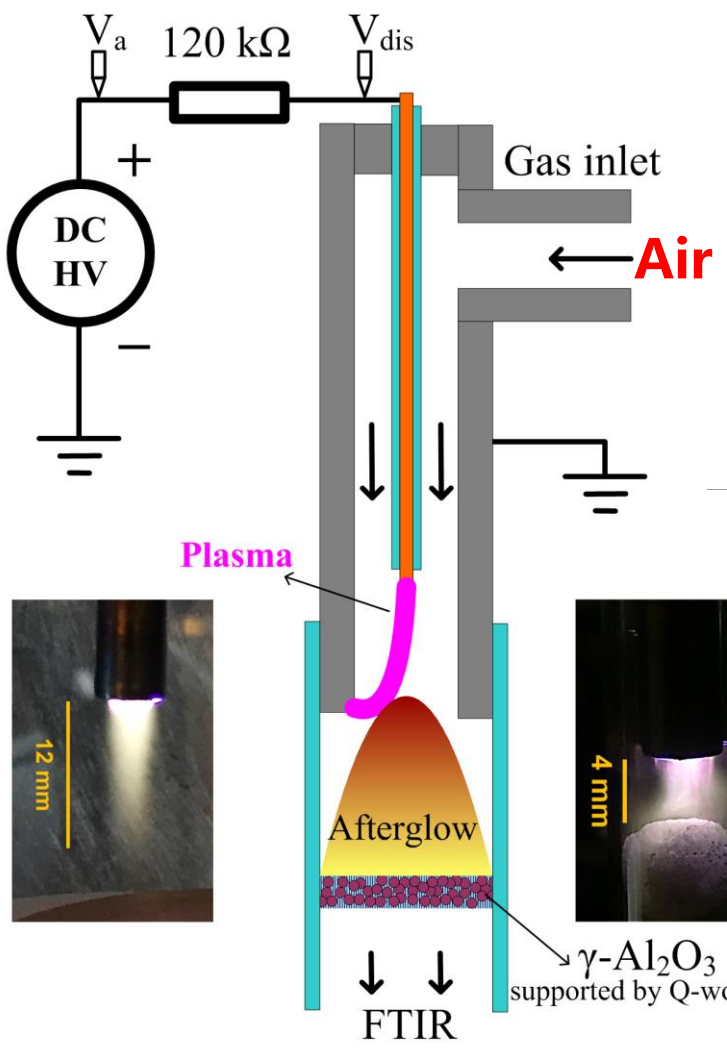
- N_2*, N

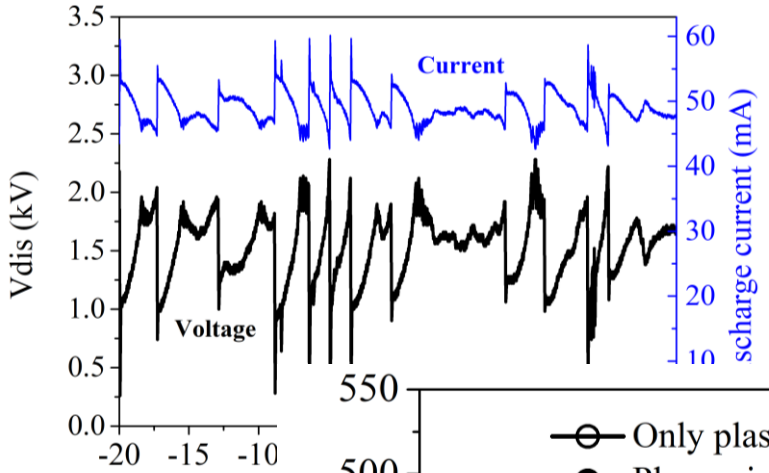


N_2* + O_2 => N_2 + O + O
N_2* + O => NO + N …

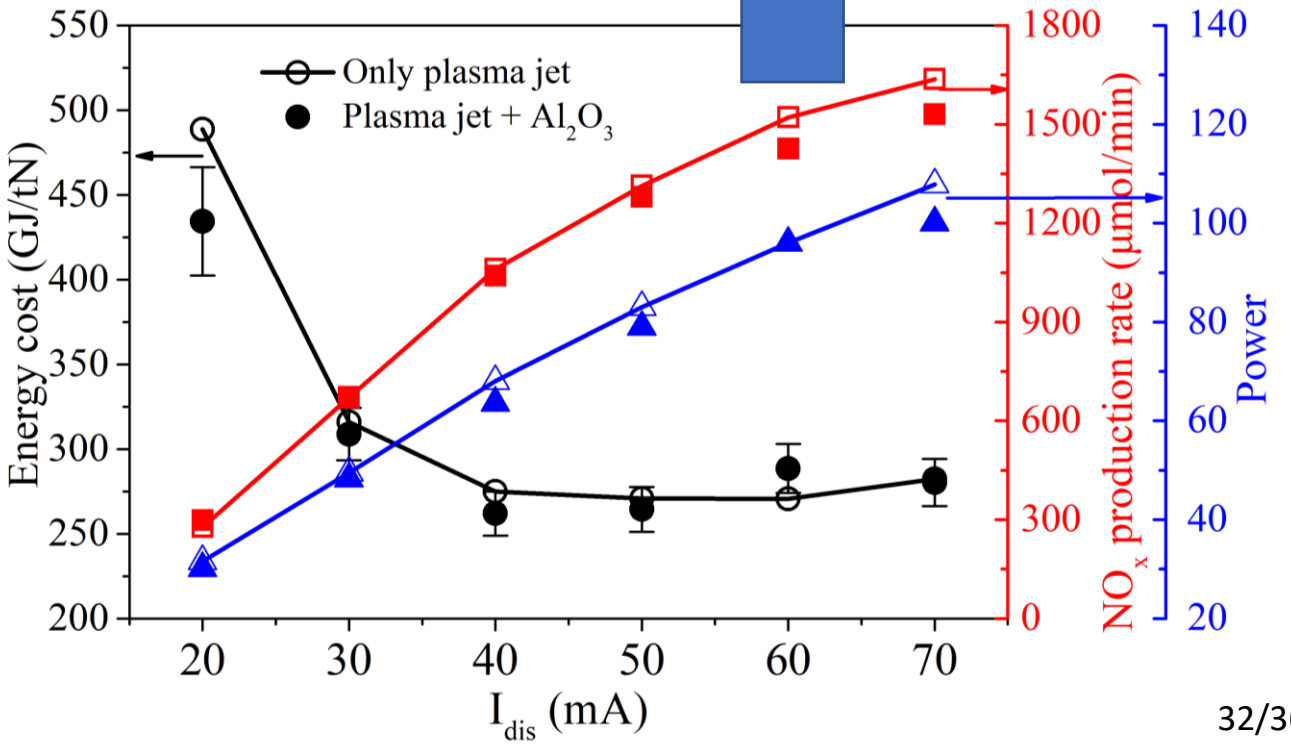


Air plasma jet coupled with catalyst



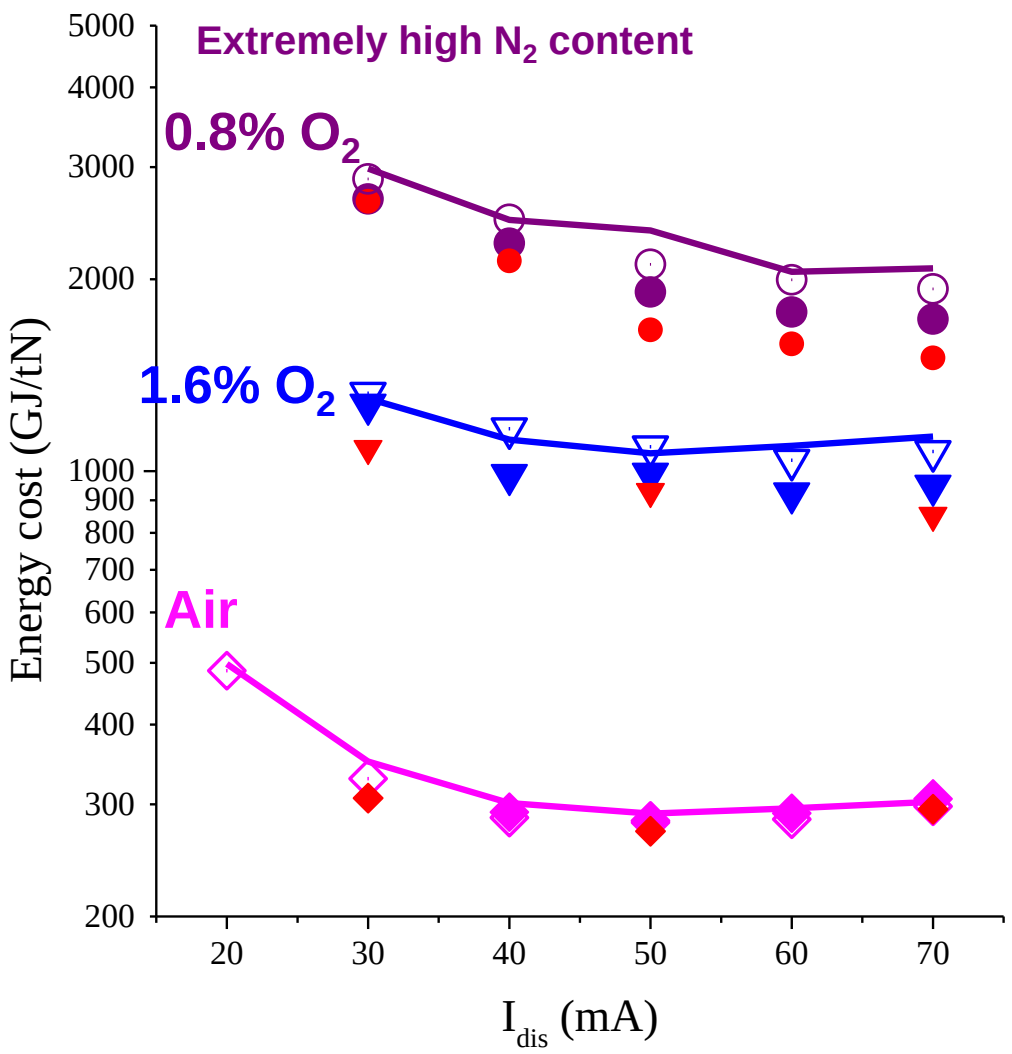


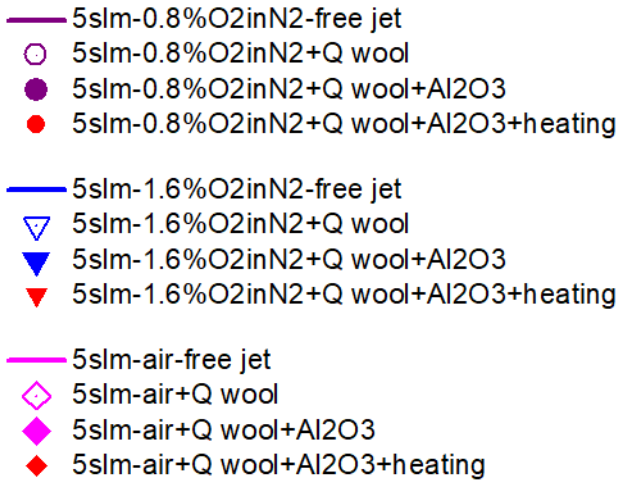
- n_{N2*} too low ?
- No catalytic effect

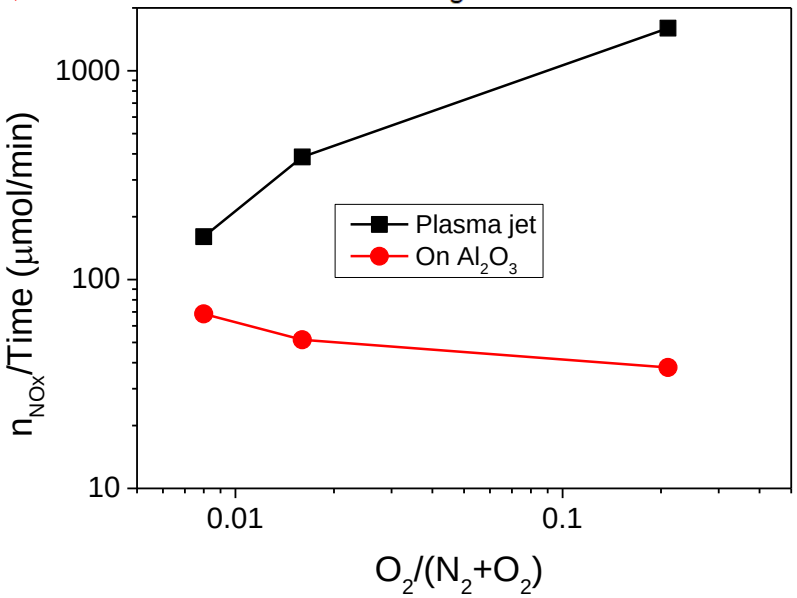


Pei X. K. et al., J. Phys. D: Appl. Phys. (Preparing to submit).

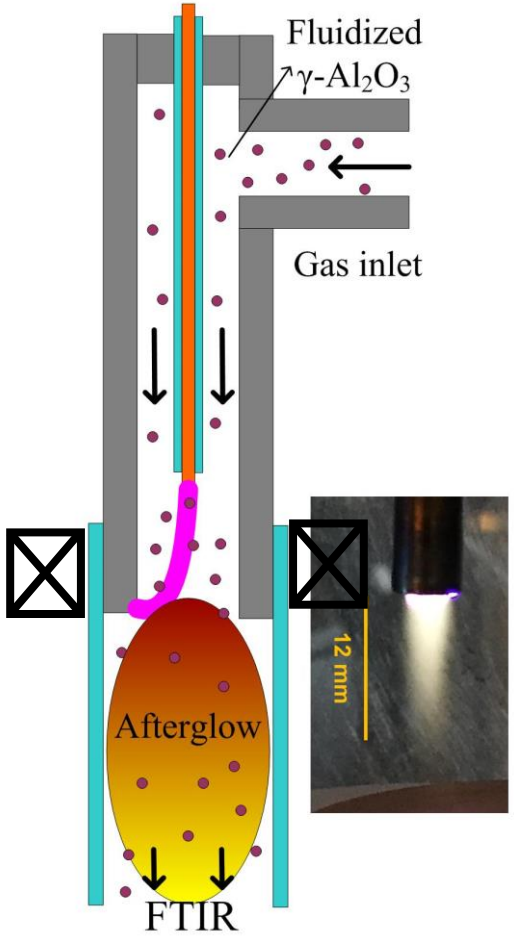
Influence of N2/O2 ratio

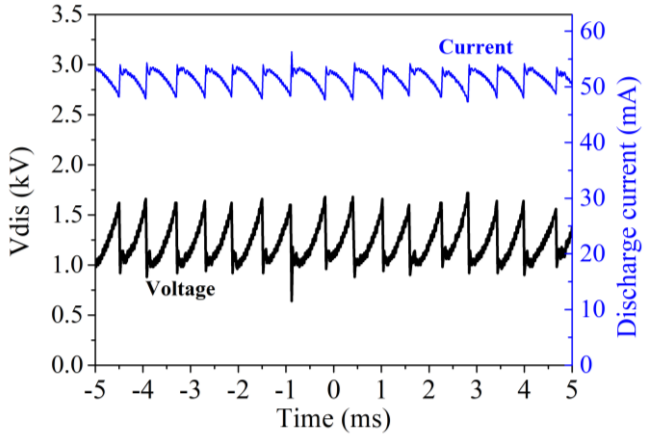




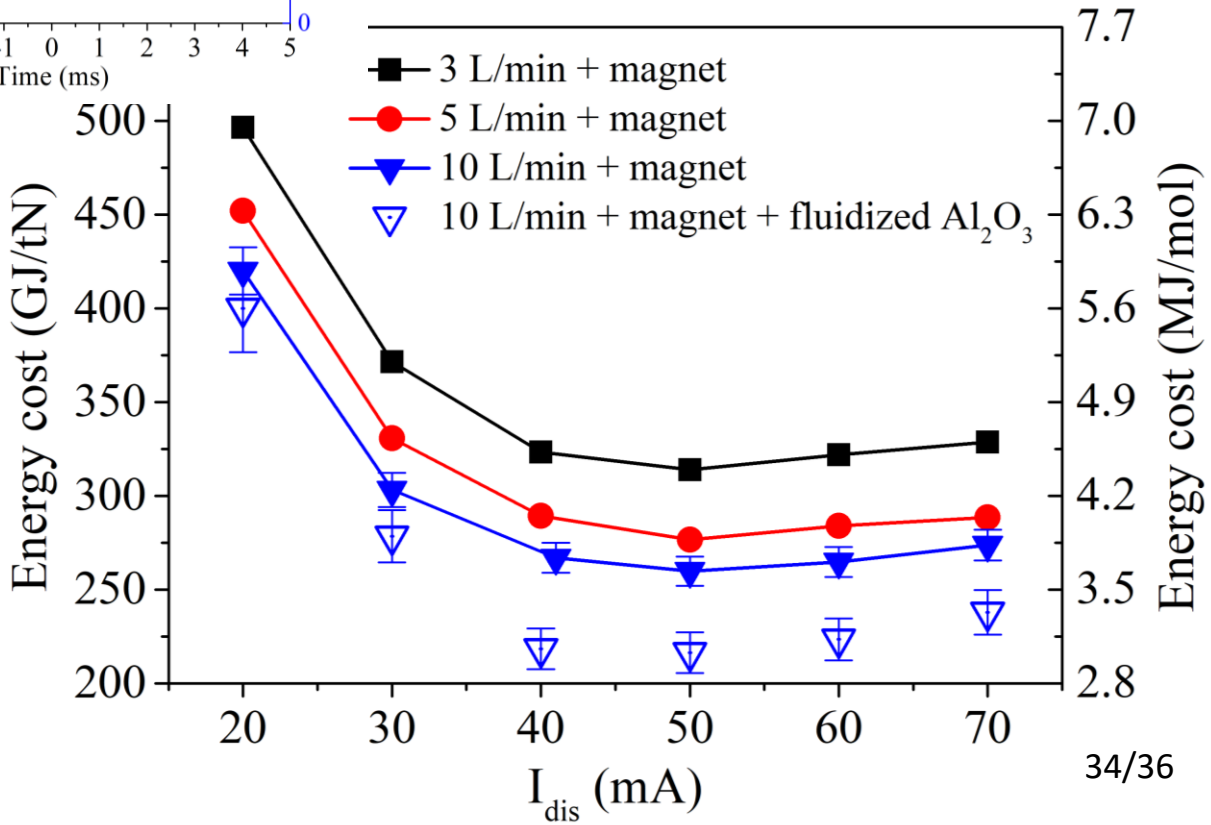


Fluidized catalyst + Magnet to stabilize





Lowest: 210 GJ/tN
2.9 MJ/mol



X. Pei et al., J. Phys. D: Appl. Phys. (Preparing to submit).

Concluding remarks

- χ factor appears to serve as a simple, effective means of correlating NO_x production energy cost across a broad range of discharges, but still poorly understood its physical and chemical mechanisms;
- 'Warm' plasma combined with catalyst can reduce the energy cost;
- 'Fluidized' catalyst improves the energy efficiency for NOx formation significantly in the air plasma jet system, more work need to do.

- Lowest energy cost for NO_x production in our air plasma system: **210 GJ/tN**. (2.9 MJ/mol)

Acknowledgements

Plasma Systems and Engineering GRAVESLab

Prof. David B. Graves

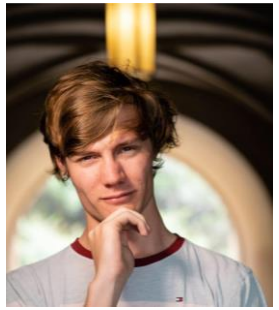
Dr. Dogan Gidon

Dr. Yaojhen Yang

Dr. Zilan Xiong

Prof. Nozomi Takeuchi

Eliot Foss



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