Development of a collisional-radiative model for microdischarges in gas bubbles

Andrew R. Gibson[1] , Florens Grimm[1], Vera Bracht[2] Jan-Luca Gembus[1] and Peter Awakowicz[2]

[1] *Research Group for Biomedical Plasma Technology, Ruhr University Bochum, Germany*
[2]*Chair of Applied Electrodynamics and Plasma Technology, Ruhr University Bochum, Bochum, Germany*

Abstract: Microdischarges taking place in bubbles within liquids are of interest for a range of applications. Optical emission-based diagnostics are one of the few methods available to quantify the properties of these discharges but are challenging to interpret due to the complex chemical and physical environment. This work will present the current state of development of a collisional radiative model for line emission of O atoms in these systems, with a view to improving the analysis of optical diagnostic measurements.

Keywords: collisional-radiative models, plasma-liquid interactions, plasma electrolytic oxidation, optical emission spectroscopy, global modelling.

1. Introduction

Microdischarges in bubbles within liquid environments can be formed in a variety of different ways and are present in a range of scenarios relevant to future plasma-liquid applications. Typical application areas include wastewater remediation, chemical processing, and material modification. While applications in these areas are promising, the knowledge of fundamental plasma properties in bubble-based microdischarges is still relatively limited compared to other plasma sources such as jets or dielectric barrier discharges. Key reasons for this include the dynamic environment in which the discharge forms, and the small sizes of the discharges themselves. Together, these features make experimental diagnostics of these systems highly challenging. Further, the complex multi-phase fluid dynamics are also difficult to simulate in a fully self consistently, limiting the insights that can be obtained from purely simulation-based approaches.

Of the methods available to study such systems experimentally, optical emission approaches are generally favoured as they are fully passive and any influence on the microdischarges can be avoided. Such methods can be used to measure electron densities and temperatures, for example [1]. Details on the temporal evolution of these microdischarges and associated gas bubbles can also be obtained by high-speed camera imaging [2,3]. Further, a combination of high speed detectors and optical filters can be used to determine temporally resolved emission of specific species [4]. In [4] it was shown that emission lines from different species vary both in magnitude and in their temporal dynamics. These complex dynamics are not easily explained without a detailed understanding of the pathways towards excited state formation in these systems.

In this contribution, the development of a collisional radiative model for atomic species emission in bubble-based microdischarges is presented. Here, the focus is on microdischarge conditions of relevance to plasma-electrolytic oxidation (PEO) processes.

2. Simulation methods

Simulations are carried out using the 0-D plasma chemical kinetics model GlobalKin [5]. The size, and power deposition of microdischarges as a function of time throughout a typical microdischarge event are informed by experimental measurements. These measurements are carried out in a specialised single microdischarge setup, utilising a high-speed camera synchronised to current-voltage measurements [6]. This system is described in detail in the contribution of J.-L. Gembus *et al*. For the lifetime of a microdischarge ordinary differential equations are solved for the densities of charged and neutral species as a function of time. The electron energy equation is also solved to yield the mean electron energy in the microdischarge. The electron energy distribution function and rate constants for electron-driven processes are derived from the solution of the two-term approximation of the Boltzmann equation. The gas temperature is assumed constant at 2000 K, and the pressure is assumed constant at 1 atm. These values are also informed by experimental measurements. However, the assumption of constant gas temperature and pressure is unlikely to be fulfilled in the experimental setup. The incorporation of the temporal variation of these quantities into the simulations is planned in future work. Microdischarges are assumed to form in a pure water-vapour environment. The plasma-chemical reaction scheme used is based on the water vapour scheme published in [7,8] for atmospheric pressure plasma jet sources. Here, this scheme is adapted for the different conditions expected in the bubble-based discharges. The overall modelling approach will be discussed in more detail in the contribution of F. Grimm *et al*. In this work, the basic scheme is extended to incorporate a simple collisional radiative model for O atom emission. Specifically, the densities of the $O(3p^5P)$ state, which emits at 777.4 nm, and the $O(3p^3P)$, which emits at 844.6 nm, are considered simulated. Both emission lines are typically observed in the corresponding experimental measurements.

3. Results

Figure 1 shows the temporal variation of the simulated densities of the $O(3p^3P)$ and $O(3p^5P)$ states. The large peak in both states at around 25 µs is a result of the maximum in power deposition per unit volume around this point in time. The definition and calculation of the power per unit volume is discussed further in the contribution of F. Grimm *et al*. Around this time point, the electron density and atomic oxygen density peak, leading to a maximum population rate of each excited state via direct electron impact

excitation of the atomic oxygen ground state. At later times, the power deposition and electron density decrease, leading to a strong decrease in the excited state densities, which are depopulated by collisional quenching and spontaneous emission. The strong variation of the excited state densities as a function of time has implications for spectroscopic diagnostics. In particular, when time-integrated spectroscopic measurements are performed on such systems, the signal will correspond to the total emission integrated over the microdischarge lifetime. In cases such as that simulated here, where excited state densities have a significant variation as a function of time, the information derived from time-integrated spectra will be weighted towards time periods of high state densities and emission i.e., in these cases early stages of the microdischarge formation. It should also be kept in mind, as demonstrated in [4], that the temporal variation in densities may differ between different lines and species, meaning that diagnostics performed on different species will probe different temporal regions of the discharge. This offers both opportunities, when these temporal dynamics are known, and limitations when they are not known.

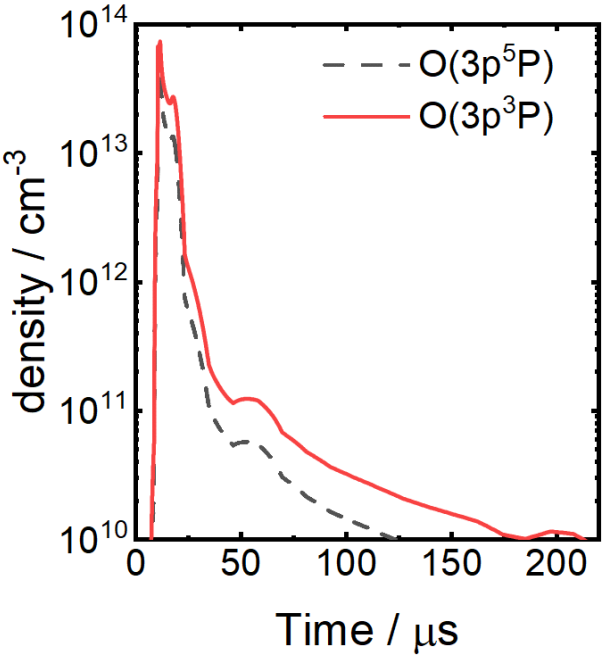

Figure 1: Temporal variation of the excited oxygen atom densities during the microdischarge lifetime. Simulations correspond to a power deposition profile taken from the single microdischarge setup operated with an Al anode, a voltage of ≈ 540 V, an electrolyte consisting of 1 g/l KOH and 10 minutes of coating time.

4. Conclusions

In this work, a simple collisional radiative model for O atom emission has been implemented into a 0-D plasma-chemical kinetics simulation of a microdischarge embedded inside a gas bubble. Simulation input parameters are informed by experimental measurements in a single microdischarge setup. The densities of excited oxygen atoms are found to exhibit complex temporal dynamics, which has implications for how spectroscopic measurements focused on these emission lines are interpreted. Future work in this area will include the extension of the collisional radiative model through the inclusion of more processes, as well as excited states of other species such as hydrogen atoms. Time-resolved, wavelength-selective diagnostic measurements are also planned to compare with simulated emission intensity profiles. Limitations and data needs for the further development of such collisional radiative models will also be discussed.

5. Acknowledgements

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