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Generation and loss of reactive oxygen species in low-temperature atmospheric-pressure RF He + O₂ + H₂O plasmas

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Online at stacks.iop.org/JPhysD/45/172001**Abstract**

This study focuses on the generation and loss of reactive oxygen species (ROS) in low-temperature atmospheric-pressure RF (13.56 MHz) He + O₂ + H₂O plasmas, which are of interest for many biomedical applications. These plasmas create cocktails of ROS containing ozone, singlet oxygen, atomic oxygen, hydroxyl radicals, hydrogen peroxide and hydroperoxyl radicals, i.e. ROS of great significance as recognized by the free-radical biology community. By means of one-dimensional fluid simulations (61 species, 878 reactions), the key ROS and their generation and loss mechanisms are identified as a function of the oxygen and water content in the feed gas. Identification of the main chemical pathways can guide the optimization of He + O₂ + H₂O plasmas for the production of particular ROS. It is found that for a given oxygen concentration, the presence of water in the feed gas decreases the net production of oxygen-derived ROS, while for a given water concentration, the presence of oxygen enhances the net production of water-derived ROS. Although most ROS can be generated in a wide range of oxygen and water admixtures, the chemical pathways leading to their generation change significantly as a function of the feed gas composition. Therefore, care must be taken when selecting reduced chemical sets to study these plasmas.

(Some figures may appear in colour only in the online journal)

1. Introduction

One of the fastest growing fields in low-temperature plasmas is 'plasma medicine', an emerging scientific discipline that exploits the interaction of gas plasma with biological targets for therapeutical purposes. The number of potential applications in this field has risen in recent years, and expands from sterilization of abiotic and biotic surfaces for health care and food processing industries to alternative approaches to wound healing, dentistry and cancer therapy [1, 2].

In the context of plasma medicine, plasmas are required to operate at atmospheric pressure and remain at low-temperature so that human tissue can be treated without inducing thermal damage. These requirements are typically achieved using noble gases as a background carrier, adjusting the input power and changing the distance between the treated target and the plasma source. In this study He is considered as a carrier gas due to its excellent thermal conductivity.

Although the potential of plasma medicine has already been demonstrated by a growing number of research groups,

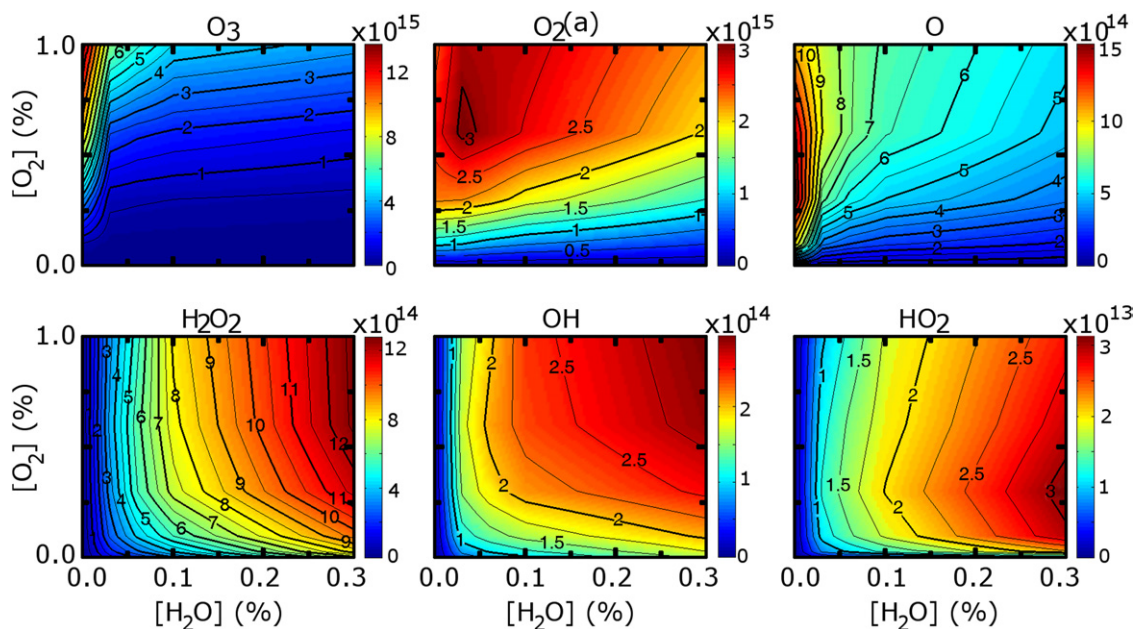


Figure 1. Density (cm^{-3}) of key ROS in atmospheric-pressure RF (13.56 MHz) He + O₂ + H₂O discharges as a function of the O₂ and H₂O concentration in the feed gas.

the underlying mechanisms leading to the observed biological responses remain largely unknown. A large number of plasma sources and biological targets have been investigated to date and there is a growing amount of literature that suggests that for low-temperature atmospheric-pressure plasmas the interaction with biological targets is mainly chemistry driven [3–5]. UV radiation and physical etching observed in low-pressure plasma treatments [6, 7] do not seem to play a dominant role at atmospheric pressure. Indeed the flux of neutral ROS to the target is orders of magnitude larger than that of ions and at atmospheric pressure the ion energy is generally small due to the large collisionality of the sheaths [8]. Nonetheless, charge accumulation on the treated surfaces may create electric fields that could lead to important biological responses such as electroporation [9], and these could interplay synergistically with the ROS chemistry.

Atmospheric-pressure plasmas can be engineered to produce reactive oxygen species (ROS) and reactive nitrogen species (RNS), which are known to play important roles in biology [10]. Here we concentrate on the generation of ROS. Oxygen is often used as a precursor of ROS in plasmas although water is also present due to ambient humidity and the moist nature of biological targets. Therefore, He + O₂ + H₂O discharges are considered in this study. It is known that both O₂ and H₂O are good sources of ROS [11, 12] and that they can be combined to create cocktails of ROS with different compositions [13]. Due to the presence of O₂ and H₂O, these plasmas tend to be electronegative and display intricate dynamics, particularly when created in small gaps [14].

In this paper the key generation and loss mechanisms of the six main ROS created in He + O₂ + H₂O plasmas are identified by means of computational simulations for a wide range of oxygen and water admixtures.

2. Computational model

The plasma source considered in this study is similar to the ones used in a number of recent experimental studies of low-temperature atmospheric-pressure RF discharges [15, 16]. It consists of two stainless steel electrodes, each being at least 2 cm in diameter and a discharge gap between the two electrodes of 1 mm. Since the electrodes are much larger ($> \times 10$) than the gap between them, glow-like discharges created in this device are amenable to one-dimensional computational studies.

The computational model used here is a conventional one-dimensional fluid model which solves the continuity equation (drift-diffusion approximation) for each species, the electron energy equation, and Poisson's equation [14]. The model incorporates 61 species and 878 reactions, which encompasses all those identified in our previous studies of He + O₂ [11], He + H₂O [12] and He + O₂ + H₂O [13] plasmas.

To determine the influence of the feed gas composition on the ROS concentration and the main chemical pathways at play, the oxygen content in the feed gas is varied from 0% to 1% and the water content from 0% to 0.3%, i.e. from dry conditions to $\sim 40\%$ relative humidity at room temperature. In all cases, the discharge is sustained at 13.56 MHz at a constant input power of 1 W cm^{-2} . This is consistent with typical experimental conditions.

3. Results and discussion

3.1. Key reactive oxygen species

Figure 1 shows the space-time averaged densities of the most abundant ROS created in He + O₂ + H₂O plasmas as a function of oxygen and water concentration in the feed gas. These ROS

are ozone (O_3), singlet oxygen ($O_2(a^1\Delta_g)$), atomic oxygen (O), hydroxyl radicals (OH), hydrogen peroxide (H_2O_2) and hydroperoxyl radicals (HO_2). For convenience, we will use the term O-ROS to refer to oxygen-derived ROS, i.e. O_3 , $O_2(a^1\Delta_g)$ and O, and H-ROS to refer to hydrogen containing ROS, i.e. OH, H_2O_2 and HO_2 . Not surprisingly, H-ROS require the presence of water as no hydrogen is present in pure He + O_2 discharges. On the other hand, O-ROS can be generated, at least to some extent, even in the absence of O_2 by decomposition of H_2O .

The density of H-ROS increases with water content in the feed gas and that of O-ROS with oxygen content (except for O at high oxygen concentrations in pure He + O_2 discharges, as has been observed in previous studies of He + O_2 plasmas [11]). Interestingly, for a given water concentration, the presence of oxygen also favours the production of the main H-ROS (OH and H_2O_2). On the other hand, for a given oxygen concentration, the presence of water decreases the net production of O-ROS (except for $O_2(a^1\Delta_g)$ at low water concentrations around 0.03%).

Figure 1 shows these trends and provides useful maps to determine which feed gas composition should be used for the maximum generation of a particular ROS. In general, O-ROS can be generated in larger quantities than H-ROS, although cocktails rich in H-ROS have a larger oxidation potential (E^0) due to the presence of OH ($E_{OH}^0 = 2.8 \text{ V} > E_{O_3}^0 = 2.1 \text{ V}$).

3.2. Generation and loss mechanisms of the key ROS

Unravelling the chemical pathways that lead to the generation and loss of each ROS would provide valuable information for future optimization of He + O_2 + H_2O plasmas. This is very difficult to determine experimentally but computationally it is possible to quantify the contribution of each reaction to the balance of a particular species. Here, we have selected the main reactions that contribute to the generation and loss of each of the ROS shown in figure 1, so that collectively all these reactions account for at least 90% of the generation and loss of each ROS. The relative contribution of each reaction to the generation or loss of each ROS is shown in figure 2.

In general, the chemical pathways that lead to the creation and destruction of ROS change as a function of the oxygen and water concentration in the plasma.

3.2.1. Ozone. Regardless of the water content in the feed gas, the generation of O_3 is mainly due to the combination of atomic and molecular oxygen. In He + O_2 discharges, O_3 is long lived and it is mainly lost by diffusion outside the discharge region. The presence of water, however, introduces an additional loss mechanism: reduction of O_3 by H atoms. As a result the net O_3 production rapidly decreases as the water content in the discharge increases (see figure 1).

3.2.2. Singlet oxygen. Electron-impact excitation of oxygen molecules is the main generation mechanism of $O_2(a^1\Delta_g)$ for all gas mixtures. In He + O_2 discharges $O_2(a^1\Delta_g)$ is lost mainly by diffusion outside the plasma. The incorporation of some water in the discharge results in efficient quenching

of $O_2(b^1\Sigma_g^+)$ by water molecules and that enhances the production of $O_2(a^1\Delta_g)$. This results in an initial increase in the net production of singlet oxygen when water is introduced in the discharge (figure 1). However, as water continues to increase, quenching of $O_2(a^1\Delta_g)$ by hydroperoxyl radicals (HO_2) quickly becomes the main loss mechanism and the net production of singlet oxygen decreases as water concentration increases above 0.03% (figure 1).

3.2.3. Atomic oxygen. The generation of O remains mostly unchanged when water is introduced into the discharge and it is dominated by electron-impact dissociation of molecular oxygen. Water, however, leads to the formation H-ROS, which readily react with O. As a result, the net production of O rapidly decreases with increasing content of water in the feed gas (figure 1).

3.2.4. Hydrogen peroxide. The main mechanism leading to the formation of hydrogen peroxide is the combination of two OH radicals. H_2O_2 is fairly stable and diffusion out of the active plasma region is a significant loss mechanism. At high water concentrations volume decomposition by OH radicals becomes important and the presence of oxygen in the feed gas also leads to the decomposition by atomic O. The enhanced production of OH when O_2 is present, however, compensates for these additional loss mechanisms and the net H_2O_2 production increases with oxygen content.

3.2.5. Hydroxyl radical. OH is not generated in pure He + O_2 discharges since it contains hydrogen, and in pure He + H_2O discharges it is formed primarily by electron-impact dissociation of H_2O and H_2O_2 . In the presence of O_2 , however, an additional generation mechanism is introduced and the main chemical pathway for the generation of OH shifts to water dissociation by excited atomic oxygen ($O(^1D)$). The presence of O_2 also affects the loss mechanisms. While in pure He + H_2O plasmas the main loss of OH is a combination to produce hydrogen peroxide (H_2O_2), the presence of oxygen in the feed gas introduces an additional loss mechanism since OH reacts readily with atomic O to form hydroperoxyl radicals HO_2 . Nonetheless, the contribution of the additional generation mechanism dominates and the net production of OH increases with oxygen content in the discharge.

3.2.6. Hydroperoxyl radical. HO_2 is less abundant than the other ROS considered above. It requires water for its formation and the addition of O_2 in the feed gas affects its generation and loss mechanisms. In He + H_2O plasma hydroperoxyl radicals form primarily as a result of the decomposition of H_2O_2 by OH radicals but with oxygen in the feed gas, the generation shifts towards reduction of O_2 by hydrogen atoms. This additional generation mechanism introduced by the presence of O_2 initially enhances the net production of HO_2 . In He + H_2O plasmas, HO_2 is quenched by H and OH whereas when oxygen is introduced in the feed gas, O and $O_2(a^1\Delta_g)$ become more significant quenchers.

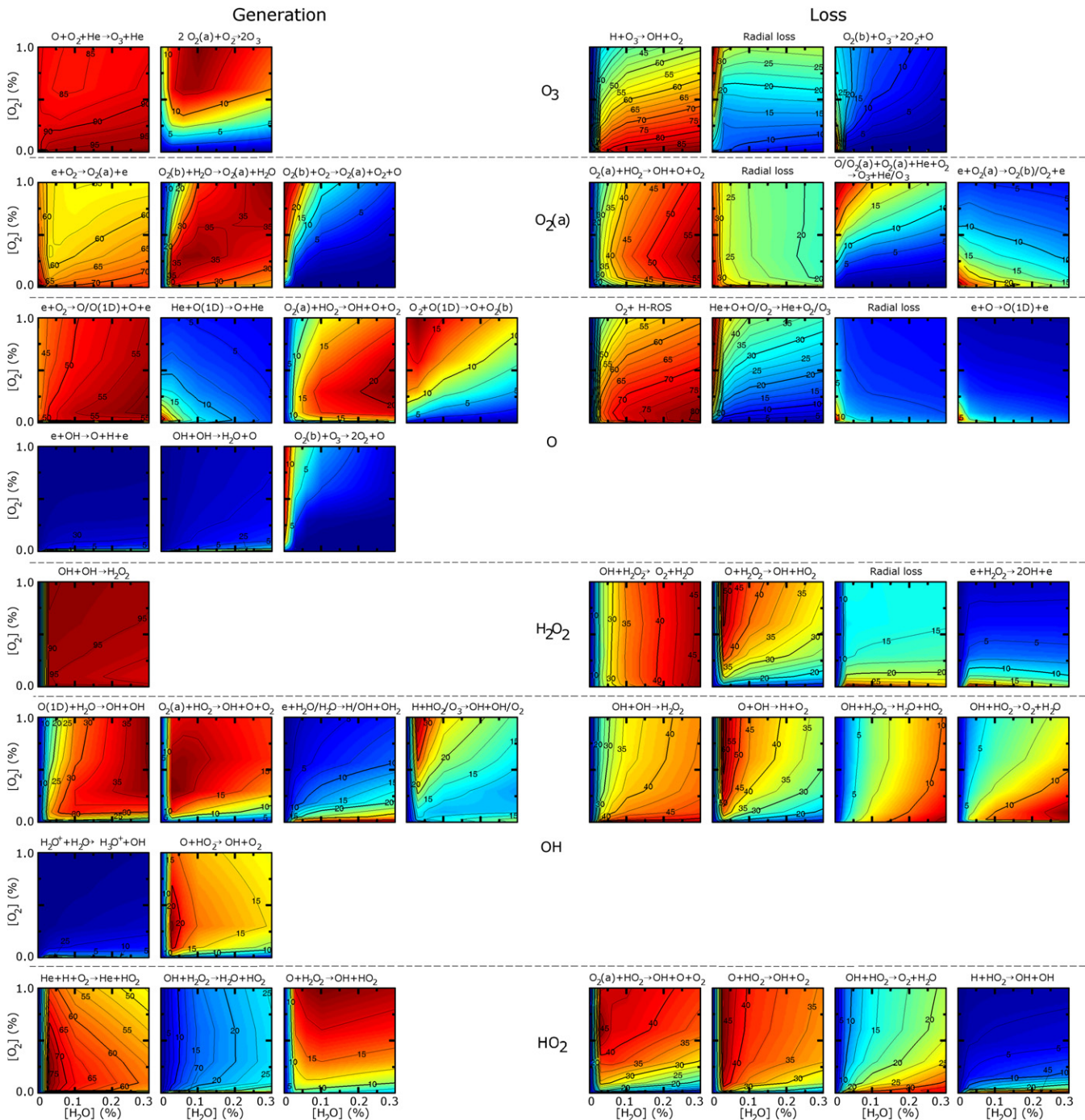


Figure 2. Main generation and loss mechanisms for the six most abundant ROS in a He + O₂ + H₂O plasma. Each plot represents the relative (percentage) contribution to the generation (or loss) of a particular ROS. For example, the first graph describes the contribution of O + O₂ + He to the generation of ozone and it shows that for all the O₂ and H₂O admixtures considered here this reaction contributed to at least 85% of the ozone production. For brevity, O₂(a) is used to denote singlet oxygen O₂(a ¹Δ_g) and O₂(b) is used to denote O₂(b ¹Σ_g⁺).

4. Conclusions

Pure He + O₂ plasmas are a good source of ozone, singlet oxygen and atomic oxygen, with densities of these species increasing as oxygen content increases. He + H₂O plasmas offer an interesting alternative to He + O₂ plasmas as a source of reactive oxygen species (ROS), and they produce significant amounts of hydrogen peroxide, hydroxyl radicals and hydroperoxyl radicals, which increase with increasing

water content. Admixtures of O₂ and H₂O lead to richer cocktails of ROS that combine all these species.

The addition of oxygen into a He + H₂O plasma generally leads to new pathways for generation and loss of OH, H₂O₂ and HO₂ but results in higher density of hydrogen containing ROS. On the other hand, addition of water to a He + O₂ discharge mainly introduces new quenching reactions for O₃, O₂(a ¹Δ_g) and O, and therefore the density of these ROS decreases with water content. The optimum discharge conditions would

depend on the actual application but the general trend is that a higher density of ROS is obtained at low water concentration and cocktails with higher oxidation potential at high water concentrations. The chemical pathways that lead to the generation and loss of these ROS have been identified out of a comprehensive list of 878 reactions and it has been shown that these change depending on the feed gas composition. This information is expected to be valuable in the optimization of He + O₂ + H₂O plasma sources for particular applications.

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