Complex Structure of the Carbon Arc Discharge for Nanomaterial Synthesis

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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

Discharge current 60 A
Discharge voltage 20 V

Atmosphere Helium 500 Torr
Plasma density ($n_e$) $10^{14} - 10^{16}$ cm$^{-3}$
Temperature ($T_e$) 1 eV

Ionization degree
- $\nu_{e-i}$
- $\nu_{e-a}$
- $mnp_{e-i}$
- $mnp_{i-a}$
- $\lambda_D$

- $10\%$
- $10^{12}$ s$^{-1}$
- $10^{11}$ s$^{-1}$
- 1 μm
- few μm
- 100 nm

Fullerenes
Graphene
Carbon nanotubes

10 μm

A
B

0.36 nm

0.25 μm

1 μm

1-2 nm

2-25 nm
Run time: 1 min; Voltage 24 V, Current 60 A

Recording with filter at 656 nm, playing at 500 fps
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

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

![Graph of Ablation vs. Deposition](image)


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

![Images of arc oscillations](image)
**Synthesis arc: Status Quo**

- Synthesis requires flux of **feedstock** material and temperature

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

- 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)

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Low frequency oscillations in arc
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Brief summary

**Plasma arc core parameters:**

**Optical emission spectroscopy**
- Plasma density $n_e$ profiles from Stark broadening of hydrogen H$_\alpha$ 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:
- $H_\alpha$ @ 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.

- $H_\alpha$ radiation diameter: < 4 mm

* 90% of discharge current is conducted within $\approx$ 3 mm

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

Temperature range 2000-3000 K
Schematic of planar LIF

Laser sheet

Arc structure - planar Laser Induced Fluorescence

Planar LIF: spectral image of carbon dimer ($C_2$) spontaneous emission at 470 nm

(a) anode 2 mm

(b) anode 2 mm

2D CFD simulation*

- 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 ($C$, $C_2$, $C_3$?)
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.

![Graph showing Ablation and Deposition rates vs Current]

**Arc voltage vs current when the arc length is fixed**

![Graph showing Arc voltage vs Current]
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

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)

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

$I_{m-2}^{\text{meas}}$ and $I_{n-2}^{\text{meas}}$ - measured intensities

\[ kT_e = -\frac{E_m - E_n}{\log \left( \frac{k_{mn}^{\text{sys}}}{K_{mn}} \right)} \]

$K_{mn} = \chi_{mn} \lambda_{m-2} \sum g_m A_{m-2} \frac{1}{\lambda_{m-2}} \sum g_n A_{n-2}$

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

Arc ignition
Gap formation
Arc operation

Electron temperature, $T_e$ [eV]

Energy [eV]

Current, [A] Voltage, [V]
Anode position, [mm]

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

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

Hydrogen Balmer series (∞..3→2)
**Arc core parameters – Stark spectroscopy**

**Recorded spectral image of H_α**

**Spectral line shape profile**

**Radial plasma density profile**

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

\[
V(\lambda) = A \int \exp \left( -\frac{4 \ln 2 (\lambda' - \lambda_0)^2}{G_w^2} \right) \frac{L_w^2}{4 (|\lambda - \lambda'| - \lambda_0)^2 + L_w^2} d\lambda'
\]

\[
L_w = \Delta \lambda_{\text{Stark}} + \Delta \lambda_{\text{WV}}
\]

\[
G_w = \sqrt{(\Delta \lambda_{\text{Doppler}})^2 + (\Delta \lambda_{\text{Instr}})^2}
\]

**Voigt function**

\[
V(\lambda) - \text{Voigt function}
\]

\[
G(\lambda) - \text{Gaussian function with FWHM } G_w
\]

\[
L(\lambda) - \text{Lorentzian function with FWHM } L_w
\]

**Plasma electron density n_e**

- **low ablation mode:** \(8 \cdot 10^{14} - 8 \cdot 10^{15} \text{ cm}^{-3}\)
- **high ablation mode:** \(5 \cdot 10^{15} - 3 \cdot 10^{16} \text{ cm}^{-3}\)

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.

This work is funded by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and Fusion Energy Sciences.
Acknowledgments

Thank you to:

Alex Merzhevskiy (engineering)

Dr. Alexander Khrabry

Dr. Shurik Yatom

Dr. Igor Kaganovich

This work is funded by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and Fusion Energy Sciences.