Production of O and H radicals in an atmospheric-pressure nanosecond pulsed discharge in helium with water vapour admixtures

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Abstract: Densities of O and H radicals were studied in a pin-to-pin discharge in He with admixtures of water vapour by experiment (TALIF) and modelling (1D fluid). O and H densities peak only about 1 µs after the end of the current pulse, even though the HV pulse is only 90 ns long. They remain nearly constant over 10 µs before decaying. Modelling explains the reaction pathways that lead to this behaviour: the built up of O and H densities continues after electron-impact dissociation processes with significant additional afterglow processes.

Keywords: Atmospheric-pressure, pulsed discharge, radicals, TALIF, 1D fluid model.

1. Introduction

Plasma-produced O-, H- and N-species that have a high oxidative power and play major roles in biological functions are extensively studied for applications. In particular, plasmas containing water vapour are studied for the production of reactive species such as OH, H₂O₂, HO₂ [1]. Even though the plasma chemistry is complex and not fully understood, it is clear that atomic oxygen and hydrogen radicals play a crucial role in these plasmas.

The aim of this work was to investigate the kinetics of reactive O and H radicals in a fast pulsed discharge (rise rate \sim 80 V/ns) generated at atmospheric pressure in humid Helium (up to 0.25% H₂O). O and H densities are obtained experimentally by ps-TALIF (Two-Photon Absorption Laser Induced Fluorescence) and are combined with 1D fluid modelling to investigate the reaction mechanisms for O and H production.

2. Methodology

Plasma discharge

The discharge setup is schematically shown in figure 1.



Fig. 1. Schematic of the discharge setup consisting of 2 conical stainless-steel electrodes, connected to a high-voltage pulse power supply. The chamber is filled with Helium gas with H₂O admixtures. Adapted from [2]

A pin-to-pin electrode geometry with a gap of 2.2 mm is positioned in a 0.3 litre vessel. Both electrodes are made of stainless steel. They have a conical shape with a tip of radius of curvature of around 500 μ m. Helium (99.996% purity) is injected in the vessel sideways to the axis of the electrodes (about 3 cm from the discharge axis) at a flow of 1 l/min. Water vapour is admixed to the gas flow by guiding a fraction of the total helium flow through a glass bubbler filled with distilled water as in [3]. The amount of water vapour is calculated using the vapour pressure at room temperature and the flow rate through the bubbler.

A positive high-voltage nanosecond pulse is applied to one of the pins. The pulse has a voltage of about 2 kV, 35 ns rise time (10-90%) and 90 ns duration FWHM at 0.1%H2O (80 ns at 0.25% H₂O) The energy dissipated in the discharge is kept constant at 90 μ J by adjusting the voltage amplitude. The discharge is run at 5 kHz.

TALIF diagnostic

Two-photon Absorption Laser Induced Fluorescence (TALIF) is used to measure the densities of O and H radicals. Details of this method can be found in [4,5]. A schematic of the experimental arrangement is shown in figure 2.



Fig. 2. Experimental arrangement for the TALIF diagnostic. Adapted from [4].

A laser system generates 30 ps-laser pulses of up to a few hundreds of μ J that can be tuned in the range 193 to 2300 nm with a spectral bandwidth of about 4 cm⁻¹, at 10 Hz. The laser pulse energy is controlled over time with a pair of rotating attenuators coupled to an energy meter.

The laser beam is focused using 30 cm focal length lens into the discharge gap. The fluorescence emission is collected at 90° by a doublet of achromatic lenses and imaged onto an ICCD camera (Stanford Computer Optics, 780×580 array, 8.3 µm2 pixels, S25IR photocathode). An interference filter is placed in front of the camera to eliminate stray light and fluorescence at other wavelengths. To increase the signal to noise ratio, the fluorescence signal of 30 to 300 shots has been accumulated on the ICCD. To be able to derive absolute densities of O and H, the measurements are performed in the non-saturated regime using the noble-gas calibration technique [6].

1D fluid model

The one-dimensional plasma fluid model that was used in this work follows a common approach, similar to e.g. [7]. Full details can be found in [5]. In short, the model is based on a system of differential equations. These are the equations of continuity of the flux density of electrons, electron energy, ions, and neutral species, and Poisson's equation.

The model uses the local mean energy approximation, which states that the macroscopic electron swarm characteristics vary only with the local average electron energy. Solution of the local steady state two-term Boltzmann equation gives electron transport and reaction coefficients [8].

The reaction kinetic scheme is based on [9] with reactions involving nitrogen removed and reactions involving H2 and H included from [10]. Transport coefficients for ions and electrically neutral heavy species were taken from [11,12]. Electron collision cross sections were used to determine the transport and reaction coefficients for the electrons.

The model is solved on a computation domain that corresponds to the 2.2 mm interelectrode dimension. Boundary conditions at the anode describe the absorption of a thermal flux of plasma species and the electron energy density, and a condition describing applied voltage pulses. The boundary conditions used for the plasma species were derived in reference [13]. The boundary conditions at the grounded electrode describes the absorption of a thermal flux of plasma species and electron energy density, secondary electron emission, and zero electrostatic potential.

Initial modelling revealed the build-up of O_2 and H_2 over successive pulses until a quasi-steady state was reached. Initial conditions of 170 ppm of O_2 , and 70 ppm of H_2 , for 0.1% H₂O, and 190 ppm of O_2 , and 75 ppm of H₂ for 0.25%H₂O were used to account for this build-up and represent a situation in steady state. The model was run for 10 pulses, with the results of the final pulse presented.

The plasma model was implemented using the commercial finite element analysis software COMSOL Multiphysics.

3. Results

The results of the TALIF experiments and the 1D fluid modelling are presented in figures 3 and 4. Figure 3 shows the temporal evolution of the O density from both the

experiment and the model for H_2O admixtures of 0.1% and 0.25%. Figure 4 shows the equivalent H densities.



Fig. 3. Temporal evolution of O density for 0.1% and 0.25% water admixture. Both modelling and experimental results are presented.



Fig. 4. Temporal evolution of H density for 0.1% and 0.25% water admixture. Both modelling and experimental results are presented.

The model and experiment have a reasonable agreement, within a factor of 2 for both densities. From both figures it is clear that the main production of O and H occurs after the voltage pulse has finished. For 0.1% water, the O density builds up over \sim 1-2 µs to a value of approximately 2x10¹⁶ cm⁻³. From 10-100 µs, the O density decays again. For 0.25% water content the O density is enhanced by roughly 40%. In the experiments, the peak in O density occurs earlier, at about 0.3 µs. This is not reproduced in the modelling.

The situation for H is similar, for both water admixtures there is a rapid increase in H density in the early pulse afterglow (<1 μ s). Densities of the order of 0.2–1.0x10¹⁶ cm⁻³ are observed, with the densities for 0.25% water being 50-100% higher than 0.1% water.

3. Discussion and conclusion

The delay of the production of O and H relative to the voltage pulse is surprising since it is often assumed that the dominant production mechanism is direct electron-impact dissociation. Analysis of the reaction pathways from the modelling show that there is a distinct change in reaction mechanisms during the discharge cycle. During the voltage pulse O is predominantly produced through electron-impact dissociation of O₂. For H, the dominant mechanism is electron-impact dissociation of H₂O. However, most of the O and H radicals are produced in the early afterglow (up to 1 μ s) through recombination processes of O₂⁺ and H₂⁺. It can therefore be concluded that not only the discharge itself, but also the (early) afterglow of pulsed discharges need to be considered when studying O and H-based plasma chemistries.

Acknowledgments

The authors acknowledge the support of the Engineering and Physical Science Research Council (Project No EP/S026584/1 and EP/S025790/1).

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