Complex Structure of the Carbon Arc Discharge for Nanomaterial Synthesis

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Outline

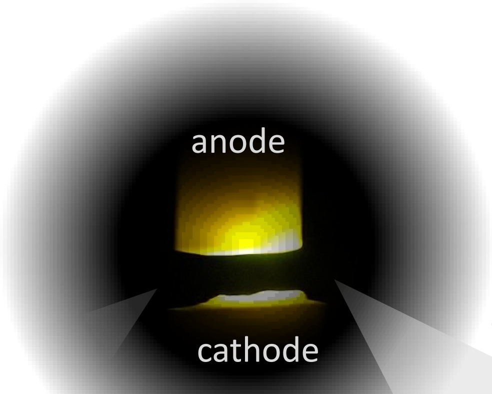
1. **Introduction**
   - **Plasma assisted nanomaterial synthesis**
   - **Current state of carbon arc research & open questions**
2. Brief description of results & applied diagnostics
   - Experimental setup
3. Arc structure
   - Filtered fast frame imaging
   - Planar laser induced fluorescence
4. Enhanced anode ablation mode
   - Formation of positive anode layer
   - Method to determine anode fall
5. Arc core
   - Plasma density and temperature measurements
6. Summary

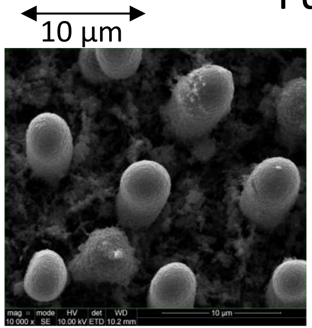
Arc discharge for nanomaterials building

Arc method :
- **Simple to implement**
- **High nanomaterial yield**
- **Variety of synthesized nanostructures**

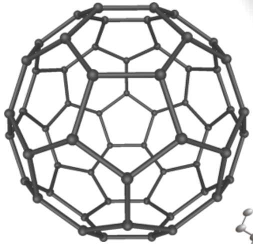
Atmosphere Helium	**500 Torr**
Plasma density (n_e)	**$10^{14} – 10^{16}$ cm^{-3}**
Temperature (T_e)	**1 eV**
Ionization degree	**10%**
$\nu_{e\text{-}i}$	**10^{12} s^{-1}**
$\nu_{e\text{-}a}$	**10^{11} s^{-1}**
$mnp_{e\text{-}i}$	**1 µm**
$mnp_{i\text{-}a}$	**few µm**
λ_D	**100 nm**

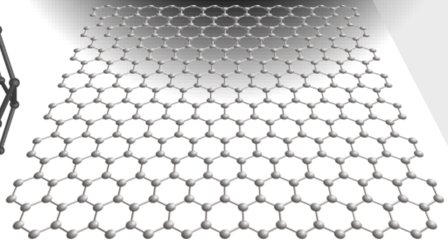
Discharge current	**60 A**
Discharge voltage	**20 V**





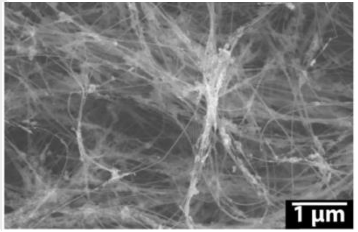
Fullerenes

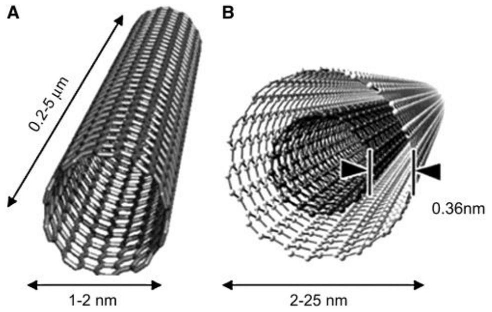




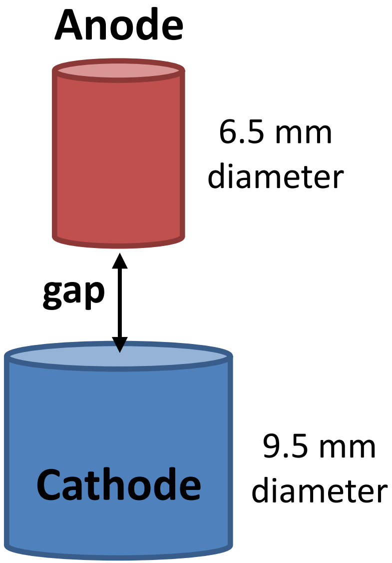
Graphene

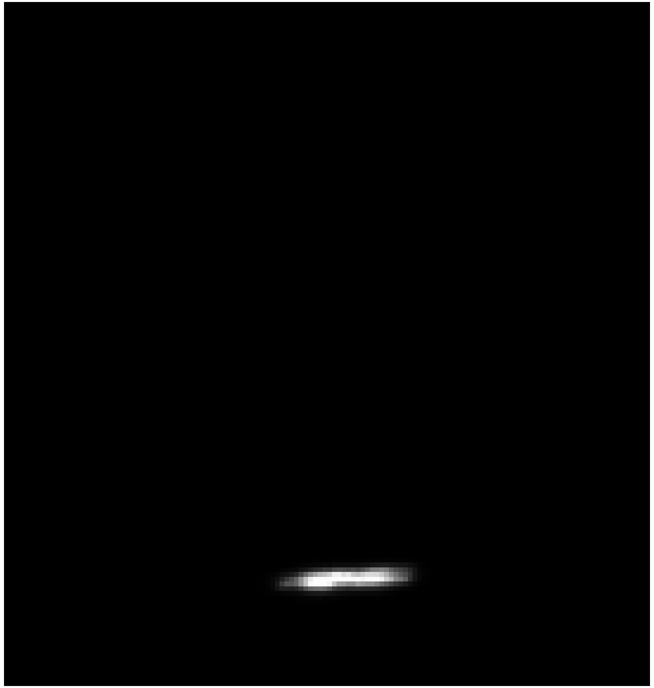
Carbon nanotubes





Run time: 1 min; Voltage 24 V, Current 60 A





Recording with filter at 656 nm, playing at 500 fps

*more details at **http://nano.pppl.gov/**

Plasma role in nanostructure synthesis?

- What are plasma properties?
- How feedstock material is formed?
- What growth conditions are realized in the arc?

10:45 WE 1.4-3 : Alexander Khrabry

SELF-CONSISTENT NUMERICAL SIMULATION OF CARBON ARC FOR NANOPARTICLE SYNTHESIS

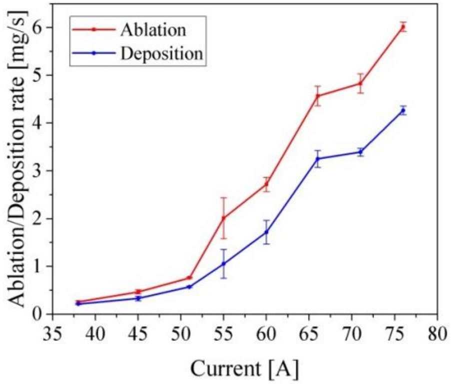
TU Posters-27 : Tianyuan Huang

EXPERIMENTAL STUDY OF TIME DEPENDENCE OF ABLATION RATE IN ATMOSPHERIC PRESSURE DC CARBON ARC DISCHARGES

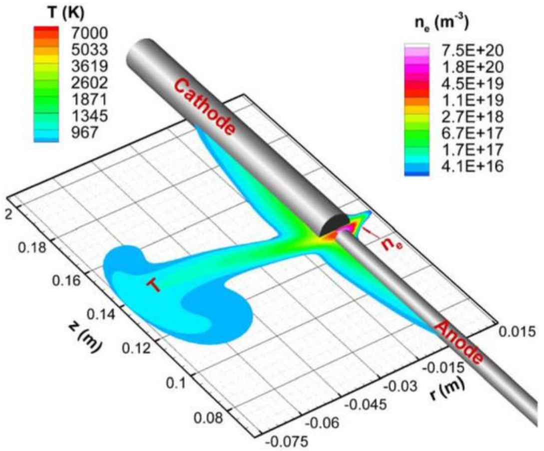
Synthesis arc: Status Quo

- Synthesis requires flux of feedstock material and temperature
- Plasma simulations show monotonic density and temperature distributions in dc arc reactor
- dc arc is … unstable arc attachments to electrodes, arc channel exhibit complex motions (oscillations)

Two modes of arc operation:
- ***Low (small) anode ablation***
- ***High (enhanced) anode ablation***



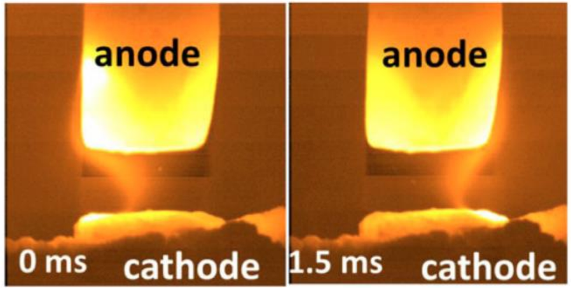
A. J. Fetterman, Y. Raitses, and M. Keidar, Carbon **46**, 1322 (2008).



M. Kundrapu, J. Li, A. Shashurin, and M. Keidar, J. Phys. D: Appl. Phys. **45** (2012).

Two modes of arc oscillations:
- ***Low frequency (<1 kHz)***
- ***High frequency (>1 kHz)***

Low frequency oscillations in arc

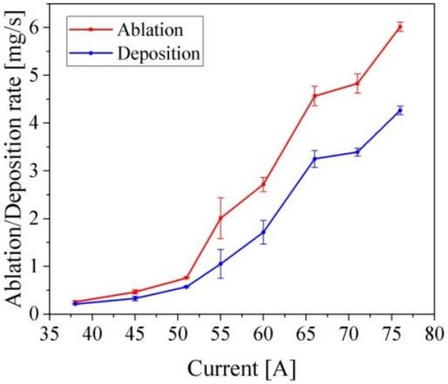


S. Gershman and Y. Raitses, J. .Phys. D: Appl. Phys. **49**, 345201 (2016).

Synthesis arc: Status Quo

- Synthesis requires flux of feedstock material and temperature
- Numerical calculations of near-cathode region in Argon arc with W electrodes at 1 atm
- dc arc is … unstable arc attachments to electrodes, arc channel exhibit complex motions (oscillations)

Two modes of arc operation:
- ***Low (small) anode ablation***
- ***High (enhanced) anode ablation***



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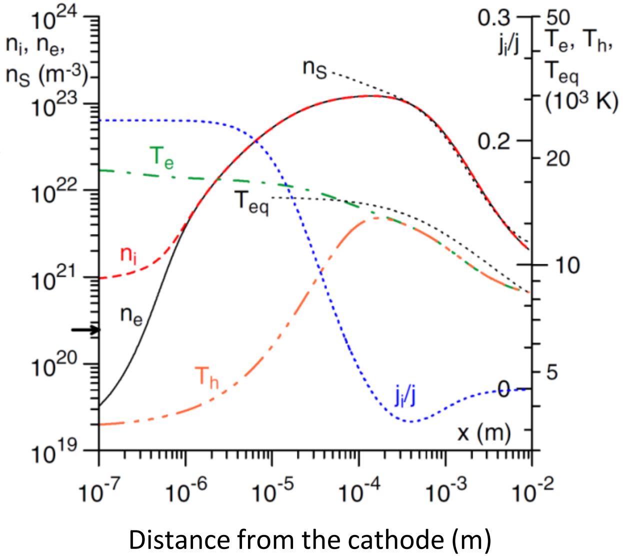

N. A. Almeida, M. S. Benilov, and G. V. Naidis, J. Phys. D: Appl. Phys. **41** (2008).

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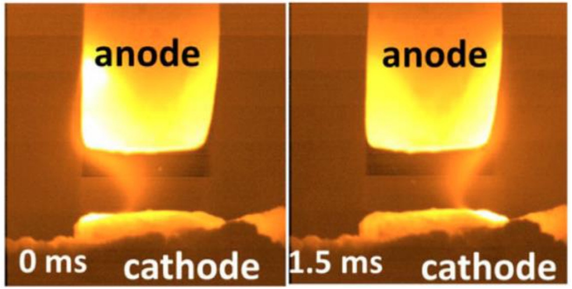

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Brief summary

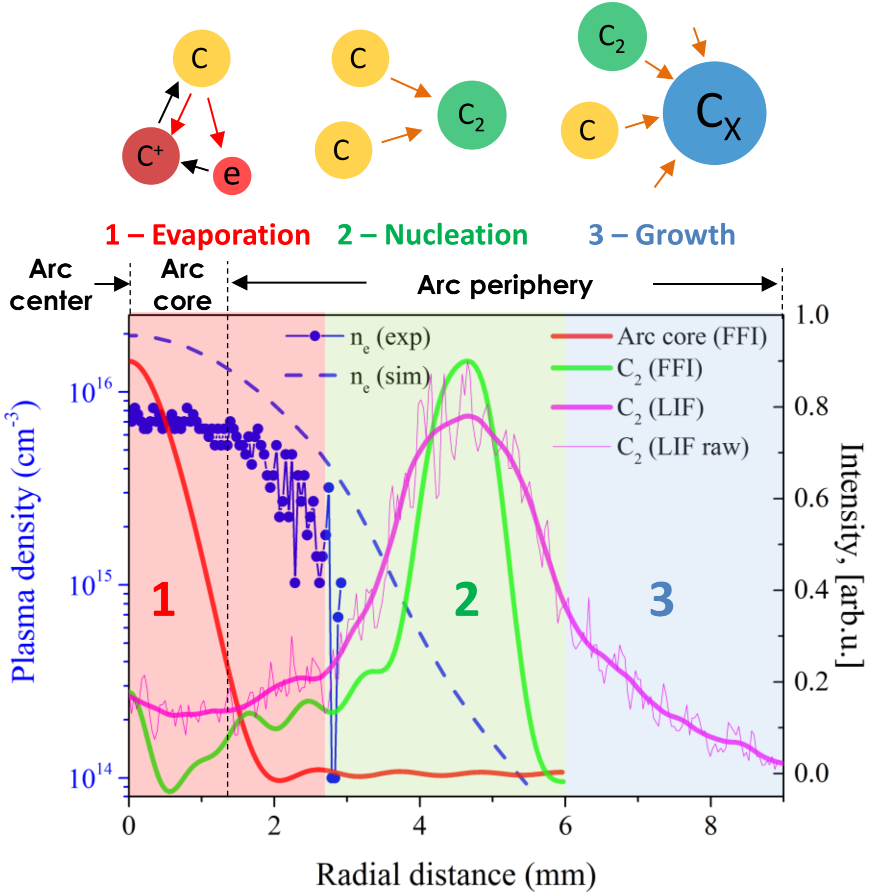
Plasma arc core parameters:

Optical emission spectroscopy

- Plasma density n_e profiles from Stark broadening of hydrogen H_α line
- Plasma temperature T_e from line intensity ratio method

Electrical measurements

- Arc Volt-Ampere characteristics



Time- and space- resolved structure of the carbon arc:

Filtered Fast Framing Imaging

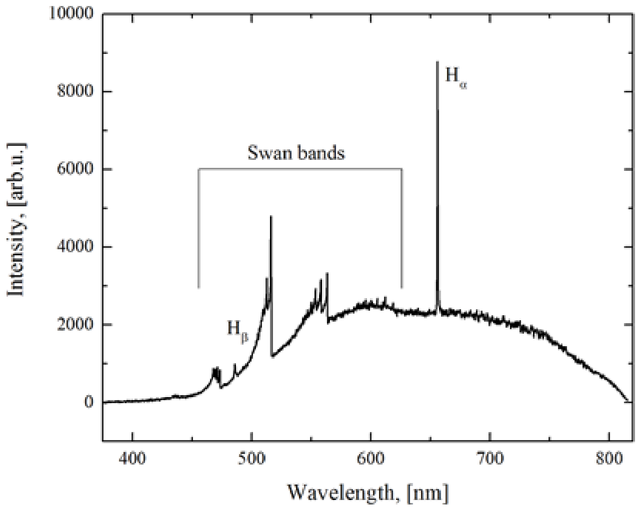
- Line integrated irradiance of plasma species

Planar Laser Induced Fluorescence

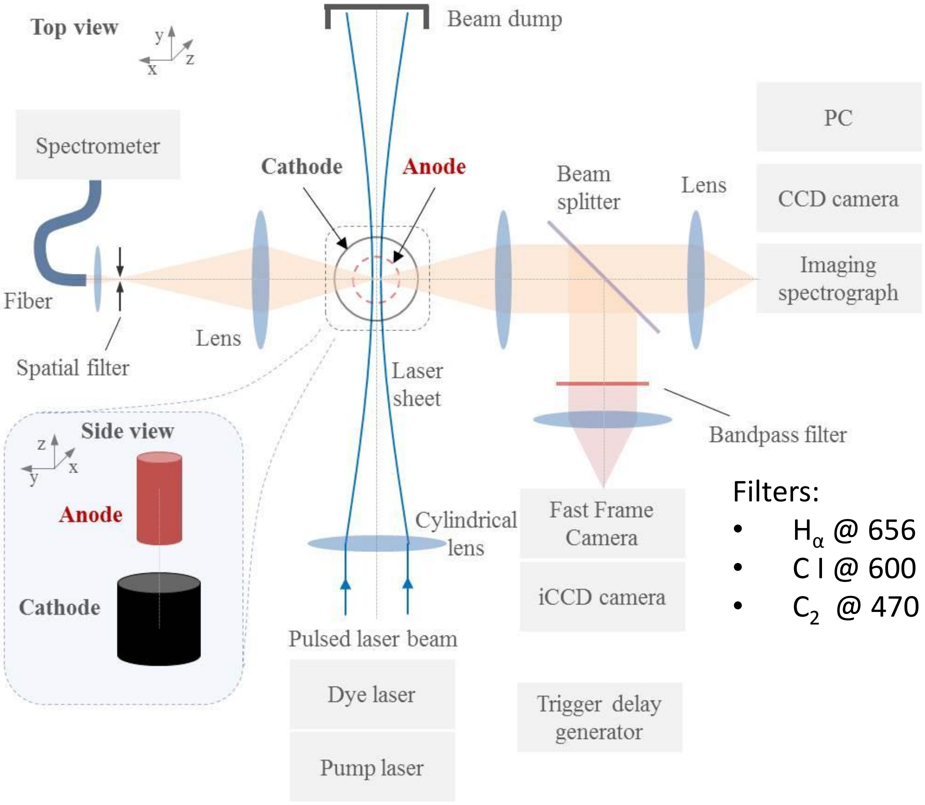
- Distribution of heavy plasma species (carbon dimers in arc periphery)

Experimental setup. Arc broadband spectrum

Typical arc spectrum



C_2 Swan band – strongest lines
C neutrals & ions – present
H – added (5%) to facilitate spectroscopy
He – very small contribution



Filters:

- H_α @ 656 nm
- C I @ 600 nm
- C_2 @ 470 nm

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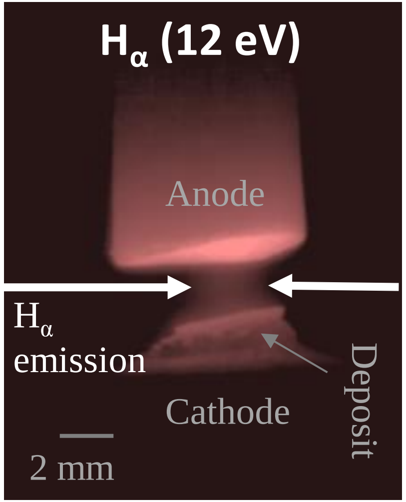
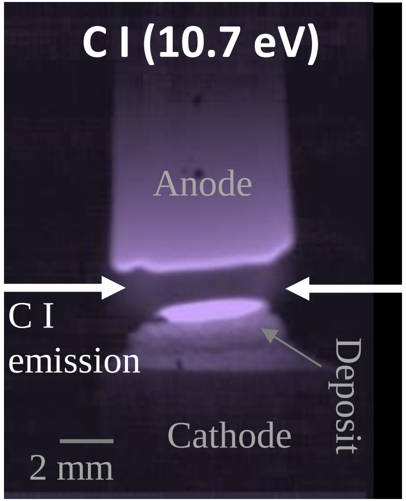
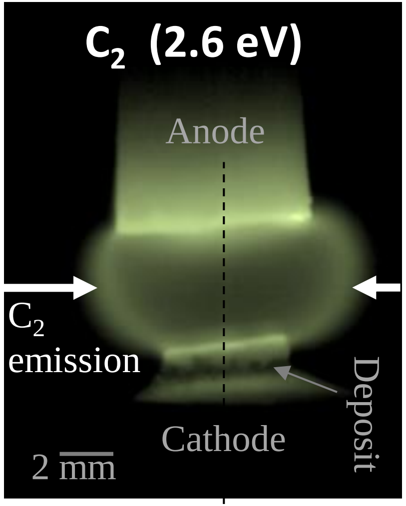
Arc structure - Filtered Fast Frame Imaging





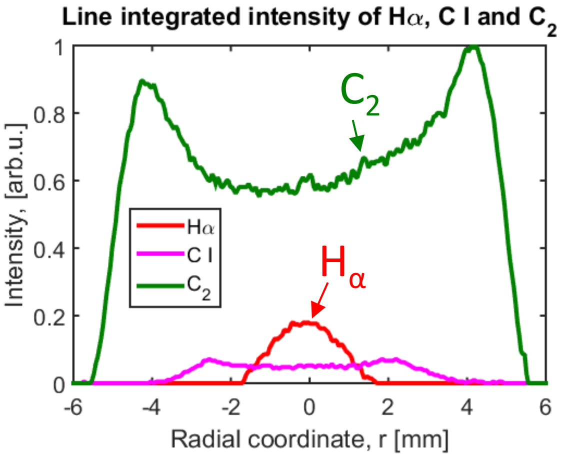


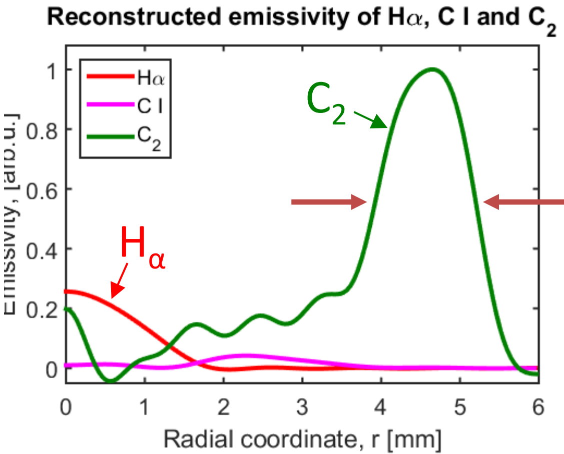
Line integrated spectral images of plasma species radiation were reconstructed using Abel inversion method to obtain distribution of plasma species emissivity

Carbon dimers form bubble-like shape around the arc core

- **H_α radiation diameter: < 4 mm**

*** 90% of discharge current is conducted within ≈ 3 mm**



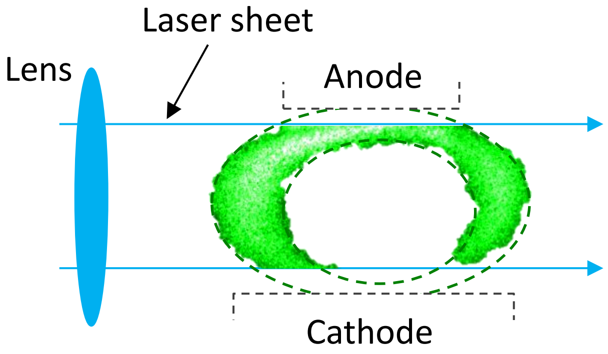


Temperature range 2000-3000 K

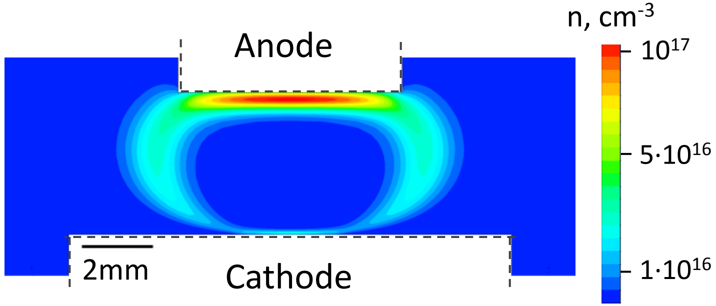
* Y. W. Yeh, Y. Raitses, and N. Yao, Carbon **105**, 490-495 (2016)

Arc structure - planar Laser Induced Fluorescence

Schematic of planar LIF

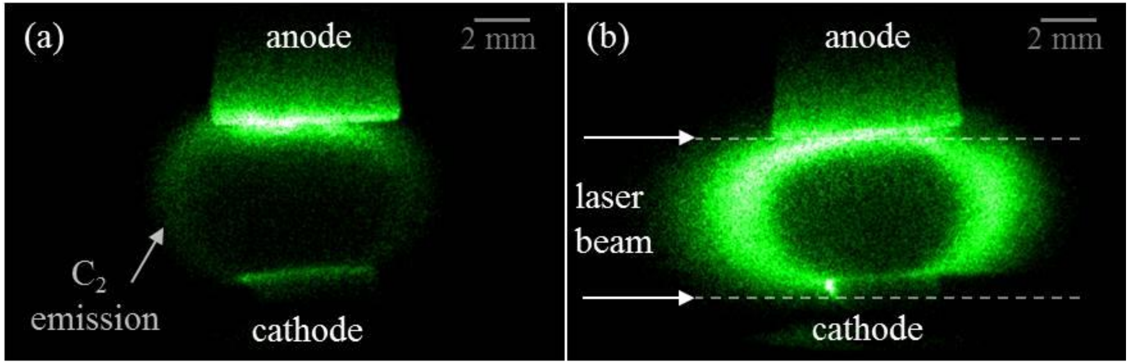


2D CFD simulation*



Spectral image of carbon dimer (C_2) **spontaneous** emission at 470 nm

Planar LIF: spectral image of carbon dimer (C_2) emission at 470 nm (laser at 437 nm)



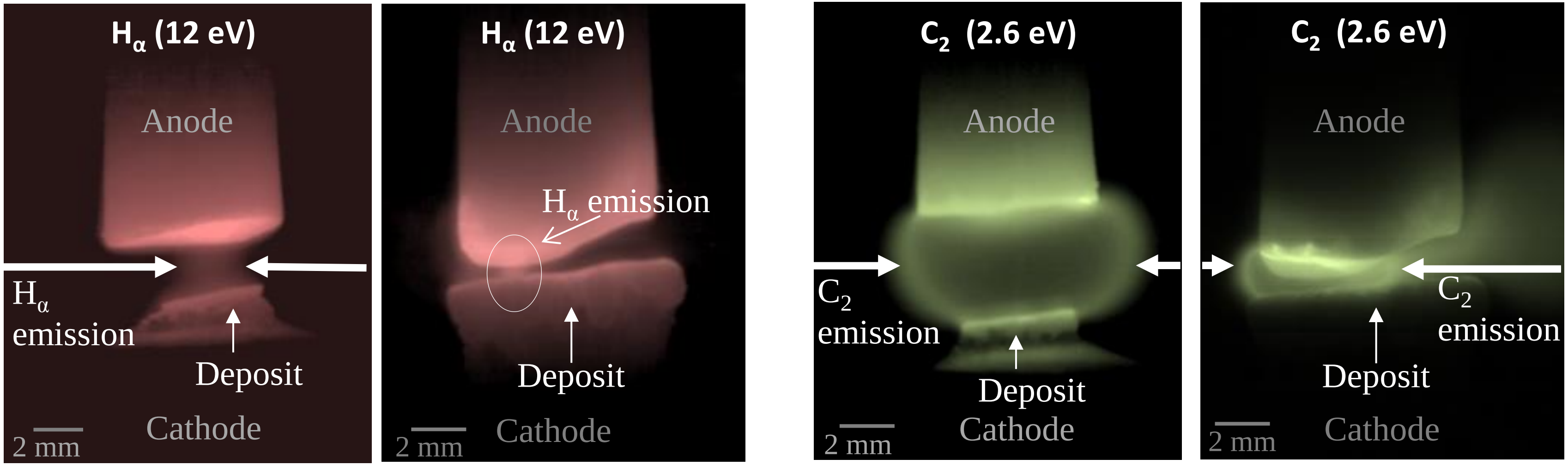
- **Carbon dimer distribution has a bubble-like shape around the arc core**
- **Presence of carbon dimer near the anode surface supports multi-species evaporation model of graphite (C, C_2, C_3?)**

Arc core

Low ablation mode | **High ablation mode**

Arc periphery

Low ablation mode | **High ablation mode**



The layered structure of the arc is preserved in most of operation modes

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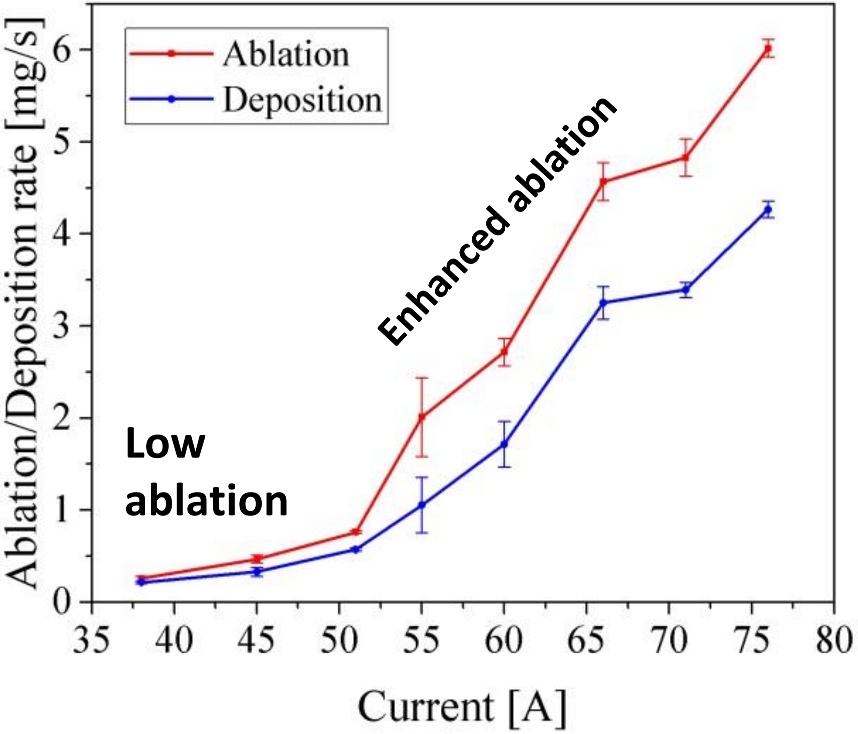
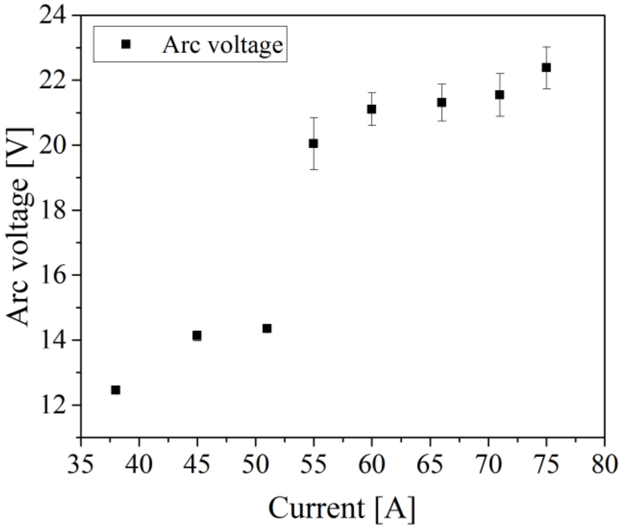
Transition Low-to-High (enhanced) ablation mode

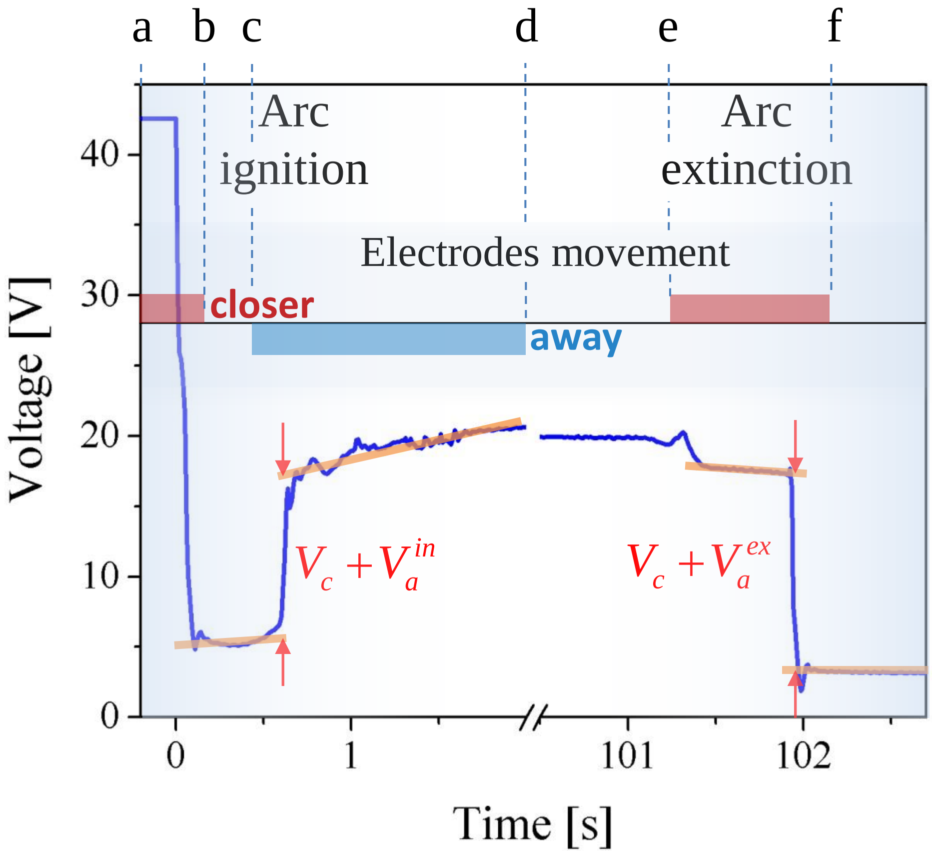
Arc exhibits sharp increase of the anode ablation rate with increase of the discharge current. Other parameters are kept the same



Arc voltage vs current when the arc length is fixed

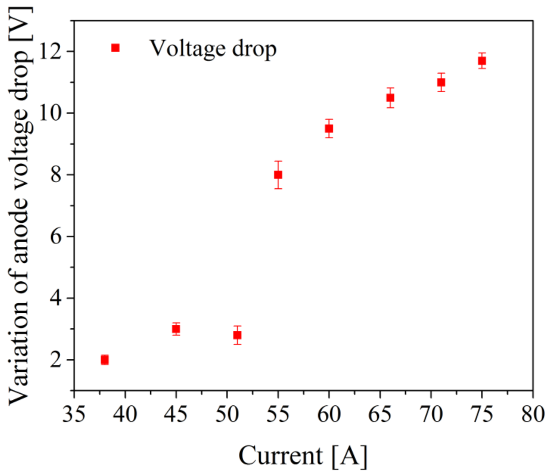


Anode fall voltage measurements



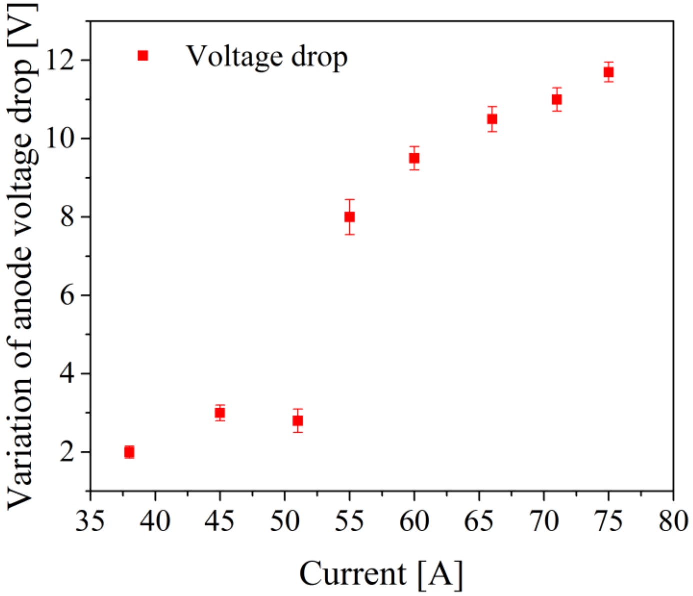
- Discharge voltage waveform (blue line) during arc **ignition** (**a-d**) and **extinction** (**e-f**).
- Electrodes are moving towards each other during (**a-b**) and (**e-f**) and outwards during (**c-d**).
- Red arrows indicate measurement points

$$\Delta V_a = V_a^{ex} - V_a^{in}$$

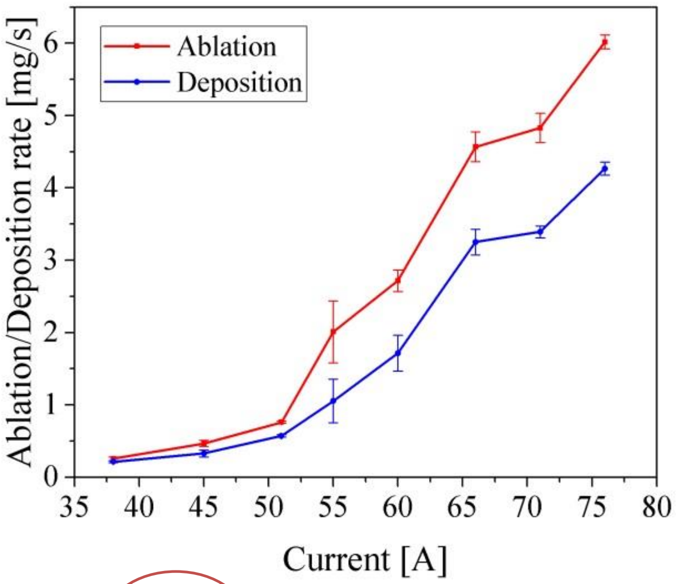


Correlation between anode fall and anode ablation

Variation of the anode voltage drop vs discharge current



Anode ablation rate vs discharge current



$$q_a^e = j_e\left(2.5T_e + \phi_w + V_a^{in} + \Delta V_a\right)$$

Enhanced ablation of the anode material can be induced by increase of the anode fall voltage (and current density)

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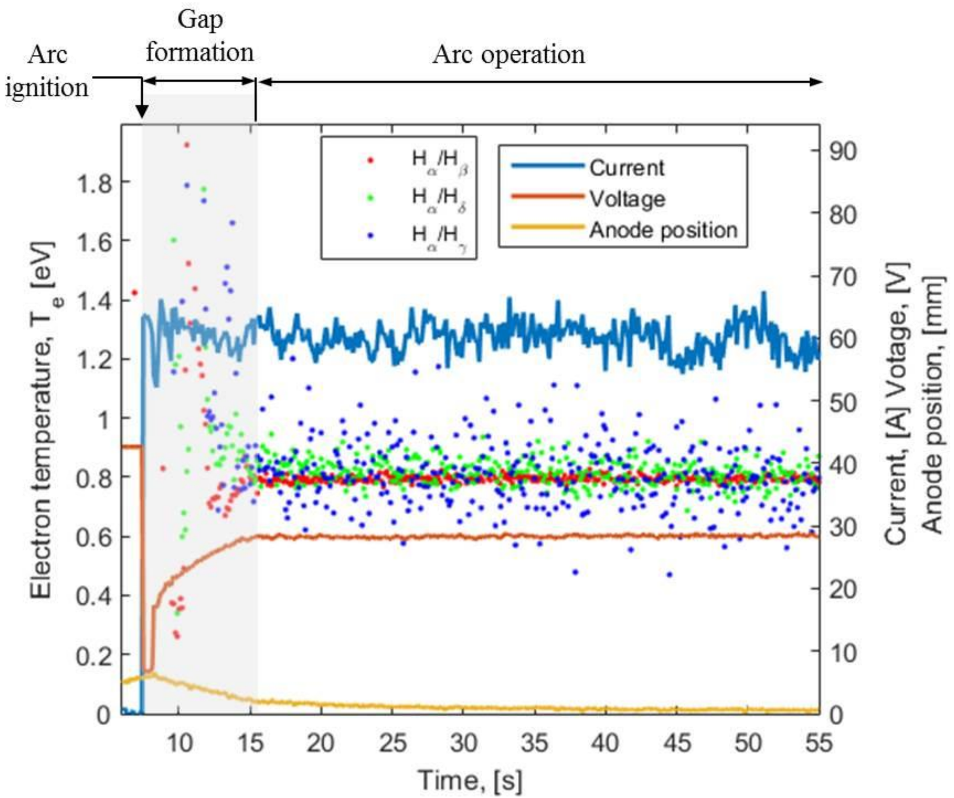
Arc core parameters – Temperature



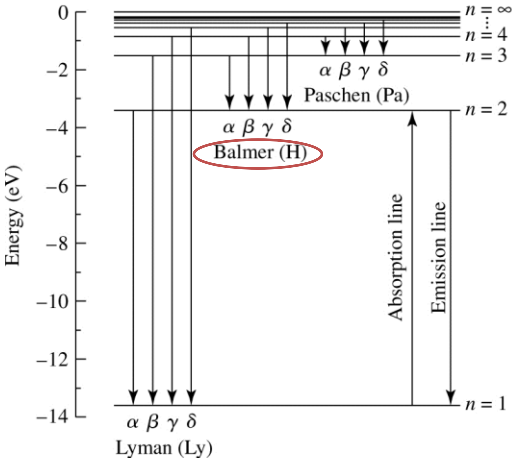
Low ablation mode

0.8±0.1 eV

High ablation mode

0.9±0.2 eV

Hydrogen Balmer series (∞..3→2)



$$kT_e = -\frac{E_m - E_n}{\log\left(\frac{k_{sys}^{mn}}{K_{mn}}\frac{I_{m-2}^{meas}}{I_{n-2}^{meas}}\right)}$$

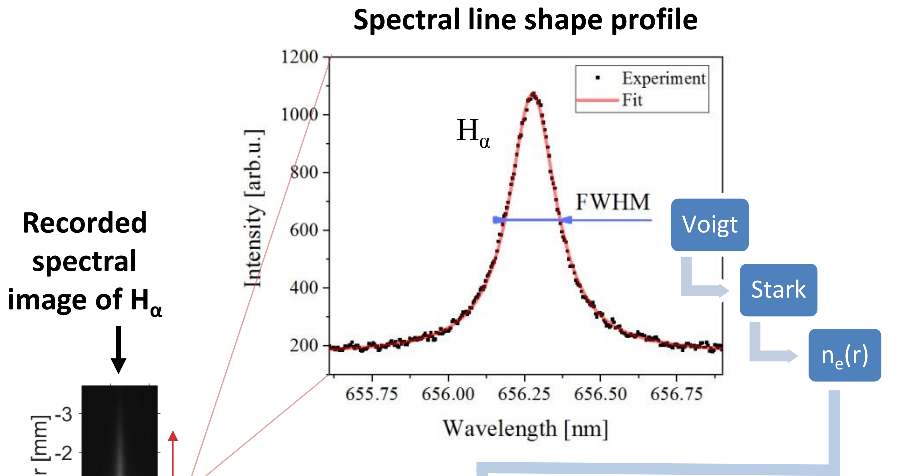
m,n – are quantum numbers of considered levels with energies E_m and E_n.

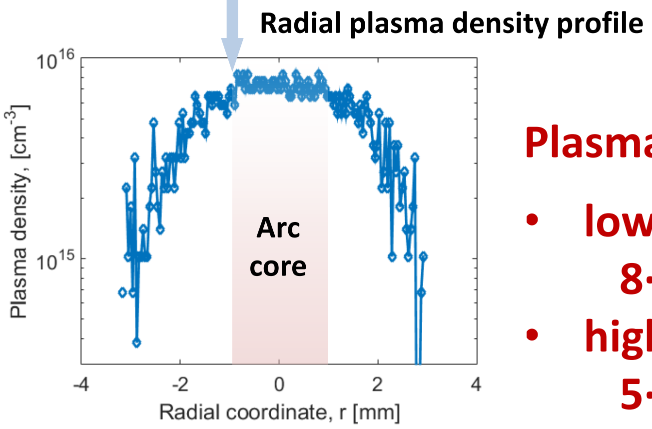
$I_{n-2}^{meas}, I_{m-2}^{meas}$ - measured intensities

$$K_{mn} = \chi_{mn}\frac{\lambda_{n-2}\cdot\sum g_m A_{m-2}}{\lambda_{m-2}\cdot\sum g_n A_{n-2}}$$

k_{sys}^{mn} - spectral response function of acquisition system

Arc core parameters – Stark spectroscopy





Experimental spectral line profile should be properly de-convolved to obtain Stark broadening component

$$\begin{cases} V(\lambda) = A\int \exp\left(-\dfrac{4\ln 2(\lambda' - \lambda_0)^2}{G_w^2}\right)\dfrac{L_w^2}{4(|\lambda - \lambda'| - \lambda_0)^2 + L_w^2}\,d\lambda' \\ L_w = \Delta\lambda^{Stark} + \Delta\lambda^{WV} \\ G_w = \sqrt{(\Delta\lambda^{Doppler})^2 + (\Delta\lambda^{Instr})^2} \end{cases}$$

$V(\lambda)$ - Voigt function

$G(\lambda)$ - Gaussian function with FWHM G_w

$L(\lambda)$ - Lorentzian function with FWHM L_w

$\Delta\lambda^{Doppler}$ - Doppler broadening

$\Delta\lambda^{WV}$ - Van-der-Walls broadening

$\Delta\lambda^{Instr}$ - Instrumental broadening

Plasma electron density n_e

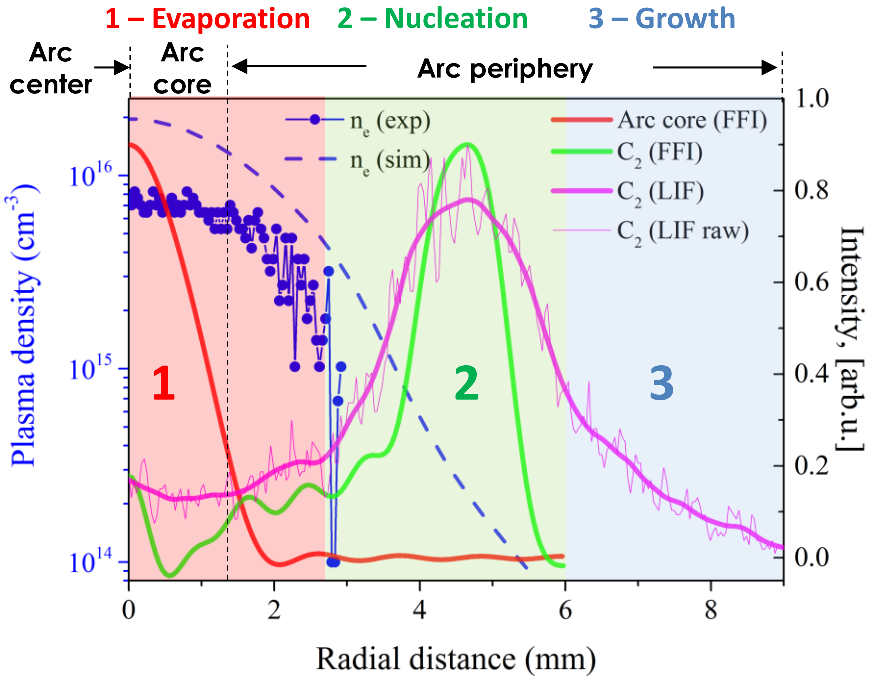
- **low ablation mode:**
  $8\cdot10^{14}$ - $8\cdot10^{15}$ cm^{-3}
- **high ablation mode:**
  $5\cdot10^{15}$ - $3\cdot10^{16}$ cm^{-3}

$$\Delta\lambda^{Stark} = f(n_e)$$

M. A. Gigosos, M. A. Gonzalez, and V. Cardenoso, Spectrochim Acta B **58**, 1489-1504 (2003).

Summary

- **First direct measurements of the arc core plasma density and temperature**
- **Arc structure and evolution of the arc core parameters in low- and high-ablation modes were obtained.**
- **Enhanced ablation of the anode material is induced by increase of the anode fall voltage and current density.**



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Alex Merzhevskiy (engineering)

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Dr. Shurik Yatom

Dr. Igor Kaganovich

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