Dynamics of reactive oxygen and nitrogen species in atmospheric-pressure and low-pressure plasmas

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Abstract: An atmospheric-pressure dielectric barrier discharge and a low-pressure double inductively coupled plasma are studied with respect to the absolute densities and chemical kinetics of reactive oxygen and nitrogen species. Absolute densities are acquired by various optical diagnostics. The results reveal a complex balance of the densities of the reactive species and are complemented by two dedicated global models of chemical reaction kinetics.

Keywords: dielectric barrier discharge, inductively coupled plasma, reactive oxygen and nitrogen species, absorption spectroscopy, chemical kinetics modelling

1. Introduction

The concentration of reactive oxygen and nitrogen species (RONS) in air and other mixtures of nitrogen and oxygen plays a significant role in the chemical interaction of such gas mixtures with treated media. Such treatments include environmental applications, such as purification of air and water by atmospheric pressure DBDs and jets, as well as biomedical applications, like treatment of wounds, cancers, or skin diseases, and technical applications, in the form of thin film deposition or plasma sterilization in lowpressure plasmas. [1]

While direct application in medicine typically requires the use of atmospheric pressure systems, there are a number of applications that can be carried out at either atmospheric pressure or low-pressure. Aside from practical differences in the implementation of the application, it is expected that the mechanisms of action of low-pressure and atmospheric pressure plasma sources will differ due to different densities and fluxes of reactive components in each case. In general, reactive oxygen and nitrogen species, such as ozone and nitrogen oxides, represent important active agents in many cases. The aim of this work is to compare and contrast the quantities of reactive oxygen species produced in plasma sources formed in nitrogen and oxygen mixtures at atmospheric and low pressure. For this purpose, a surface dielectric barrier discharge (SDBD) is used as a prototypical atmospheric pressure source, and a double inductively coupled plasma (DICP) as a prototypical low-pressure source. [2-6]

In order to achieve a broad characterization of different reactive oxygen and nitrogen species, a variety of different methods are used, which differ between the two sources. For the atmospheric pressure source, absolute ground state densities of selected reactive species are determined by optical absorption spectroscopy (OAS). For the lowpressure source, the measurement of NO by laser induced fluorescence spectroscopy (LIF) is planned. In addition, two zero-dimensional models, dedicated to the two types of discharges, are used to simulate absolute densities of the selected RONS, amongst other species. A semi-empirical atmospheric pressure model is used for the SDBD and complements the results acquired from OAS. The temporal resolution of these measurements, in combination with the model, enables the interpretation of different balances of reactive species, the corresponding dominant reaction pathways, and extension of the measured results towards species that can or have not be measured yet.

In the case of the DICP, a global model is used to simulate the electron and heavy particle kinetics of the discharge, which provides information on not just neutral reactive species densities, but also ionic species. This enables the determination of species densities that cannot be measured directly at a possibly greater accuracy than the semi-empirical model for the SDBD system. This model for the DICP system is planned to be validated by the densities of NO determined by LIF.

2. Experimental Setups

The atmospheric pressure twin SDBD setup consists of a thin aluminum oxide plate with two symmetrical metal grids screen-printed onto either side. When a sufficient difference in electric potential is applied to the two grids, a DBD ignites on the surface of the dielectric aluminum oxide plate and along the metallic grid lines. The electrode configuration is mounted in a stainless steel chamber, limiting the gas flow to the vicinity of the discharge and ensuring a defined gas mixture. For more detail on the experimental setup, see [3].

The low-pressure DICP source consists of a cylindrical stainless steel chamber with a flat lid and base made from quartz. Outside of the vacuum, directly above and below the lid and the base, two coplanar copper coils are placed, each driven by a 13.56 MHz power generator with a radio frequency (RF) matching system. A detailed outline of this setup is given in [5-6].

At low power coupling, the discharge ignites in the socalled E-mode and then, as the power coupled into the gas increases, crosses into the higher-density H-mode. The Hmode of the ICP discharge allows for higher densities of reactive species, with respect to comparable capacitively coupled discharges, while also allowing for biologically significant vacuum UV (VUV) radiation to reach any samples, which is not the case for the atmospheric pressure DBD.

3. Diagnostic Methods

Measurements at atmospheric and low pressure focus on two different techniques: optical absorption spectroscopy for the atmospheric pressure SDBD system, and laser induced fluorescence for the low-pressure DICP discharge. Those techniques have in common that they utilize the unique optical absorption bands of molecular species, albeit in different ways.

The OAS method used here is described in detail in [7]. Briefly, a broadband laser-driven light source (EQ-99X LDLS, Energetiq Technology Inc., United States) with plano-convex quartz collimating lenses (#48-274, Edmund Optics Ltd., United Kingdom) is used to generate a parallel beam of light, which is guided through the center of the chemically active region above the SDBD. A photodiode (APD440A2, Thorlabs Inc., United States) is used to detect the intensity of the light, which is transmitted through different band-pass filters (misc. interference filters, Edmund Optics Ltd., United Kingdom), in order to select a specific absorption region that corresponds to a certain reactive species. An absolute particle density n of the selected reactive species can be calculated by use of the Lambert-Beer law (see Eq. 1), where I_0 is the intensity of the light when the plasma is turned off, I_1 is the intensity with the plasma turned on, σ is the wavelength dependent absorption cross-section, and *l* is the absorption length.

$$n = -\frac{\ln\left(\frac{l_1}{l_0}\right)}{\sigma(\lambda) \cdot l} \tag{1}$$

While OAS directly utilizes the absorption of light at a certain wavelength LIF, on the other hand, makes use of the induced fluorescence of certain electronic levels within a molecule of interest. These measurements are currently being planned, following the scheme described in [8]. Briefly, these will utilise a nanosecond pulsed dye-laser (Narrowscan, RadiantDyes Laser GmbH, Germany) for the excitation of the NO ground state. The intensity of the fluorescence signal will then be correlated to a concentration of NO species, by calibration with respect to a known concentration. Overall, the major species considered in this work include O₃, NO, NO₂, NO₃, N₂O₄, and N₂O₅. [7]

4. Modelling

The results obtained with both experimental setups, respectively, will be compared to values obtained by two dedicated models of chemical kinetics. In the case of the SDBD, the discharge is not simulated itself, and instead an empirically determined constant density of atomic oxygen is used as the main input parameter of a semi-empirical chemical kinetics model written in Julia language. That model includes neutral nitrogen and oxygen species, as well as the nitrogen oxides. The calculated densities of the reactive species are given as functions of time from a few seconds, to several hours, and can be calculated in less than a second by use of the Julia specific Catalyst.jl library. This model is developed based on a scheme described by Park et al. in [9].

The low-pressure model used for the DICP discharge is a zero-dimensional model based on the particle balance equation and the electron energy balance equation in molecular gases, including neutral and ionized species, as well as wall-reactions (see details in [10-11]). The chemical kinetics ($N_2(v<7)$ and $O_2(v<7)$), where v is the vibrational level) used for DICP are adopted from those in [12]. In contrast to the atmospheric pressure model, the low-pressure model computes stationary results after a runtime on the timescale of minutes and is written in MathWorks MATLAB.

5. Results

The results of the atmospheric pressure SDBD case include temporally resolved measured and simulated densities of O₃, NO, NO₂, NO₃, N₂O₄, and N₂O₅ at different gas flow rates and flow speeds. The densities measured by optical absorption spectroscopy are used to benchmark and optimize the parameters of the semi-empirical model for the SDBD system. Furthermore, a transition in the reaction pathways for different flow speeds is demonstrated in the experiment and accurately depicted in the model, despite its simplicity. Such insights are beneficial for the targeted production of desired or undesired reactive species for different applications, such as air purification or biological decontamination.



Fig. 1. Exemplary time resolved absolute densities of selected RONS in the SDBD reactor as calculated by the semi-empirical atmospheric pressure model at a synthetic airflow rate of 10 standard litres per minute.

An exemplary graph of time resolved absolute number densities for selected RONS, determined by the semiempirical atmospheric pressure model, is given in Fig. 1.

In the case of the low-pressure DICP discharge, exemplary number densities simulated by the model for the DICP discharge in steady state are given in Fig. 2. The same species are shown as for the SDBD in Fig. 1. Comparing the two cases, it can be shown that the relative RONS composition of the two sources differs significantly. In the SDBD source, O_3 is present at the highest density, while N₂O is present at the highest density in the DICP. Further, the relative density of NO is much higher in the DICP compared to the SDBD source.





6. Conclusions

Various methods have been used to characterize the RONS chemistry in prototypical atmospheric and lowpressure plasma sources. It is found that the relative composition of RONS in each source differs significantly, which is likely to have implications for the mechanisms of action of these sources in applications such as plasmabased disinfection or sterilisation.

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