U.R.S.I. France JS 24

WAVES FOR PLASMA
PLASMAS FOR WAVES

Caractérisation spectroscopique de micro-décharge DBD en système microfluidique pour la synthèse chimique
Spectroscopic characterization of DBD micro-discharge in microfluidic system for chemical synthesis

Abderzak el-Farsy[1], Siméon Cavadias[1], Xavier Dutin[2], Gabriel Morand[1], Stéphanie Ognier[1], Michael Tatoulian[1]

[1]Institut de Recherche de Chimie Paris (IRCP), UMR 8247, 2PM group Chimie ParisTech-PSL, PSL Université Paris, CNRS. 11 rue Pierre et Marie Curie, 75005, Paris, France. abderzak.el-farsy@chimieparistech.psl.eu, michael.tatoulian@chimieparistech.psl.eu
[2]Laboratoire des Sciences des Procédés et des Matériaux, Institut Galilée, Université Paris 13, 99 avenue Jean-baptiste Clément, F-93430 Villetaneuse

Mots clés : Décharge à barrière diélectrique, microfluidique, caractérisation de plasma, spectroscopie d'émission optique.
Keywords: Dielectric barrier discharge, microfluidic, plasma characterization, optical emission spectroscopy

Abstract/Résumé

Ce travail présente la caractérisation spectroscopique d'une décharge DBD dans un système microfluidique en flux continu pour la chimie fine/pharmaceurique. Dans les procédés plasma en interaction avec liquide, la température de gaz influe la pression de la vapeur saturante des réactifs et joue un rôle protagoniste dans le rendement du procédé. Etant une technique non-destructive et adaptée à caractériser les microplasmas, la spectroscopie d'émission optique a été utilisée pour mesurer la température de gaz *via* la simulation de la bande rotationnel de N_2 (second positive system, (0,2) R branche). L'influence de diffèrent paramètres comme puissance déposée et débit de gaz sur la température de gaz a été étudié.

This work presents a spectroscopic characterization of DBD discharge combined with a microfluidic system for chemical synthesis. In plasma processes interacting with liquid, the gas temperature influences the saturation pressure of the reactants and plays a key role in the yield of the process. Being a non-destructive technique and suitable for characterizing microplasmas, optical emission spectroscopy was used to measure the gas temperature *via* the simulation of the second positive band of N_2. The influence of different parameters such as deposited power and gas flow rate on the gas temperature was studied.

1 Introduction

In the current socio-economic and environmental context, the chemical industries are seeking to push their practices to make them more ecologically, and ethically efficient, less expensive and dangerous. Therefore, optimizing the manufacturing processes or developing new technologies compatible with green chemistry are of great interest. Combining non-equilibrium cold plasma at atmospheric pressure conditions with the microfluidic system responds to these needs.

Being composed of ions, radicals, and neutrals which are excited to different electronic, vibrational, and rotational states, cold plasma is a rich reactive state. This strong reactivity can be used in contact with a liquid to produce chemical reactions, such as functionalization, polymerization, coupling reactions, etc. Generated at atmospheric pressure using a dielectric barrier discharge (DBD) for a wide variety of gases, plasma could be a relevant activation energy source for chemical synthesis. DBD plasma allows for avoiding the transition to "arc" in which electrons and ions are in thermodynamic equilibrium. The ions remain generally cold and near neutral species temperature. Compared to low-pressures discharge where the plasma is almost diffuse, the discharge at atmospheric pressure tends to become inhomogeneous "filamentary mode" [1]. Its generation has several difficulties leading to the miniaturization of plasma in this context: the gap between the electrodes is the order of the millimeter.

For organic chemistry which involves the liquid phase, continuous-flow is particularly efficient when made at a small scale, i.e., so-called microfluidics. The latter ensures a maximized mass and heat transfer to obtain an improved and controlled liquid/gas thanks to a larger ratio between their surface and volume [2]. In addition, many other advantages rise with continuous-flow such as high product quality, periodic flow and ability to safely handle toxic and explosive reactions. According to Paschen law, for plasmas created within submillimeter scales in at least one dimension the breakdown voltage is reduced because of the reduced distance between the electrodes. Compared to the overmillimeter scale, this can lead to an increase in the electron's temperature and a decrease in the gas temperature.

Due to the small size of microplasmas and discharges, electrical measurements using electrostatic probes are not suitable and can disturb the plasma and change its properties [3]. Therefore, active optical diagnostics which are based on the interaction of light with the species are needed in many cases to obtain direct measurements of species densities and temperatures. Optical emission spectroscopy (OES) is a common and nonintrusive plasma diagnostic technique. It is widely used for chemical analyses and quantification (e.g., the evaporation of compounds vs alloys)[4], to characterize plasmas and plume formation when a metal vapor expands under vacuum (e.g., ablation). OES measures the electron densities and temperatures using excited species (atoms and molecules, neutral or ionized) in a plasma based on their radiative emission lines [5,6]. When the plasma contains molecular gas, OES gives access to rotational and vibrational temperatures. In atmospheric pressure cold plasma, the rotational temperature of a diatomic molecule is assumed to be the translational temperature.

This work focuses on the study of DBD plasma in interaction with liquid generated in microfluidic chips. Using OES, the effect of gas flow rate, the applied voltage and its waveforms have been characterized. Furthermore, gas temperature has been measured and the chemical composition of the plasma in interaction with Ethyl acetate has been characterized.

2 Experimental setup

The microreactor used in this work consists of on a serpentine channel (100 μm × 300 μm) as shown in Figure 1. The DBD cell comprises two rectangle plane-parallel of ITO (Indium tin oxide) electrodes deposited on the glass by magnetron sputtering, the distance between electrodes is 100 μm. The upper electrode is connected to the high voltage, whereas the lower electrode is grounded. The discharge is created by high voltage generator (made in-house) triggered by a low frequency signal generator, the frequency was fixed to 2 kHz with different waveforms (sine, square and triangle). The gas (Ar + 1%N_2) and liquid (Ethyl acetate) flows were controlled with a flowmeter and syringe driver.

The chemical species present in the plasma were determined by OES measurement using an Acton Research Corporation SpectraPro-500i equipped with a PIMAX4® ICCD camera (Blue Intensified). The second positive system of N_2 [$C^3\Pi_u - B^3\Pi_g$ (0,2) was used to assess the rotational temperature by Specair Software.

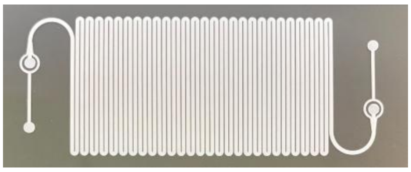

Figure 1: picture of the microfluidic chip

3 Results

The emission spectrum obtained during a plasma of pure Ar at different voltages (peak to peak) is shown in Figure 2a. It reveals the presence of various Ar excited states, the deposited power and Ar I intensity at 696 nm increase with the applied voltage (Figure 2b).

Figure 3 shows the effect of the voltage waveform on the plasma glow. From those averaged measurements, the plasma created by the square wave is denser compared to the sine or triangle wave. The Ar intensity is an order of magnitude higher with a square wave. It seems that plasma density (electron density) is proportional to voltage variation. OES measurements herein are integrated over 10 milliseconds. The fast voltage variation induces high current and high deposited power. Time-resolved optical and electrical measurements are required to better understand this difference.

Figure 4a shows the effect of the gas flow rate on the plasma glow. The Ar intensity increases with the gas flow rate. Two regimes could be distinguished, a strong increase until 0.8 ml/min and a slow increase for higher gas flow rate (Figure 4b). This effect is surprising and requires rapid imaging to understand.

Figure 5 shows the gas temperature at the middle and the end of the channel. The measured temperature depends slightly on the applied voltage, on the position in the channel but also on the gas flow rate. The temperature in the canal is around 330 K.

The emission spectrum obtained during the Ar plasma in interaction with Ethyl acetate is shown in Figure 6a. It reveals the presence of various atomic and molecular excited species originated from the dissociation of Ethyl acetate molecules (Figure 6b). These include the presence of Ar emission lines, with a peak at 383 nm corresponding to the transition ($B^1\Sigma - A^1\Pi$ (0,1)) of CO Angtsrom system, and a peak at 518 nm corresponding to the transition ($A^3\Pi_g -\ X'^3\ \Pi_u$) of C_2 SWAN system.

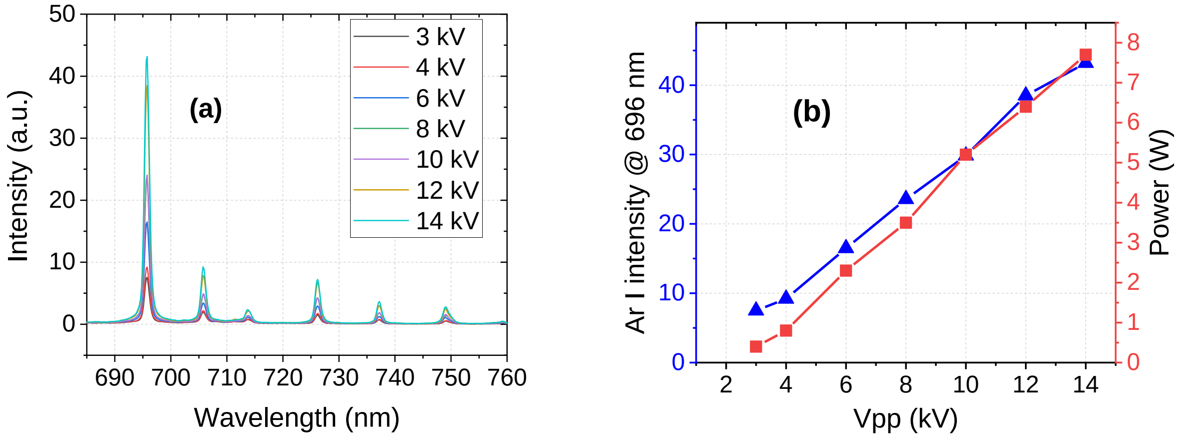

Figure 2: (a) OES spectrum of a microfluidic plasma in pure Ar for various Vpp, frequency of 2 kHz, sine waveform and Ar flow rate of 0.8 ml/min. (b) Intensity of Ar neutral exited state at 696 nm and deposited power as function of V_{pp}.

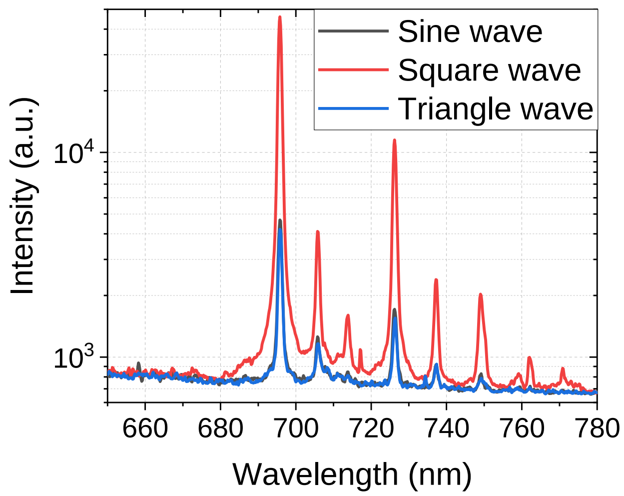

Figure 3: OES spectrum of a microfluidic plasma in pure Ar for sine, square and triangle wave. Vpp = 6kV and Ar flow rate of 0.8 ml/min.

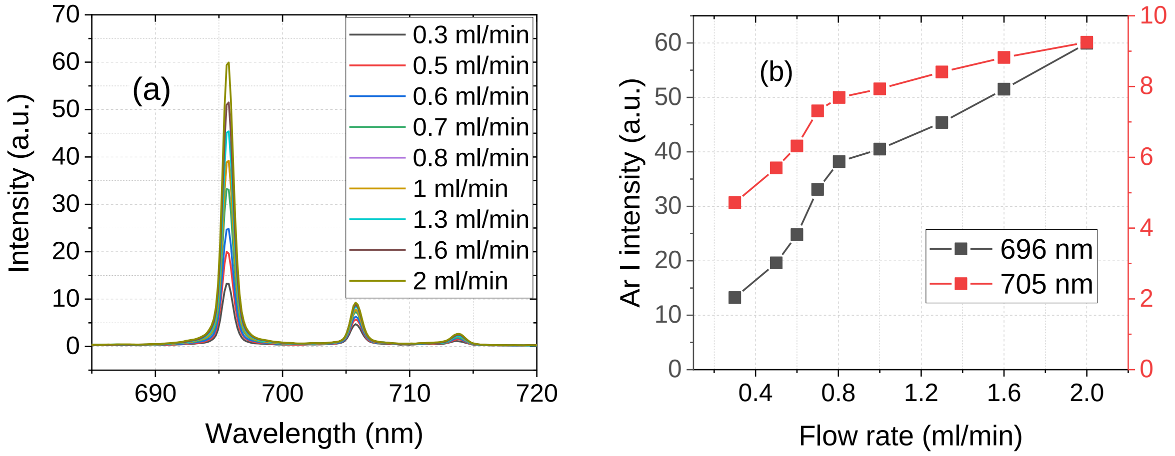

Figure 4:(a) OES spectrum of a microfluidic plasma in pure Ar for various gas flow rate. Vpp = 6kV and deposited power of 6 W, the deposited power does not change with the flow rate. (b) Evolution of the Ar neutral exited state as function of the gas flow rate.

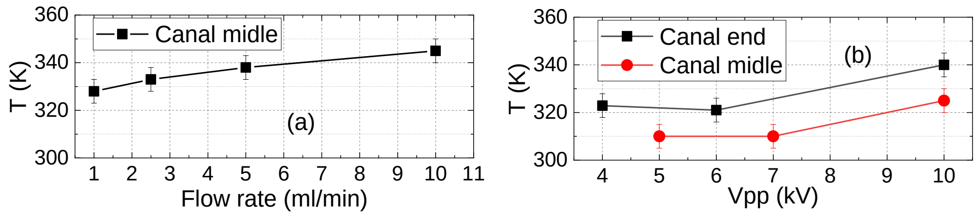

Figure 5: Gas temperature at the end and middle of the canal as function of flow rate (a) and the voltage (b).

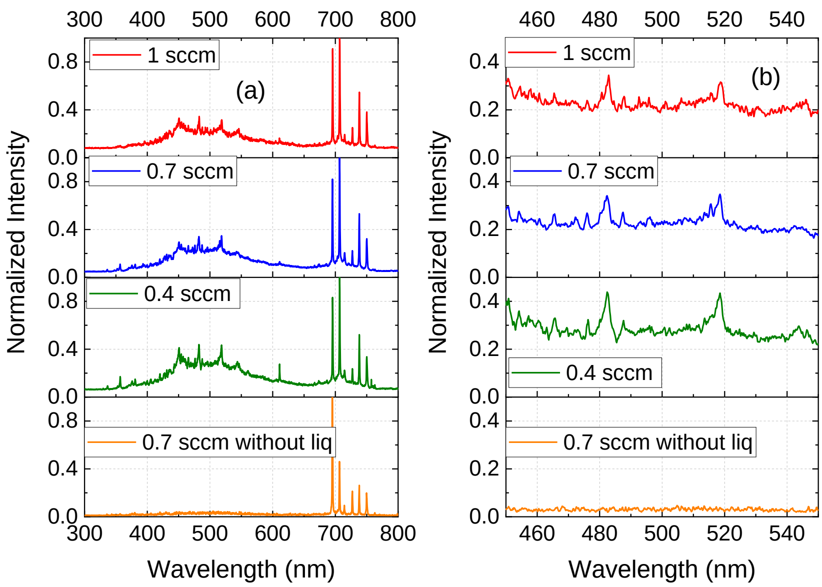

Figure 6 : (a) OES spectrum of a microfluidic plasma in pure Ar with liquid for various gas flow rate. The flow rate of liquid (Ethyl acetate) was kept 0.12 ml/min. The bottom panel is a pure Ar plasma. (b) OES spectrum for 450-550 nm

4 Conclusion

This study focuses on the microfluidic plasma using dielectric barrier discharge under an Ar gas and Ethyl acetate liquid. The effect of the applied voltage amplitude and waveform, gas flow rate was characterized. The chemical composition of the plasma in interaction with liquid confirm the creation of radical that can be used for molecules' functionalization.

References

[1] Brandenburg R 2017 Dielectric barrier discharges: progress on plasma sources and on the understanding of regimes and single filaments *Plasma Sources Sci. Technol.* **26** 053001

[2] Dupont V, Ognier S, Morand G, Ollivier C, Fensterbank L and Tatoulian M 2023 Direct Amination of Benzene with Ammonia by Flow Plasma Chemistry *Chemistry A European J* **29** e202301666

[3] Bruggeman P and Brandenburg R 2013 Atmospheric pressure discharge filaments and microplasmas: physics, chemistry and diagnostics *J. Phys. D: Appl. Phys.* **46** 464001

[4] Dilecce G, Martini L M, Ceppelli M, Scotoni M and Tosi P 2019 Progress on laser induced fluorescence in a collisional environment: the case of OH molecules in ns pulsed discharges *Plasma Sources Sci. Technol.* **28** 025012

[5] Junjuri R, Rashkovskiy S A and Gundawar M K 2019 Dependence of radiation decay constant of laser produced copper plasma on focal position *Physics of Plasmas* **26** 122107

[6] Lacroix D, Jeandel G and Boudot C 1997 Spectroscopic characterization of laser-induced plasma created during welding with a pulsed Nd:YAG laser *Journal of Applied Physics* **81** 6599–606