Simulation of Chemical Reaction Kinetics, and Diffusive and Electrostatic Mass Transport in Plasma-Treated Water

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Abstract: In this work, we report results of a coupled reaction-diffusion-electrostatics model for reactive species transport in plasma-treated water, and investigate liquid composition during and after treatment with a noble gas μ-APPJ with admixture of water. Results demonstrate that the production of short-lived species during treatment are dominated by OH consumption processes, while after treatment hydrogen peroxide dominates.

1. Introduction

Plasma-treated water has been shown to have many applications, one of which is direct degradation of biological or persistent organic contaminants (for example PFAS). To gain a mechanistic insight into deconstruction pathways of these contaminants, the liquid composition and electrical properties during and after treatment need to be known. Benchmarked modelling can bridge this gap providing in-depth knowledge on the liquid environment. Models have previously been developed for reactive species (RS) transport, fluid flow and heat transfer [1-2], but little has been reported for combined reaction-diffusion-electrostatics models within the liquid phase.

Here, we demonstrate a first step into developing a plasma treated liquid model for this purpose, presenting RS production and transport through a liquid water sample during plasma treatment.

2. Methods

A coupled liquid-phase reaction-Poisson-Nernst Planck model in 1D was used to simulate plasma treatment of water. Parallel electrode geometry was assumed (e.g. COST μ-APPJ), with gas flow impinging normal to the liquid surface, meaning simulated plasma treatments contained only neutral species [3]. A helium plasma with admixture of water was assumed throughout, with simulated treatments consisting of H_2O_2 (Case 1), and H_2O_2 with OH (Case 2). This was considered analogous to treatments with species in the far effluent of a COST μAAPJ (Case 1 - long-lived only), and with species in the near effluent (Case 2 - long and short-lived). Other plasma-produced RS (i.e. H, H_2, O_3) are excluded due to their low solubility in comparison to those mentioned above [3-4].

3. Results and Discussion

Figure 1 displays RS produced in water due to plasma treatment for Case 1 and 2 as outlined above. In Case 1 treatments, the plasma-delivered H_2O_2 and its conjugate base HO_2^- largely dominate. Reactions between HO_2^- and the H_2O solvent leads to an increased concentration of OH^- in comparison to that produced due to the autoionization of the water solvent. In addition, the dissociation of H_2O_2 temporarily forming OH, is followed by the production of HO_2 and O_2^- in very small concentrations. In Case 2 treatments, OH is largely consumed in the first 100 nanometres and converted (through reactions with H_2O_2) into HO_2, which permeates through diffusion and leads to the increased production of O_2^-/H^+ deeper in the liquid.

Further chemical reaction network analysis demonstrates that only OH^- originates from hydrogen dissociated from the H_2O solvent. All other species in both cases are directly produced in the liquid through plasma-delivered H_2O_2, OH and HO_2, and their products as shown in Figure 1 (bottom).

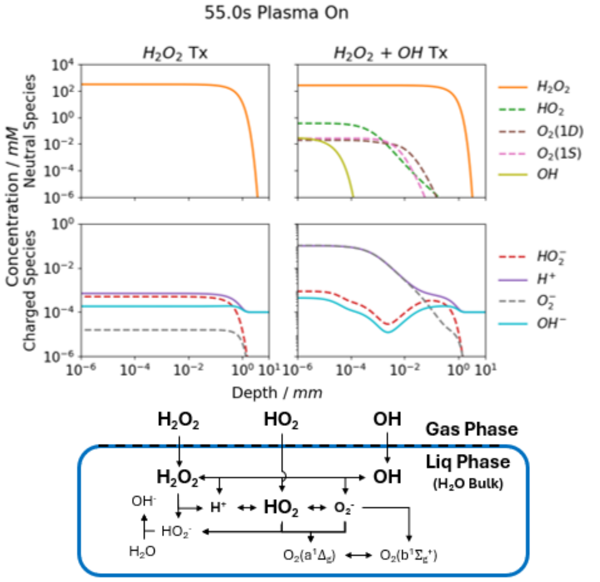

Fig. 1. Spatial profile of reactive neutral (top) and charged species (middle) for treatment with a noble gas plasma with admixture of water, including H_2O_2 only (Case 1 - left column) and H_2O_2 with OH (Case 2 - right column) after 55s of plasma treatment.

4. Conclusion

For a noble gas (e.g. helium) plasma with admixtures of humidity, although H_2O_2 is the most abundant RS in the liquid phase due to its high solubility, highly reactive OH dominantly leads to increased short-lived RS production during treatment. OH is rapidly consumed leading to the production of HO_2 almost immediately upon entering the liquid phase, with HO_2 and its conjugate base O_2^- propagating further into the liquid through diffusion. After treatment, the liquid composition is dominated by H_2O_2.

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