Improved production and selection of reactive species using a nanosecond pulsed gas bubble discharge in liquid

X.J. Dai¹, C.S. Corr², S.B. Ponraj³, M. Maniruzzaman¹, T.A. Arun¹, Z.Q. Chen¹, L. Kviz¹, R. Lovett¹, G.D. Rajmohan¹, D. Rubin de Celis¹, M.L. Wright¹, P.R. Lamb¹, Ya.E. Krasik³, D.B. Graves⁴, W.G. Graham⁵, R. d’Agostino⁶, and X.G. Wang¹

¹ Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia
² Research School of Physics and Engineering, Australian National University, Canberra, Australia
³ Physics Department, Technion, Haifa, Israel
⁴ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, USA
⁵ Centre for Plasma Physics, School of Mathematics and Physics, Queen’s University, Belfast, UK
⁶ University Aldo Moro of Bari, Bari, Italy

Abstract: Higher production and improved selection of reactive oxygen and nitrogen species has been obtained in a nanosecond pulsed plasma in water using a needle point-to-plate bubble discharge and different gases. A high density of H₂O₂ was produced by Ar plasma, while high densities of NO₃⁻ and NO₂ were generated by air plasma, in good agreement with observations of emission spectra. Possible mechanisms are proposed.

Keywords: reactive species, nanosecond pulsed plasma, bubble discharge

Electric discharge plasmas in liquid have many potential applications in areas such as biomedicine, nanoscience, and agriculture. Reactive oxygen and nitrogen species generated by creating plasma in a liquid, particularly hydrogen peroxide (H₂O₂) and nitrate ion (NO₃⁻), have been found to play critical roles in these processes [1]. Various discharge setups, including electrodes immersed in liquid and/or above liquid, and their effect on hydrogen peroxide yield have previously been examined [2]. The physics of these discharges and the plasma-induced chemistry have been studied to help determine the underlying mechanisms [3, 4]. However, selectivity for the desired reactive species and efficient production are still the challenges for specific applications.

In order to tailor the process for specific applications (e.g., milk sterilization, plant growth, nanomaterial formation), this work has focused on: (1) enhancing the interface reaction between gas plasma and liquid, as the interface plays a critical role in controlling chemical reactions, and (2) achieving a selectable and controllable level of the required reactive species. We implemented needle point-to-plate (mesh) electrodes in liquid and used a nanosecond pulsed discharge, as shown in Figure 1. Different gases, fed through the needle to produce bubbles in the liquid, were used to generate plasma inside the bubbles. Due to a large difference in dielectric constants in gas and water, the electric field is enhanced in bubbles leading to plasma discharge formation at those locations. This dynamic bubble setup increases interface reactions between gas-plasma and water with fast mass transport from plasma to liquid so that more of the required reactive oxygen or nitrogen species can diffuse into the liquid. Using different gases gives different gas phase reactive species enabling selective production of the required oxygen or nitrogen species.

The concentrations of hydrogen peroxide (measured by UV-Vis absorbance spectra), and nitrate and nitrite (measured by photometric assay), as well as the conductivity and pH of treated de-ionized (DI) water were measured. An ICCD camera was used to capture the formation of the plasma discharge, and a spectrometer to obtain emission spectra. The analysis of this data has helped in the understanding of underlying mechanisms.

![Fig. 1. Schematic of the experimental setup, 10 ns pulse, applied voltage 18kV (mesh +9 kV, needle –9 kV), inner dia. of needle 0.44 mm, gas flow rate 100 sccm, DI water 100 ml.](image)

We found that Ar plasma in this setup produces a much higher density of H₂O₂, while air plasma produces a higher density of nitrogen dioxide and nitrate ions. As expected, air plasma also produces a much higher density of ozone, as well as a much higher conductivity but lower pH, than Ar plasma. As H₂O₂ and NO₃⁻ are the most important products, we only present results for these two species (Figure 2).
Using Ar gas, the most energetic species in the Ar plasma (energetic electrons, excited Ar atoms, Ar-ions, UV radiation) directly interact with water (the boundary of the Ar gas bubble is the dielectric surface), which results in decomposition of the water to produce OH radicals. Hydrogen peroxide is then formed by the recombination of OH either in gas phase or in water. Due to the bubble movement, H2O2 molecules are rapidly transferred into the bulk water enabling a high density to be achieved. Using air, N and O are generated. They combine in the plasma to form nitric oxide (NO) in the gas phase, which however readily combines with oxygen to form nitrogen dioxide (NO2). Nitrogen dioxide is well known to disproportionate in H2O forming NO3\(^-\), NO and H+ according to the reaction in solution:

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3\text{NO}_2 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{NO}_3^- + \text{NO} + 2\text{H}_3\text{O}^+.
\]

Again due to the bubble movement, NO2 rapidly diffuses into the bulk water so that a high density of NO3\(^-\) and an acid solution is achieved, which was quantified by pH measurement. Figure 2 also shows that higher frequency operation of the pulsed generator results in higher densities of H2O2 in Ar plasma and higher densities of NO3\(^-\) in air plasma. As more ozone was generated at higher power in air plasma, less H2O2 was found in the treated water. Very little ozone was found in Ar plasma treated water. All these results are in good agreement with the observed emission spectra (see Figure 3). Ar plasma generates a high intensity of hydrogen and oxygen species while the air plasma spectrum is dominated by the second positive band of nitrogen between 300 nm and 400 nm. In addition, the large ratio between the intensities of the H\(\alpha\) and H\(\beta\) spectral lines indicates a low temperature (~1 eV) of the plasma electrons (assuming an optically thin plasma and Boltzmann energy level population).

In conclusion, this improved method has enabled the selection and increased production of the reactive species required for specific applications, such as milk sterilization, plant growth, and nanomaterial production. Some of these results will be presented elsewhere in the conference.
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References