Interaction of Atmospheric Pressure Plasma Jets with Liquids

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In this work, the interaction of atmospheric pressure plasmas with liquids is investigated. On the example of hydrogen peroxide, generation and transport mechanisms are studied from the plasma to the gas- and liquid phase. Interaction with the ambient surroundings is investigated and effects of nitrogen and oxygen species on the plasma dynamics a well as on the reactive species generation in the liquid phase are discussed

Keywords: atmospheric pressure plasma jet, plasmas and liquids, reactive species, optical diagnostics

1 Introduction

Atmospheric pressure plasma jets have been in the focus of research for over a decade now due to exciting new research areas such as plasma medicine [1]. Here the equilibrium chemistry invoking highly reactive species at low gas temperature can be utilized for inactivation of bacteria [2] or the treatment of wounds [3]. These types of applications raise the hope in a new kind of technology in medical areas. For research in plasma medicine, in-vitro studies of biological systems in cell culture medium are key issue for an understanding of relevant processes [4]. Thus, a fundamental understanding of the interaction of plasma jets with liquids poses a vital pillar of this research area. The work describes interactions of tailored plasmas with liquids and follows the reaction pathway of the most relevant reactive components produced by atmospheric pressure plasma jets.

2 Experimental

Plasma jet

In this work, a kinpen atmospheric pressure plasma jet is investigated [5]. This plasma jet is typically operated in argon at a frequency around 1 MHz. It has been determined recently that this plasma jet emits even at 1 MHz plasma 'bullets' [6]. To the plasma jet's feed gas argon, a small molecular admixture of oxygen or nitrogen or water vapor is admixed. For a control of the surrounding atmosphere, a shielding gas device is constructed around the

jet. With this, a gas curtain can be established around the active effluent zone and the precursors for reactive components can be controlled.

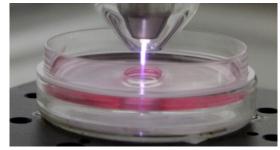


Fig.1: Argon plasma jet (kINPen) in contact with liquid (buffer solution)

Gas- and Liquid Phase Diagnostics

Fourier transform infrared (FTIR) absorption spectroscopy

As gas phase diagnostics, Fourier transform infrared (FTIR) absorption spectroscopy is performed. For this, the effluent of the plasma jet is guided into a mixing cell, from which the plasma generated reactive components are sampled into an about 30 m absorption length multi pass cell [7]. Here, the resulting gas mixture is analyzed at a pressure between 100 and 600 mbar. From a fit of Hitran Database data to the measured spectrum, the quantity and type of infrared active molecules in the multi pass cell can be derived.

Laser induced fluorescence spectroscopy

As a space resolved diagnostics, laser induced

fluorescence (LIF) spectroscopy is applied. For this, a Nd:YAG pumped dye laser is used to develop a laser sheath, which illuminates a thin plane within the plasma effluent. The resulting fluorescence radiation is imaged onto an intensified camera [8]. The LIF system is used on the one hand to detect flow profiles of the feed and curtain gas, as well as OH and NO in the effluent of the plasma jet.

Chemical Kinetics Modeling

An insight into the fundamental mechanisms of the long living reactive species, a simple chemical kinetic model is applied. It consists of the two fitting parameters, density of Argon Metastables and Argon Excimers and contains 21 species in 46 reactions.

Liquid Diagnostics

For liquid diagnostics, electron paramagnetic resonance spectroscopy was used to detect radical generation in liquids and colorimetric methods were applied for nitrite and nitrate measurements using the Griess assay. H₂O₂ measurements were performed by an Amplex red assay.

3 Results

Argon plasma jets at atmospheric pressure usually are filamented - despite the fact that they might appear homogeneous to the eve as homogeneous plasma plume. In the imaging work, present during excitation period reveals the streamer like structure of the plasma effluent. Several subsequent images reveal that the streamer path is changing with the flow field. Former measurements comparing these OH-planar laser induced images to fluorescence measurements show that the streamer path is coinciding with ambient impurities.

For the investigations regarding the long living gas phase species with FTIR spectroscopy and chemical kinetics modelling, the shielding gas was varied regarding the humidity and the oxygen to nitrogen ratio.

With this parameter range, a fit of the chemical kinetics to the molecular measurements could be achieved.

It can be observed that regarding the oxygen to nitrogen ratio, a maximum in the NO₂ production occurs for a gas composition closer to a nitrogen dominated regime.

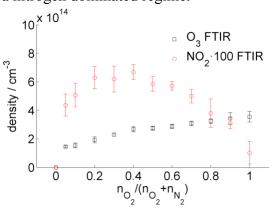


Fig.2: FTIR measurements of NO_2 and ozone as a function of gas curtain composition [7]

With this toolbox, several liquids were treated. The findings showed that the reactive species generation inn the gas phase could be reflected in the liquid phase.

For the generation of H_2O_2 , it could be shown that the net production rates of liquid and gas phase agree. Here it is shown that H_2O_2 is mostly generated in the gas phase and subsequently transported into the liquid phase. [9]

The bell shaped curve of the nitrogen to oxygen variation in the NO₂ response is also reflected in the liquid generation of nitrite and nitrate [7, 10]. This is also independent of the type of liquid treated. A slight shift of the maximum can be observed which could be attributed to different precursors and scavengers in the respective liquid systems.[11]

4 Conclusion

A study of the generation and interaction of plasma with ambient surroundings was presented and the resulting effect and generation pathways of reactive species were shown. Plasma reactive species composition can be tailored in the gas phase as well as in the liquid phase. Transport and generation mechanisms have to be studied in greater detail. For application, this approach can be used to study

and de-correlate the effect of respective reactive species groups.

Acknowledgements

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REFERENCES

- [1] von Woedtke T, Reuter S, Masur K, Weltmann K.D, Plasmas for medicine, Physics Reports, 530 (2013) 291-320.
- [2] Matthes R, Bender C, Schluter R, Koban I, Bussiahn R, Reuter S, Lademann J, Weltmann K.D, Kramer A, Antimicrobial efficacy of two surface barrier discharges with air plasma against in vitro biofilms, PloS one, 8 (2013) e70462. [3] Kramer A, Lademann J, Bender C, Sckell A, Hartmann B, Münch S, Hinz P, Ekkern-kamp A, Matthes R, Koban I, Partecke I, Heidecke C.D, Masur K, Reuter S, Weltmann K.D, Koch S, Assadian O., Suitability of tissue tolerable plasmas (TTP) for the management of chronic wounds, Clinical Plasma Medicine, 1 (2013) 11-18.
- [4] Reuter S, Tresp H, Wende K, Hammer M.U, Winter J,Masur K, Schmidt-Bleker A, Weltmann K.D, From RONS to ROS: Tailoring Plasma Jet Treatment of Skin Cells, Ieee T Plasma Sci, 40 (2012) 2986-2993. [5] Weltmann K.D, Kindel E, Brandenburg R, Meyer C, Bussiahn R, Wilke C, von Woedtke T, Atmospheric Pressure Plasma Jet for Medical Therapy: Plasma Parameters and Risk Estimation, Contrib Plasm Phys, 49 (2009) 631-640.

- [6] Reuter S, Winter J, Iseni S, Peters S, Schmidt-Bleker A, Dünnbier M, Schäfer J, Foest R, Weltmann K.D, Detection of ozone in a MHz argon plasma bullet jet, Plasma Sources Science and Technology, 21 (2012) 034015.
- [7] Schmidt-Bleker A, Winter J, Iseni S, Dünnbier M, Weltmann K.D, Reuter S, Reactive species output of a plasma jet with a shielding gas device-combination of FTIR absorption spectroscopy and gas phase modelling, J. Phys. D: Appl. Phys., 47 (2014) 145201.
- [8] Iseni S, Schmidt-Bleker A, Winter J, Weltmann K.D, Reuter S, Atmospheric pressure streamer follows the turbulent argon air boundary in a MHz argon plasma jet investigated by OH-tracer PLIF spectroscopy, Journal of Physics D: Applied Physics, 47 (2014) 152001.
- [9] Winter J, Tresp H, Hammer M.U, Iseni S, Kupsch S. Schmidt-Bleker A, Wende K, Dünnbier M, Masur K, Weltmann K.D, Reuter S, Tracking plasma generated H₂O₂ from gas into liquid phase and revealing its dominant impact on human skin cells, J. Phys. D: Appl. Phys., Accepted for publishing (2014).
- [10] Reuter S, Winter J, Schmidt-Bleker A, Tresp H, Hammer M.U, Weltmann K.D, Controlling the Ambient Air Affected Reactive Species Composition in the Effluent of an Argon Plasma Jet, IEEE T Plasma Sci, 40 (2012) 2788-2794. [11] Tresp H, Hammer M.U, Reuter S, Weltmann K.D, Effect of atmosphere shielded plasma jet on different biological relevant liquids, Plasma Medicine, accepted (2014).