

Optical and electrical diagnostics of microdischarges at moderate to high pressure in argon

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Microdischarges at moderate to high pressure in argon were investigated. A hole opening diameter of 500 μm direct current (dc) microhollow cathode discharges (MHCD) were characterized by electrical measurements and optical emission spectroscopy (OES) for pressures ranging between 90 and 800 Torr and current from 5 to 20 mA. Current-voltage characteristic curves were obtained as a function of the pressure for this hole diameter. MHCD enables stable dc discharges for molybdenum electrodes material at constant Ar + 2% H_2 flow of 0.03 ℓ/min . Optical emission spectroscopy and analysis of the spectral line broadening of plasma line emissions were performed in order to measure gas discharge parameters. Electron number densities were obtained from H_β Balmer line ($\sim 10^{14} \text{ cm}^{-3}$). For the above mentioned discharge conditions, gas temperature was estimated to be 550 – 850 K from OH rotational bands. Excitation temperature was measured based on two lines method (from atomic Mo lines) and from 4p - 4s and 5p - 4s Ar radiative transitions. Hydrogen atom temperature was measured for 800 Torr ($\sim 12000 \text{ K}$).

Keywords: Microdischarges, microhollow cathode discharges; optical emission spectroscopy.

1. INTRODUCTION

Following Schoenbach group studies about microdischarges - notably of microhollow cathode discharges (MHCD) at moderate to atmospheric pressure - the operation and applications of these kinds of microplasmas has attracted the attention of researchers worldwide due to the convenience and easiness of operation, besides the low cost [1-10]. These non-thermal microplasmas, where the electron temperature is much higher than the gas temperature (here, electron temperature is associated with the mean electron energy), allied to small size and low power consumption, is an attractive to the plasma applications possibilities in industry, like surface treatment, generation of UV and VUV radiation, reduction of pollutants, gas lasers, biological decontamination, thin film deposition, mainly in a high pressure operation [1,2].

These microdischarges consist of a cathode with a bore-hole and an arbitrarily shaped anode, separated by an insulator, where a hole is drilled through a cathode-mica-anode sandwich structure. Both current-voltage characteristics and Paschen's curves have been studied previously [6-8] for different pressures and hole diameters. They showed three distinct modes of operation: abnormal (at low current), self-pulsed and normal. Stable atmospheric pressure operation is easily obtained in small holes or by employing a certain constant gas flow (dynamic mode). As an example, for a flow of 0.7 ℓ/min it was possible to ignite a discharge in a 200 μm diameter hole using rare gas [11]. For atmospheric pressure operation, the hole diameter should be in the order of 100 μm

in a static mode of operation (without gas flowing) [3].

The understanding of physical and chemical processes occurring in this kind of plasma is fundamental for the optimization of the some industrial applications. Reliable MHCD operating at low voltage seems to be useful and important both for industrial and research applications. It is important to notice that at high-pressure, the cathode heating and sputtering is a problem in these devices mainly in static mode of operation, diminishing the lifetime. Therefore, low gas temperature at higher current operation is desirable to avoid these issues. The investigation of plasma parameters, like electron number density (n_e), gas temperature (T_g), electron temperature (T_e) and excitation temperature (T_{exc}) generated in MHCD is important to understand the mechanisms that govern these new high-pressure discharges and at the moment, there are no systematic experimental results of plasma parameters (n_e , T_g , T_e and T_{exc}) in the literature.

Recent works have shown results on plasma parameters and applications for high pressure (p) quasi-static MHCD, or in a low argon flux, and now they will be presented. For diagnostics and application of an analytical plasma, Miclea *et al* [12] have measured $n_e = 9 \times 10^{15} \text{ cm}^{-3}$, $T_g = 2000 \text{ K}$, $T_e = 1.2 \text{ eV}$ for discharge current $I_d = 3 \text{ mA}$ in dc MHCD at atmospheric pressure. Limitation in these applications is the low current and reduced lifetime of the microstructures due to overheating, or sputtering of the micro-hole, at high pressure. Investigating excimer emission from MHCD, Moselhy *et al* [13] found $n_e = 1 \times 10^{15} \text{ cm}^{-3}$ in atmospheric pressure, for flowing argon at a rate of 0.04 ℓ/min in the gas chamber (gas temperature was not measured). These authors estimated $T_e = 1.2 \text{ eV}$ for dc operation and 2.25 eV in the pulsed mode. Naming micro-structured-electrode arrays, Penache *et al* [14] have investigated static dc MHCD in pure

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Ar for pressure ranging from 50 to 400 mbar. From spectroscopic measurements of the absorption line profiles they found $T_g = 1100$ K and $n_e = 5 \times 10^{15} \text{ cm}^{-3}$ at $p = 400$ mbar. In a device for water treatment, Yamatake *et al* [15] implemented dc-driven MHCD in argon flow rate 1ℓ/min for 200 μm hole diameter and they have only measured the current-voltage characteristics, showing abnormal mode of operation. Otherwise, we showed that a dynamic mode MHCD can be operated with intense gas flow in a low gas temperature [11].

In this work optical emission spectroscopy (OES) is used to diagnose the microplasma. In order to measure the basic discharge parameters, an open dc MHCD was used with Ar/H₂ = 98/2 at moderate to high pressure and total flow 0.03 ℓ/min. Plasma parameters were determined from spectral line intensity and broadening. Stark and van der Waals broadenings of the Hydrogen H_α, H_β, and argon atom Ar 603.213 nm and 565.070 nm lines were used to measure the gas temperature and electron number density of the microplasma for a range of pressure and current. Therefore, we study the variation of the electron number density with pressure and current. In order to analyze the radiation emission from the cathode surface, Mo sputtered and excited atoms could be used to determine T_{exc} and through OES of OH (from residual water vapor) the gas temperature could be estimated.

2. EXPERIMENTAL SET-UP

The electrodes are made of approximately 100 μm thick molybdenum foils separated by a 250 μm spacer of mica with 500 μm hole diameter. Sustained glow discharge voltages were in the range of 200 – 400 V for Ar/H₂ = 98/2 gas mixture at 0.03 ℓ/min total gas flow. The discharge currents I_d varied between 1 and 20 mA. The operating gas mixture was running from moderate to high-pressure, between 90 and 800 Torr. The electrode system was placed in a cylindrical quartz chamber with 10 cm diameter and 16 cm length. Before each experiment the chamber was cleaned, dried and evacuated to about 1 mTorr. Then, the discharge chamber was filled with pure argon gas and placed at the desired pressure. Ballast resistors of 55 KΩ were located to the cathode side and were used to limit the discharge current. A picoammeter model Keithley 414S and Minipa digital voltmeter were used to measure the current and voltage in the prebreakdown phase.

Figure 1 shows schematically the MHCD device and the optical apparatus for emission spectroscopy measurements. For spectral investigations the radiation emitted from the cathode borehole was focused onto the optical fiber 1mm i.d. aperture by means of convergent lens. This radiation was sent onto the entrance slit (width of 100μm) of 1 m Czerny-Turner (Jobin-Yvon) monochromator (THR1000). The radiation was collimated at the exit slit where a photomultiplier tube (PMT) converts photons into an electric signal. The current generated by the PMT was sent to data acquisition electronics, where the signal was processed by software. The apparatus function was obtained from Ar low-pressure lamp and found to be 0.0463 nm.

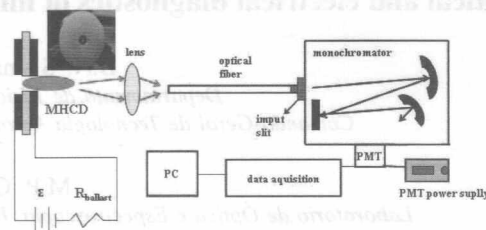


FIG. 1: Experimental set-up showing MHCD and light acquisition; inset: end-on photography of MHCD.

TABLE 1: FWHM for various broadening mechanisms for H_α, H_β, Ar 603.213 and 565.070 nm lines, at atmospheric pressure (n_e in cm^{-3} , T in K).

Line (nm)	$\Delta\lambda_{\text{Stark}}$ (nm)	$\Delta\lambda_{\text{van Der Waals}}$ (nm)	$\Delta\lambda_{\text{Resonant}}$ (nm)	$\Delta\lambda_{\text{Doppler}}$ (nm)
H _β – 486.130	GIG-CARD MAPS	$4.528T_g^{-0.7}$	$0.513T_e^{-0.7}$	$3.48 \times 10^{-4} T_g^{0.5}$
H _α – 656.232	GIG-CARD MAPS	$5.203T_g^{-0.7}$	$0.610T_e^{-0.7}$	$4.70 \times 10^{-4} T_g^{0.5}$
Ar I – 603.213	See text	$3.931T_g^{-0.7}$	0	$6.83 \times 10^{-5} T_g^{0.5}$
Ar I – 565.070	See text	$3.310T_g^{-0.7}$	0	$6.40 \times 10^{-5} T_g^{0.5}$

The main mechanisms responsible for H_α, H_β, Ar 603.213 and 565.070 nm lines broadenings were previously investigated [9]. The full-width at half-maximum (FWHM) for these lines are given in Table 1. In our experimental conditions, both Ar 603.213 and 565.070nm lines are substantially broadened by van der Waals and Stark effects, allowing the estimation of n_e and T_e simultaneously. The gas temperature could be measured both by van der Waals broadening of Ar 603.213 nm line and OH radicals Q₁ branch. The excitation temperature was determined from the two Mo lines method and from the well-known Boltzmann-plot method using strong Ar 4p – 4s and 5p – 4s transition lines.

In MHCD, where the electron density is about 10^{14} cm^{-3} at atmospheric pressure, Stark and van der Waals contributions are the most important for these lines broadening, because the line shape is influenced by interactions of the radiating atoms with surrounding particles. Natural and resonance broadening of these lines are usually negligible. The Doppler and instrumental contributions give origin to Gaussian shape line profiles. Stark and van der Waals contributions generate Lorentzian component. The convolution of the Gaussian and Lorentzian components results in a Voigt profile. The GIG-CARD maps [16] for H_β line enable to determine the electronic density. In our MHCD, excited non-hydrogenic neutral atoms like Ar lines 603.213 nm and 565.070 nm may be used for diagnostic purposes because they are intense and well isolated. Using quasi-static approximation, Griem [17] took into account the small contribution of ion broadening in addition to the electron impact broadening of an isolated line profile. For the line Ar 603.213 nm the Stark width (FWHM) can be given by:

$$\Delta\lambda_S(\text{nm}) = 2(0.2206 + 1.77 \times 10^{-4} T_e - 1.072 \times 10^{-8} T_e^2 + 2.408 \times 10^{-13} T_e^{13}) [1 + 1.75 \times 10^{-4} n_e^{1/4} \times (0.0628 + 0.1042 \exp(-T_e/4216.168)) \times (1 - 0.068 n_e^{1/6} T_e^{1/2})] \times 10^{-17} n_e \quad (1)$$

and the Stark width (FWHM) for the Ar 565.070 nm line is:

$$\begin{aligned} \Delta\lambda_S(\text{nm}) = & 2(0.2093 + 1.231 \times 10^{-4}T_e - 6.045 \times \\ & \times 10^{-9}T_e^2 + 1.323 \times 10^{-13}T_e^3 - 1.042 \times 10^{-18}T_e^4 \\ & \times [1 + 1.75 \times 10^{-4}n_e^{1/4} \times (0.00299 + 0.01513 \times \\ & \times \exp(-T_e/1128.45) + 0.00399 \exp(-T_e/14592.93)) \times \\ & \times (1 - 0.068n_e^{1/6}T_e^{-1/2})] \times 10^{-17}n_e \end{aligned} \quad (2)$$

Solving simultaneously these equations, one can obtain n_e and T_e , presuming that the widths of these lines are previously known. Atmospheric-pressure microplasmas are generally in near-partial-local thermodynamic equilibrium (PLTE) [17,18]. The excitation temperature may be determined from Ar emission lines intensities using the well-known Boltzmann plot method. The two-line method was used for this purpose because the cathode surface sputters Mo excited atoms into the negative glow. The estimation of the excitation and gas temperature are fundamental to obtain the electron number density and other parameters of the plasma.

The rotational temperature (T_{rot}) was measured by using the $OH(A^2\Sigma^+, v=0 \rightarrow X^2\Pi, v'=0)$ emission band at 306.357 nm [9]. The OH radical emissions in atmospheric pressure plasma are result of water vapor naturally present as impurity in the gas and can be formed by electron impact dissociation ($e(> 4.4\text{eV}) + H_2O \rightarrow H + OH$). In MHCD it was observed emission band between 306 and 312 nm. The T_{rot} value may be taken from the slope of the plot $\ln(I_0\lambda/A)$ as a function of the upper state energy. Here, I_0 is the line intensity, λ is the transition wavelength and A the transition probability. The standard deviation on T_{rot} is less than 10%. Finally, from n_e , T_{rot} and T_e one can use GIG-CARD maps for H_α to estimate H ($n=3$) atom temperature.

3. RESULTS AND DISCUSSION

In Fig. 2 is shown the evolution of the current with applied voltage to an open MHCD for pressure ranging from 12 to 800 Torr. Additionally, in Fig. 3 the discharge appearances for different currents and specifically for 40 Torr pressure are presented. As can be seen low current abnormal mode is present, which is characterized by a positive differential resistance, for pressure up to 40 Torr (Fig. 3a). A self-pulsed mode appearing for currents up to 1.5 mA can be remarked by a voltage drop with current increase, i.e. negative differential resistance, for pressures ranging from 100 to 800 Torr. This region is characterized by high efficiency in producing of ions and metastables species inside the cathode cavity. The confinement of the discharge inside the hole can be seen by the optical appearance of the glow (Fig. 3b). Increasing the discharge current, one can observe a gradual expansion beyond the cavity, covering the cathode surface (Fig. 3c – d). The normal glow discharge mode is seen for currents greater than 1.5 mA, where the voltage is held constant as the current increases.

Three different methods were employed to measure T_e and T_{exc} [9]: 1) two Mo lines method (T_{exc}); 2) Boltzmann-plot method, for Ar 4p – 4s and 5p – 4s transition lines (T_{exc}); 3)

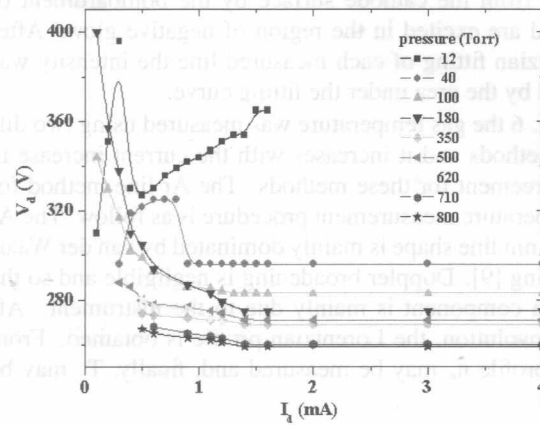


FIG. 2: V-I characteristic curve for a hole diameter of 500 μm in $\text{Ar}/\text{H}_2 = 98/2$ gas flow.

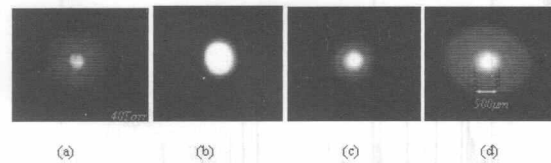


FIG. 3: End-on photography of the discharge appearance for a hole diameter of 500 μm at 40 Torr with the current increasing from 0.3 to 0.7 mA (a), 0.7 to 1.1 mA (b), 1.1 to 2.0 mA (c) and 2.0 to 4.0 mA (d) (see figure 2).

Ar 603.213nm and 565.070nm lines method, that simultaneously yields T_e and n_e (will be shown later). Based on both, Boltzmann plot and two Mo lines methods, $T_{exc} \cong (7000 \pm 300)$ K and $T_e \cong (8500 \pm 1000)$ K were obtained respectively for current ranging from 5 to 20 mA. For Boltzmann-plot the emission intensity of a series of Ar lines from 400 to 820 nm was recorded and their intensities were corrected for the spectral response of the monochromator. The emission of high intensity Ar and Ar^+ lines corresponding to the 5p – 4s and 4p – 4s (3d) transitions, respectively, indicates high electron temperatures in the investigated region. The difference between T_e and T_{exc} was already observed in the literature and the explanation is that the excitation temperature is obtained from the upper excited states distribution, corresponding to a part of electrons of the energy distribution function. T_e obtained with two Ar lines method may be associated with the electrons temperature because this method takes into account a significant part of the electrons energy distribution function. The presence of Ar^+ lines in the MHCD spectra from 400 to 450 nm (Fig. 4) shows that electrons with energies between 13 and 24 eV are present in the plasma bulk, which populates the tail of the electrons energy distribution function.

The presence of these argon ions is commonly observed in low-pressure plasmas but not in high-pressure discharges. In regards to two Mo lines method, the region of 440 to 452 nm was investigated where there are occurrences of atomic lines of excited molybdenum (Fig. 5). These Mo atoms are

released from the cathode surface by the bombardment of Ar^+ , and are excited in the region of negative glow. After a Lorentzian fitting of each measured line the intensity was obtained by the area under the fitting curve.

In Fig. 6 the gas temperature was measured using two different methods and it increases with the current increase in good agreement for these methods. The Ar line method for gas temperature measurement procedure is as follow. The Ar 603.213 nm line shape is mainly dominated by van der Waals broadening [9]. Doppler broadening is negligible and so the Gaussian component is mainly due to the instrument. After deconvolution, the Lorentzian profile is obtained. From the H_β profile n_e may be measured and, finally, T_g may be obtained.

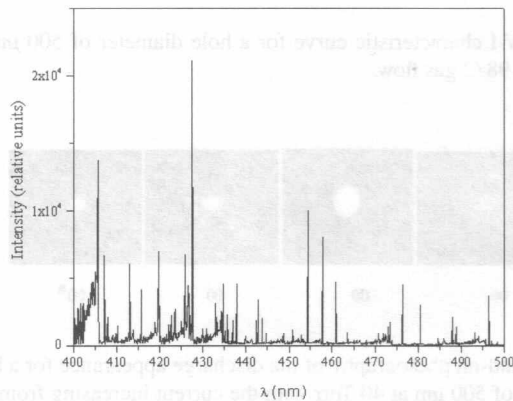


FIG. 4: Spectra of the $\text{Ar}/\text{H}_2 = 98/2$ microplasma at $I_d = 12\text{mA}$.

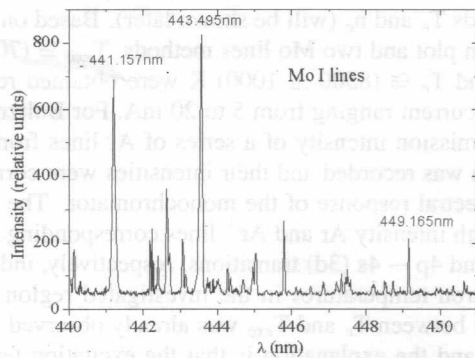


FIG. 5: Mo I lines observed in MHCD at atmospheric pressure.

The electron number density (n_e) was estimated from two methods [9]: a) H_β line and b) from Ar 603.213 nm and 565.070 nm lines methods. From H_β line method we can calculate n_e from GIG-CARD maps and it is depicted in Fig. 7 for current ranging from 5 to 20 mA and pressure from 90 to 800 Torr. From Ar 603.213 nm and 565.070 nm lines we obtain n_e and T_e for 800 Torr by solving simultaneously their Stark FWHM equations and yielded a density of 1.6 to $2.3 \times 10^{14}\text{cm}^{-3}$ and $T_e \cong (8500 \pm 1000)\text{K}$ for this range of current, showing that n_e increases with the current as must be for glow discharges. The thermal nonequilibrium $T_e \gg T_g$ in MHCD shows that this discharge operates in a glow mode

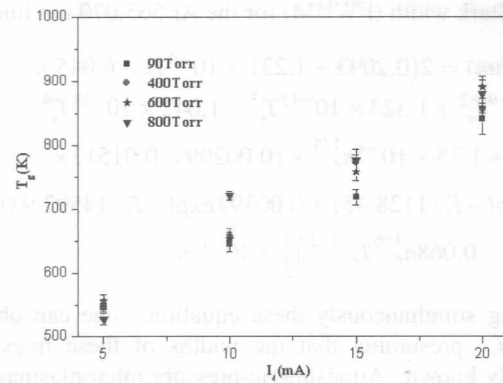


FIG. 6: Gas temperature for MHCD in argon flow for a range of pressure.

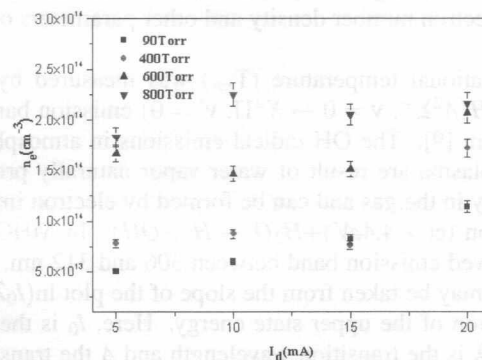


FIG. 7: Electron number density for current ranging from 5 to 20 mA.

and further glow-to-arc transition is possible only at high current. From these results, we obtain hydrogen atom temperature $T_h \cong (12000 \pm 1800)\text{K}$ from corresponding H_α line (GIG-CARD maps) for this range of current showing that the plasma heavy atoms are not in thermal equilibrium, and $T_h > T_e \gg T_g$. The creation process of excited H atoms may be formed by ion conversion and electron impact dissociation in reactions involving H^+ , H_2^+ and H_3^+ in H_2 or in Ar and excited H atoms [9]. For this magnitude of electron density, at 800 Torr, the Debye d_{De} length is about $3.3 \times 10^{-5}\text{cm}$. Therefore $(2d_{De}/D)^2 \sim 10^{-6}$ ($D = \text{hole diameter}$) and this characterize the existence of the plasma and ambipolar diffusion may be used for straightforward estimation of the electron number density $n_e(I_d)$ as function of the discharge current [11]. For MHCD hole in a cylindrical cathode configuration, neglecting any loss recombination, we used the continuity equation to deduce $n_e(I_d)(\text{cm}^{-3}) = 3.73 \times 10^{17} (I_d/D_a)$, where I_d is the current in mA and D_a is the ambipolar diffusion coefficient in cm^2s^{-1} given by Langevin formula as a function of plasma temperature [11]. For $I_d = 10\text{mA}$, $T_g = 730\text{K}$, and $D_a = 8.6\text{cm}^2\text{s}^{-1}$ one can obtain $n_e = 2.0 \times 10^{14}\text{cm}^{-3}$, which is in agreement with our optical results.

4. SUMMARY AND CONCLUSIONS

Emission spectroscopy and power measurements were employed to study dc MHCD in $Ar + 2\%H_2$ gas flow at moderate to high pressure up to 800 Torr. H_{β} Balmer line and Ar 603.213 nm and 565.070 nm lines were used to characterize the bulk plasma formed in the cathode borehole with diameter $D = 500 \mu m$. Gas temperature was estimated from OH radical Q_1 branch and from Ar 603.213 nm line. The measured gas temperature was in the ranges from 550 to 850 K

for current up to 20 mA, lower than that for static MHCD (~ 2000 K). Electron excitation temperature was estimated from both Mo two lines method and Boltzmann plot and was found to be below the electron temperature. The latter was obtained by two Ar lines (8500 K). The electron number density was measured both from H_{β} line Stark broadening and from Ar 603.213 nm and 565.070 nm lines broadenings increasing with the current. Hydrogen atom ($n = 3$) temperature for 800 Torr was already 12000 K, hotter than the gas and the electron temperature.

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