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Radio frequency (rf) plasmas operated at atmospheric pressure have received great attention in recent years for their potential use in many scientific and industrial applications. The optical emission profile of these atmospheric pressure rf discharges typically presents two bright layers, one above each of the electrodes. Although in the low-pressure regime bright layers near the electrodes are typically associated with the so-called gamma mode, these layers are observed in the alpha mode at atmospheric pressure and only after a significant increase in current, the transition into the gamma mode takes place. In the gamma mode, the bright layers are found to light up in an alternating fashion, corresponding to the excitation of radiative states by avalanches across the sheaths. On the other hand, in the alpha mode, the bright layers light up simultaneously mostly as a result of the acceleration of bulk electrons in the expanding and retreating sheath-bulk boundaries.

Interestingly, as the rf frequency increases, more power can be delivered into the discharges without transitioning into the gamma mode. This allows for more intense plasmas that have narrower and brighter emission layers. For a given constant power, however, increasing the rf frequency results in lower plasma density despite more power being coupled to the electrons and the increasing mean electron energy. This apparent paradox can be explained by the non-uniformity of the electron temperature in these atmospheric-pressure discharges.

As the discharge gap decreases, the two bright layers described earlier come closer to each other and eventually overlap and experimental results

seem to corroborate earlier simulation predictions that highlighted the presence of a large number of energetic electrons in rf microdischarges.

Despite their interesting dynamics, discharges operating in pure helium have limited application because without other gas additives the reactivity of the plasma is low. Therefore, small admixtures of O_2 and/or H_2O are typically incorporated in the discharge because these are good precursors of reactive oxygen species (ROS) and the two can be combined to create cocktails of ROS (O, OH, O_3, $^1O_2$, OOH and H_2O_2) of different compositions of interest in biomedical applications, air treatment and chemical synthesis. These plasmas tend to be electronegative and display interesting dynamics, particularly when created in small gaps.

From a practical point of view it is important to understand the chemical pathways leading to the production of the relevant ROS, as this will provide guidelines for the optimization of the plasma sources for a particular application. We have analyzed by means of 1-dimensional fluid simulations (60+ species, 850+ reactions), the key ROS and their generation and loss mechanisms in low-temperature water-containing atmospheric-pressure plasmas. Where possible, simulation results have been compared with experimental data (e.g. spectroscopy and mass spectrometry) and models with revised reaction rates and incorporation of rotational and vibrational excitation of water molecules have resulted in improved agreement with experimental observations.

The high reactivity of most of the ROS, however, limits their penetration into a treated sample and therefore encapsulation of the ROS and/or triggering of a secondary chemistry is required for the plasma treatment to reach beyond the first layers of (bio)molecules. Experimental and computational results suggest that production of ROS can be enhanced by the presence of water droplets, and combination of low-temperature plasmas with high speed droplets provide an interesting opportunity for the delivery of ROS beyond the surface of a treated sample.

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