

Reactions of singlet oxygen molecules $^1\text{O}_2$ in water irradiated by atmospheric-pressure plasmas

Kazumasa Ikuse and Satoshi Hamaguchi

Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Osaka, Japan.

Abstract: A one-dimensional simulation model has been developed to analyze the reaction and transport processes of various chemical species in water generated by the exposure of an atmospheric-pressure plasma to the water surface. In this study, the generation and loss of singlet oxygen (molecular dioxygen) are examined by numerical simulation, especially near the region of tumor cell membranes.

Keywords: atmospheric-pressure plasma, reaction-diffusion, singlet oxygen

1. Introduction

Recent research [1] has demonstrated the importance of presence of singlet dioxygen molecules ($^1\text{O}_2$) for the induction of apoptosis of tumor cells. Tumor cells have catalase (CAT) on their membranes that can efficiently block intercellular reactive oxygen/nitrogen species (ROS) that would induce apoptosis signaling. Intercellular $^1\text{O}_2$ molecules are expected to eliminate membrane associated CAT of tumor cells and simultaneously generate more $^1\text{O}_2$ molecules, inducing chain reactions of elimination of membrane associated CAT and therefore apoptosis of the tumor cells.

In this study, we examine how $^1\text{O}_2$ molecules are generated in water exposed to an atmospheric pressure plasmas (APP), using numerical simulation based on a transport-reaction model. The rate constants of all possible liquid phase reactions are quoted from past publications. For this purpose we have added a few key chemical reactions that governs the generation and loss of $^1\text{O}_2$ molecules in water to the existing simulation model that we have developed over the past few years. In a water layer near the tumor cell surfaces, the presence of surface associated enzymes may strongly affects the concentrations of intercellular RONS. Such effects can also be included in our simulation.

2. Numerical simulations

In this section, a one-dimensional simulation model that governs reactions and transport of various chemical species in water facing a gas-phase plasma is reviewed. First the influx of the gaseous species to the water surface is given as the boundary condition. Under typical conditions, we assume that the plasma is in steady state (i.e. the composition is constant in time and uniform in space at the plasma-water interface). However, time varying plasma can also be modeled by time dependent boundary conditions. The gas phase species are assumed to enter water at their thermal velocities and the outward flux of reactive species from water to the gas phase is determined from Henry's law. Typically the concentrations of the gaseous species may be taken from

experimental data. As the initial condition, the medium is assumed to be pure water (pH=7) with dissolved oxygen and nitrogen in equilibrium with air at 1 atm.

The simulation model we have developed so far is one-dimensional in space in the direction from the liquid surface to the bottom of water. The governing equations are drift-diffusion equations for various chemical species advected by water flow. They have been derived in the following manner.

Equations of the mass and momentum conservations of species i are given by

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v}_i) = \tilde{R}_i$$

$$m_i n_i \frac{d\mathbf{v}_i}{dt} = -k_B T \nabla n_i + q_i n_i \mathbf{E} - \nu_i m_i n_i (\mathbf{v}_i - \mathbf{v}_c)$$

with $i = 1, 2, \dots, N$, where n_i , t and $\mathbf{v}_i$ represent the concentration of species i , time and fluid velocity. Here $\tilde{R}_i$ is the chemical reaction term determined from the rate equations. Other parameters m_i , k_B , T , q_i , $\mathbf{E}$, ν_i and $\mathbf{v}_c$ denote the atomic or molecular mass of species i , Boltzmann constant, water temperature, electrical charge of species i , electric field, collision frequency of species i with water molecules and the convective flow velocity of water, respectively. The electric field $\mathbf{E}$ is calculated from Poisson's equation

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon}$$

where ρ is the charge density and ε is the permittivity of pure water. If collisions of chemical species with water molecules are sufficiently frequent, inertia of the momentum conservation $m_i(d\mathbf{v}_i/dt)$ can be ignored. Therefore the fluid velocity of the chemical species i can be written as

$$\mathbf{v}_i = \mathbf{v}_c + \mu_i \mathbf{E} - \frac{D_i}{n_i} \nabla n_i$$

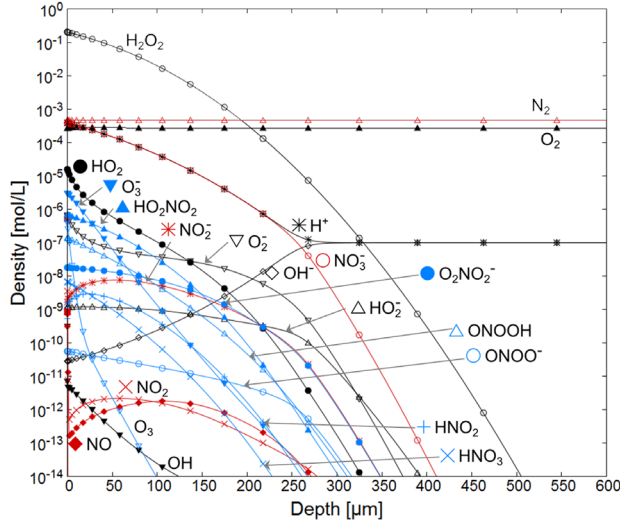


Fig. 1. The concentration distributions of the chemical species at 1 second after the water surface is exposed to a typical APP. The horizontal axis represents the depth from the liquid surface in liner scale and the vertical axis represents density in log scale.

with

$$\mu_i = \frac{q_i}{v_i m_i}$$

$$D_i = \frac{k_B T}{v_i m_i}$$

where μ_i and D_i denote the mobility and diffusion coefficient. If the water flow is incompressible, the divergence of the convective water flow velocity can be ignored, i.e.

$$\nabla \cdot \mathbf{v}_c = 0.$$

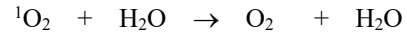
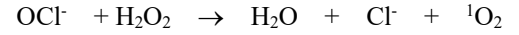
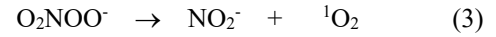
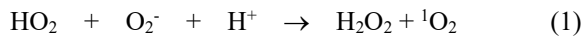
Thus the governing equation of our simulation model can be obtained from combining the mass conservation equation with the expression of velocity $\mathbf{v}_i$,

$$\frac{\partial n_i}{\partial t} = \tilde{R}_i - \mathbf{v}_c \nabla n_i - \mu_i \nabla \cdot (n_i \mathbf{E}) + D_i \Delta n_i.$$

The simulation has been parallelized based on the domain decomposition with Message Passing Interface (MPI), which allows the computation for many seconds of physical time to be completed within reasonable computational time.

Figure 1 shows the concentration distributions of chemical species in liquid at 1 second after a typical APP exposure. In this simulation, reactions of $^1\text{O}_2$ are not included. However, it is seen that the solution becomes acidic due to the generation of nitric acid (H^+ and NO_3^-), which is consistent with experimental observations [2].

It has been known [1] that singlet oxygen molecules $^1\text{O}_2$ are generated or lost from the following reactions;



As the reaction (2) is slower than (1) [1], the generation of $^1\text{O}_2$ is more likely to be triggered in acidic conditions. It is seen in reaction (3) that peroxyxynitrate anion O_2NOO^- plays an important role in the generation of $^1\text{O}_2$. Recent study of bactericidal effects of its conjugate acid, i.e., peroxyxynitric acid O_2NOOH may be related to this reaction [3].

3. Summary

The one-dimensional simulation of chemical reactions and diffusion/advection of reactive species in water exposed to a low-temperature APP has been developed with the generation and loss of singlet dioxygen molecules $^1\text{O}_2$. A small amount of singlet oxygen $^1\text{O}_2$ generated by reactions of more stable RONS generated by APP exposure to the water surface can trigger the elimination of membrane associated CAT of tumor cells as well as further generation of $^1\text{O}_2$, which may cause chain reactions of loss of CAT and apoptosis signaling in the tumor cells. Such effects will be examined more closely in the future with the model simulation developed here.

References

- [1] G. Bauer, D. B. Graves, Plasma Process. Polym. **13** (2016) 1157.
- [2] S. Ikawa, K. Kitano and S. Hamaguchi, Plasma Process. Polym. **7** (2010) 33.
- [3] S. Ikawa, A. Tani, Y. Nakashima, K. Kitano, J. Phys. D: Appl. Phys. **49** (2016) 425401.