Various types of plasmas in contact with liquid have been applied to water purification. The author and his group have developed plasma-based water treatment technologies for efficient and rapid decomposition of persistent organic compounds in water [1]. Understanding of the reaction fields in gas and liquid phases, with respect to mass transfer through their interface, is necessary to achieve efficient treatments, and a numerical simulation is a strong tool to understand such reaction fields. Numerical analyses of two types of plasmas in contact with liquid, namely, plasma generated within gas bubbles and plasma generated over a solution surface, are introduced in this abstract.

Plasma generated within gas bubbles has been used for ROS generation [2] and water purification using OH radicals [3]. There was a small hole in a ceramic plate and bubbles were produced from the hole by gas supply. Plasma was generated within the bubbles by applying a high voltage to the electrode under the hole with grounding the solution. When plasma was generated in O₂ bubbles, reactive oxygen species (ROS) such as O₃, ·OH, H₂O₂, and HO₂ were generated. It was found that the amount of produced H₂O₂ increased with increasing the discharge power while that of O₃ decreased. To understand the key reactions which determine the ROS generation, a zero-dimensional (0D) simulation model (global model) considering mass transfer between the gas and liquid phases was constructed [2]. By electron-impact dissociation of O₂ molecules, O radicals were generated. The O radicals were consumed to generate ·OH or O₃ in bubbles via a reaction with H₂O or O₂, respectively, as follows: ·O + H₂O → ·OH + O₂, O + O₂ → O₃ + O. When the water vapor concentration was increased, the calculated H₂O₂ concentration increased, whereas the O₃ concentration drastically decreased. The calculated amounts of H₂O₂ and O₃ exhibited good agreement with experimentally obtained values. Therefore, it was concluded that when the discharge power increases, the vaporization of water is enhanced based on an increased heat flux from the plasma to the solution. Higher reaction rate of ·O with H₂O results in higher concentrations of ·OH and H₂O₂. In contrast, less vaporization with a lower power results in more reactions between ·O and O₂, which generates O₃. When the plasma is driven by AC voltage, the discharge power can be controlled by using ballast capacitors. Lower power input with smaller ballast capacitances achieved a higher generation rate of O₃ [3].

Axisymmetric two-dimensional (2D) model was constructed for plasma generated over a solution surface, which was applied to decomposition of acetic acid [4]. A needle electrode was placed 1 mm above the solution surface with the gas composition of 97% Ar and 3% water vapor. Plasma was generated between the tip of the needle and the solution surface by applying a pulsed voltage. The solution contained acetic acid at a total organic carbon (TOC) concentration of 10 mg/L. The mass transfer of ROS, namely, ·OH, H₂O₂, and HO₂, through the gas–liquid interface was considered by assuming that a gas–liquid equilibrium is established in accordance with Henry’s law and that the fluxes of these species are continuous. ·OH in the gas phase was mainly generated via the dissociation of H₂O by metastable Ar atoms. Only a limited portion of the ·OH generated in the vicinity of the plasma–solution interface could diffuse into the solution, while the rest was converted into H₂O₂. Figure 1 presents the liquid-phase concentration of ·OH along the axisymmetric axis. The concentration near the plasma–solution interface peaked approximately 1 μs after the voltage increase and then decreased to 2% of its maximum value at 10 μs because of the loss reactions with ROS and acetic acid. In the simulated TOC concentration, the reaction rate of ·OH with acetic acid was one to two orders of magnitude smaller than those with ROS. Even at a depth of 0.2 μm, the concentration of ·OH was less than 1% of the maximum value near the interface. Therefore, the OH penetration depth is considered to be less than 0.2 μm and the decomposition reactions of acetic acid are like interfacial reactions at the plasma–solution interface.

Figure 1. Distribution of the concentration of liquid-phase ·OH along the axisymmetric axis [1].

References