Kinetics Mechanisms of High Electron Density Argon-Water Plasma Discharges

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The plasma kinetics in He-H\(_2\)-O mixtures in diffuse atmospheric pressure glow discharges have been developed and partially validated [1]. However, the plasma kinetics in filamentary water-containing discharges, although ubiquitous for many applications, have not been studied in detail. A major difference between diffuse and filamentary plasmas is that the higher electron and ion density results in ionic recombination processes to play an important role in the radical production compared to the dominance of electron dissociation of water in diffuse plasmas. Unfortunately the branching ratios of electron-ion recombination reactions are not as accurately known as electron-induced processes.

In this work, we measured the absolute densities of OH and H in a nanosecond pulsed Ar-H\(_2\)-O plasma by laser induced fluorescence (LIF) and two-photon absorption LIF respectively [2]. We also implemented a 0-D kinetics reaction set in Global_Kin [3]. The simulated and experimentally measured H and OH densities as a function of time are compared in Fig. 1. The 0-D model predicts the absolute values of the H and OH densities accurately. Remaining discrepancies during the discharge pulse can be explained by uncertainties in the power density input waveform. Discrepancies in OH densities in the far afterglow are due to not considering transport. The results show that the reaction set is capable of predicting the general trends in reactive species.

The remarkable 2 orders of magnitude lower OH than H density is due to electron-induced dissociation of OH during the discharge pulse and enhanced recombination of OH due to the large H and O densities. This result seems to contradict the common assumption that OH is the dominant non-selective reactive species in water containing plasmas. The outcome of this study suggests that the importance of atomic species such as H and O in water containing plasma is generally underestimated. In addition, the high concentration of atomic radicals (in access of \(10^{22} \text{ m}^{-3}\)) leads to rapid recombination and a low overall energy efficiency for the production of reactivity.

References

Figure 1 – Comparison of experimentally obtained OH and H densities in a nanosecond pulsed plasma filament with results from a 0-D global model.
KINETICS MECHANISMS OF HIGH ELECTRON DENSITY Ar-WATER PLASMA DISCHARGES

- Absolute OH and H densities measured in Ar-H₂O plasma filament generated by a nanosecond voltage pulse are compared with a 0-D kinetics simulation.
- Significantly lower OH densities are found compared to H and O densities. This result seemingly contradicts the common assumption that OH is the dominant radical in water containing plasmas.
- The energy efficiency for reactivity production in high electron density discharges is low due to fast radical recombination.

![Graph showing comparison between experimental and model results for H and OH densities.](image)

- Comparison model - experiment
- Primary plasma produced species
Solvent-Enhanced Reactive Species Treatment for Plasma-Liquid Interactions
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Biological and other effects associated with atmospheric pressure plasma-liquid interactions are often directly or indirectly due to reactive nitrogen and oxygen species, or RONS.[1] For example, maximizing RONS uptake in and, often, penetration through biological tissue is crucial for biomedical applications. However, solvation and penetration of RONS in biological and other material is typically limited by water that is present. Uptake can be limited by the solubility of of plasma produced RONS in water, while penetration is limited by reactions undergone by RONS after solvation in the aqueous phase.

One way to potentially aid in the uptake and penetration of plasma produced RONS is by surface application of a solvent with RONS solubilities much higher than those seen in water. For example, the ability of perfluorocarbons to dissolve O$_2$ and NO$_x$ at high concentrations is well known.[2] We are investigating the use of perfluorodecalin (PFD) to amplify RONS deliveries into liquids from plasma treatments. A thin layer of plasma-exposed PFD applied to a surface could significantly enhance the delivery of RONS to that surface.

One challenge in characterizing these effects is that many common liquid-phase RONS probes are not soluble in PFD. However, since dissolved gases will not ionize or undergo reactions with water, techniques such as direct UV absorption should be possible if dissolved RONS concentrations are high enough. To test this possibility, we have used an O$_3$ generator to produce O$_3$ at 2700 ppm, similar to the concentrations produced by plasmas in our previous studies.[3] UV absorption at 254 nm shows an order of magnitude more O$_3$ dissolved in PFD than in water, demonstrating both RONS solvation enhancement and the viability of UV absorption in place of liquid-phase indicators (see Fig. 1). Potential applications include the use of plasma-activated PFD to improve antimicrobial activity at surfaces.

References
SOLVENT-ENHANCED REACTIVE SPECIES FOR PLASMA-SURFACE INTERACTIONS

- Solvation of plasma-produced RONS can be limited by water solubility. Uptake and penetration can be enhanced with perfluorodecalin (PFD), which has superior gas solvation properties.
- Tests with an O$_3$ generator and UV absorption show an order of magnitude more O$_3$ dissolved in PFD than in H$_2$O.
- We have also constructed a plasma device to perform additional PFD solvation tests to study how PFD solvation enhancement functions for NO$_x$ as well as O$_3$.

- O$_3$ concentrations in liquid

- Gas-Phase O$_3$ vs NO$_x$ mode