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Habilitation Thesis

NON-EQUILIBRIUM PLASMAS AT ATMOSPHERIC PRESSURE. DIAGNOSIS AND APPLICATIONS

Summary

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Summary of Habilitation Thesis

The habilitation thesis „***Non-equilibrium Plasmas at Atmospheric Pressure. Diagnosis and Applications***” presents some of the most significant scientific results published after defending the doctoral thesis, with a focus on contributions to which I made the greatest input. Over the past 19 years, my studies have covered three main directions: (i) the diagnosis of non-equilibrium plasmas at atmospheric pressure, (ii) applications of atmospheric-pressure plasmas, and (iii) contributions to validating numerical simulations of atmospheric-pressure discharges. The scientific results included in this thesis were selected to reflect the most important personal scientific results and to give the thesis a cohesive structure.

The thesis is organized into three chapters. **Chapter I**, titled „***Investigation of the Operating Modes of DBD through Plasma Diagnosis***”, presents the experimental results related to the diagnosis of the dielectric barrier discharge (DBD) plasma, excited by pulsed voltage and produced in gas at atmospheric pressure, with the aim of identifying and investigating the discharge operating regimes. After a review of the current state of research in the field, this first chapter continues with the investigation of the glow regime of the pulsed DBD, focusing on the secondary discharge. While the primary discharge is directly powered by the external electric circuit and extinguishes due to the accumulation of electric charges on the dielectric barriers, the secondary discharge is driven by the energy stored in these memory charges and extinguishes once this energy is consumed. For these reasons, studying the conditions for secondary discharge formation is important both from the perspective of fundamental research — by contributing to the understanding of the pulsed DBD discharge mechanism — but also of applied research. The experimental results showed that the secondary discharge, like the primary discharge, exhibits all the characteristics of a pulsed glow discharge. Specifically, the presence of dielectric barriers with special properties (such as electret properties and a high secondary electron emission coefficient) leads to a more intense secondary discharge. Identifying the experimental conditions for achieving the most intense secondary discharge contributes to enhancing the efficiency of DBD discharge in applications, without additional electrical energy consumption.

Chapter I continues with the study of the pseudo-glow regime (also called multi-pulse or multi-glow) of the pulsed DBD, produced in helium at atmospheric pressure, followed by a subchapter dedicated to a systematic comparative study of the two operating regimes of DBD: (1) glow regime, obtained in a continuous gas flow (named Flowing Gas Atmosphere – FGA) and (2) pseudo-glow regime, obtained in a stationary gas (named Trapped Gas Atmosphere – TGA), with the aim of clarifying the mechanism of pulsed DBD discharge. Additionally, the importance of studying DBD in TGA mode is motivated by the specific potential applications of plasma sources generated in trapped gas at atmospheric pressure, such as the sterilization of wrapped medical instruments or the cold-plasma treatment of the packaged food.

The comparative study of the two modes of DBD discharge FGA and TGA was conducted through electrical characterization and spectral diagnosis of the discharge. From the complementary analysis of the discharge current waveforms and the spatiotemporal distribution of light radiation emitted by the plasma, the discharge regimes (glow and pseudo-glow) were experimentally identified. Also, the temporal evolution of excited species and the discharge current allowed for the investigation of elementary processes produced in the plasma volume. Then, the similarities between the effects produced by the flow rate and composition of the working gas on the discharge characteristics were analysed, and finally, the similarities between the two regimes were synthesized, proposing a mechanism to explain the discharge operation under these experimental conditions.

Special attention was paid to the elementary processes that take place in the plasma volume as a result of trapping working gas. Experimental results suggest that the Penning effect is one of the dominant processes by which N_2^+ and O are excited in the glow discharge (pulsed He–DBD produced in FGA mode), while in the pseudo-glow discharge (He–DBD in TGA mode and He+N_2–DBD in FGMA mode), electron impact excitation is dominant, because of the decrease in the density and lifetime of metastable atoms. Furthermore, the metastable lifetime reaches a critical value (∼3 µs) for which the discharge transits from the glow regime to the pseudo-glow regime, regardless of the variable parameter considered.

Chapter II, titled „***Contributions to the Applications of Atmospheric-Pressure Plasmas***”, presents three distinct applied research studies. The first subchapter is dedicated to ***the study of stable surface modification of polymers by cold atmospheric-pressure plasma***. On this topic, two representative studies are presented in the thesis. In the first study, the surface properties of natural cellulose-based polymers and a synthetic polymer (polysulfone), treated by atmospheric-pressure DBD plasma in He and Ar, were comparatively investigated. The experimental results indicate remarkably stable and efficient modifications in plasma-treated surfaces, such as wettability, adhesion, surface energy and polarity, level of oxidation, as well as surface morphology. Also, plasma provides significant oxygen uptake in cellulose-based materials that bear already prior to treatment a high amount of oxygen in their structure. The comparison between the properties of the non-permeable, homogeneous, smooth-surface synthetic polymer and those of the loosely packed, porous, heterogeneous cellulose-based polymers points to the different rates of plasma-induced modification, whereby a progressive alteration of cellulosic surface properties over much larger ranges of exposure durations is noted. Also, it was observed that this plasma treatment method reaches a limit of surface enhancement that is consistent across different polymer types.

Although plasmas generated in helium are very suitable for modifying the properties of polymer surfaces due to the high degree of crosslinking and functionalization induced on the surfaces without the physical degradation of the material, the high cost of helium and the large gas consumption caused by processing at atmospheric pressure in a continuous gas flow requires continuous optimization of both helium plasma sources and the polymer treatment method. Under these circumstances, a study was conducted to explore the possibility of overcoming the disadvantage of using an expensive continuous gas flow. The study consists of a comparative investigation of plasma-induced effects in different discharge modes—stationary gas (TGA mode) and continuous gas flow (FGA mode)—on the surface properties of four types of polymers with different structure, degree of oxidation, and functionality. The discharge characteristics, specific to each mode of operation, were analysed in correlation with the changes in the plasma treated surface characteristics. The results suggest that the hydrocarbon-type polymers treated in DBD plasma, in TGA mode, is more efficient due to improved surface functionalization (>15–40%) and more cost-effective due to considerable reduction in helium consumption.

The second applied research presented in this thesis refers to the ***biological applications of plasma for extending the shelf life of perishable foods***. This interdisciplinary study was conducted at *Risø National Laboratory for Sustainable Energy, Technical University of Denmark*, in collaboration with *Division of Industrial Food Research, National Food Institute* from Denmark. The inactivation of spoilage or pathogenic bacteria is essential for extending the shelf life of foods, and the demand for fresh and lightly preserved foods drives research into new inactivation methods, including gas discharges. Specifically, plasma treatment of perishable foods to extend their shelf life requires fulfilment of special conditions such as generating plasma in hermetically sealed containers filled with gas, like CO_2 mixed with Ar. For a systematic characterization of the plasma, a series of independent experiments were conducted to study: the effect of gas trapping on plasma parameters, the effect of molecular CO_2 gas on plasma parameters, the effect of biological samples on plasma, as well as the plasma-induced effect on fish samples inoculated with bacteria. The research concerns the effect of cold plasma on the inactivation of bacteria commonly found in fish products (*Photobacterium phosphoreum*, *Lactobacillus sakei*, and *Listeria monocytogenes*) and the optimization of plasma treatments inside a closed package to achieve a high efficiency of microorganism inactivation in fish products without negatively impacting their sensorial properties (texture, temperature, odour and colour)

Another interdisciplinary study presented in the thesis focuses on the ***plasma applications for the decomposition of gaseous pollutants*****.** This study was conducted at *Laboratoire de Physique des Gaz et des Plasmas* in collaboration with *Laboratoire de Chimie Physique, Université Paris-Sud Université Paris-Sud, France*. Compared to traditional thermal decomposition methods for gaseous pollutants, in non-equilibrium plasmas, pollutants are removed without heating the entire volume of the carrier gas. Due to this, non-thermal plasmas offer the advantage of minimal energy consumption required to remove pollutants from the ambient air. In this context, atmospheric-pressure non-equilibrium plasmas are being investigated as a feasible method for removing undesirable volatile organic compounds (VOCs) from ambient air. However, complete oxidation of pollutant molecules has not yet been fully achieved by this method. Specifically, in addition to CO_2, other by-products with lower molecular masses, which could themselves be pollutants, are also produced as a result of VOC decomposition in plasma. Since efficiency and selectivity are limited in plasma, hybrid air depollution methods, such as plasma combined with a catalyst, are necessary. Optimization of the plasma catalysis coupling can be improved if all byproducts coming from the discharge are known for each individual pollutant.

The aim of the air depollution study is to gain insight into the physico-chemical mechanism involved in the non-thermal plasma degradation process of a typical VOC, as 2-heptanone. Alongside the experimental investigation of the influence of various DBD parameters on the removal efficiency of 2-heptanone, the results lead to different decom-position mechanisms for 2-heptanone, depending on the composition of the discharge's working gas. In N_2–DBD plasma, C–C bond cleavage predominates due to interactions with electrons or excited nitrogen molecules, whereas in N_2+O_2–DBD plasma the by-products result from oxidation processes, following interactions with O and OH. Experimental results also showed that the decomposition efficiency of 2-heptanone can be increased by 30% by adjusting the proportion of O_2 in the predominantly N_2 gas mixture.

The issue of producing pollutant by-products (such as acetaldehyde or formaldehyde) during the plasma decomposition of 2-heptanone can be addressed either by using a higher specific energy or by adding suitable catalysts or additives. For this reason, the analysis was extended to the by-products, studying the decomposition of acetaldehyde in DBD plasma generated in both dry and humid air. The experimental results show that acetaldehyde oxidation in plasma depends both on the nature of the gas—where the presence of water vapor increases the proportion of OH radicals—and on the type of applied voltage, with the highest decomposition efficiency achieved in pulsed DBD.

Chapter III, titled „***Evolution and development plan of the scientific and professional career***", presents: ***university teaching activities***, specifying the subjects taught over the years, the teaching materials developed (author/co-author of 3 books of laboratory works), and students visiting in factory; ***scientific research activities***, resulting in 27 ISI articles (of which 18 as first author and 4 as corresponding author; 9 published in ISI journals from Q1 quartile, and 8 in Q2 quartile; over 530 citations; Hirsch index: 15); ***the ability to coordinate research teams*** (demonstrated by coordinating two research grants) and to explain and facilitate learning and research (demonstrated by supervising and completing 13 bachelor's theses and 5 master's theses in Plasma Physics, as well as 28 other master's theses in interdisciplinary fields, and by supervising of students who participatied in student conferences); ***international collaborations*** in teaching and scientific research. At the ond of this chapter, ***the development plan for the university teaching career and scientific research*** is presented with four research directions proposed.

The habilitation thesis contains also three appendices, which include the spectral transitions of representative excited species, reaction rates, excitation cross-sections for representative species, and a list of abbreviations used in this thesis. At the end, the bibliography is included.