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# Radical Species in Aqueous Solution for Plasma-Induced Chemical Processing
プラズマ誘起液中化学プロセスにおける液中ラジカル種の診断

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Free radicals formed in water during atmospheric-pressure plasma processing with a low-frequency (LF) HV power supply have been investigated by electron spin resonance (ESR) using a spin-trapping compound, CYPMPO. Even if the end of plasma jet does not reach the surface of water sample, hydroxyl radical (OH·) and superoxide anion radical ($O_2^{-}$·) are formed in the solution if surrounding gas contains oxygen. It suggests that plasma does not need to contact with liquid in plasma-induced chemical processing.

## 1. Introduction

A low-frequency (LF) plasma jet [1,2] is atmospheric-pressure plasma with low gas temperature and can be used for plasma processing in liquids or on liquid surfaces. With the LF plasma injected into liquids, advanced reaction fields may be created in the liquids, where reduction, polymerization, or sterilization can occur [3]. Although active ions, molecules, and radicals are formed by plasma exposure in the fields, they are usually unstable and not easily observed.

For the medical application to control the infection diseases, inactivation of bacteria in liquid is distinctly important. Successful bactericidal activity was found to be achieved if the solution is sufficiently acidic [4,5]. It is interesting to note that there is a critical pH value of about 4.7 for the bactericidal effects, below which the bacteria are efficiently inactivated and above which they are hardly affected by the plasma application. It has been also found that the presence of superoxide anion radicals ($O_2^{-}$·) in water and the air is essential. The critical pH value may be associated with $pK_a$ of the dissociation equilibrium between $O_2^{-}$· and hydroperoxy radicals (HOO·), which is known to be approximately 4.8. This means that $O_2^{-}$· can be changed into HOO·, which have much stronger bactericidal activity, in lower pH. To clarify the elementary processes, plasma-produced active species were measured and their reaction to biomacromolecules was evaluated [6]. In this paper, we discuss about the production of radical species in aqueous solution.

The spin trapping technique is one of methods to observe unstable radicals in solution. Unstable (short lifetime) radicals in liquid are trapped by spin trapping compounds to form spin adducts with a longer lifetime. In previous reports, $O_2^{-}$· and hydroxyl radical (OH·) were formed in water after plasma exposure if surrounding gas includes oxygen gas, based on electron spin resonance (ESR) measurements [7] with a spin trapping compound, CYPMPO [8]. Since the end of plasma jet reached the surface of water, intense signal intensities for both radicals were observed.

Recently, helium and oxygen mixed gases through discharge keep high activity and can be used for sterilization [9]. This suggests that such gases may also induce active species in water solution, even if the plasma does not touch the surface of water. In this work, free radicals formed in water with non-contact plasma have been investigated using a spin-trapping compound, CYPMPO with ESR.

## 2. Experimental

One end of the glass tube was inserted to the chamber where a glass cup was sealed with an O-ring. Oxygen gas was supplied from one of the side ports to the chamber. High voltage (~10 kHz and ~10 kV) was applied to the electrode on the glass tube 19 cm apart from the lower end of the tube. Most discharge was terminated near the other

electrodes for electric ground and did not reached to the chamber where oxygen flowed into the system. This means that meta-stable helium produced by plasma may react with oxygen gas in the chamber. After purging gas in the camber with helium and oxygen, the plasma discharge was kept for 3 min. The flow rates were controlled by flow controller (KOFLOC, 8500MC).

The sample was aqueous solution of a spin-trapping compound, CYPMPO (5-(2,2-dimethyl-1,3-propoxycyclophosphoryl)-5-methyl-1-pyrroline N-oxide). Reagent of CYPMPO was supplied by RADICAL RESEARCH and used without any further purification. ESR measurements were preformed at room temperature with a flat glass cell using the X-band ESR system (JEOL, JES-FA200).

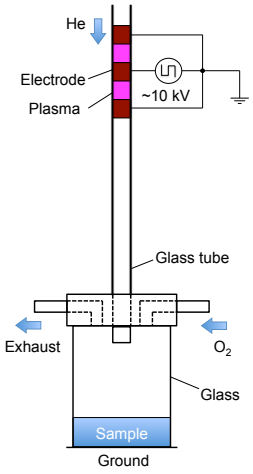


Fig. 1. A schematic illustration of the experimental setup with a straight glass tube. Oxygen was supplied to the chamber through a side port.

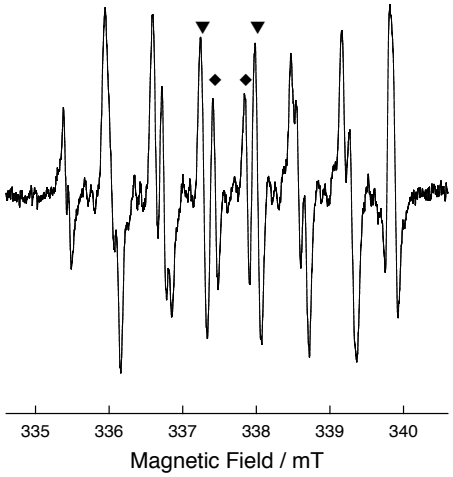


Fig. 2. Representative ESR spectrum of the solution. All signals are due to spin adducts of hydroxyl radical (OH·) and superoxide anion radical ($O_2^{-}\cdot$). The signals can be distinguished using four peaks in the middle (◆ for OH· adduct and ▼ for $O_2^{-}\cdot$ adduct).

## 3. Results and discussion

Figure 2 shows a representative ESR spectrum of the solution. ESR signals for OH· and $O_2^{-}\cdot$ adducts are observed. It indicates that active species are induced in water even by non-contact plasma.

The peak height for $O_2^{-}\cdot$ adduct is larger than that for OH· adduct in non-contact plasma. This result is strongly different from the previous one by plasma exposure directly to the water (i.e. contact plasma with the surface of the water) where an intense signal for OH· and a weak signal for $O_2^{-}\cdot$ [8]. This means that amounts of plasma-induced active species in liquid may change with the distance from the plasma discharge to the water surface.

Both radicals are reactive oxygen species. As their reactivity is different, suitable radicals induced in liquid should depend on an application. For example, sterilization in liquid with the LF jet needs $O_2^{-}\cdot$ [4]. In the case of non-contact plasma, $O_2^{-}\cdot$ may produce effectively into liquid with low yield of OH· in comparison with the case of contact plasma.

## 4. Summary

Free radicals formed in water with non-contact plasma have been investigated by ESR using a spin-trapping compound, CYPMPO. Hydroxyl radical (OH·) and superoxide anion radical ($O_2^{-}\cdot$) are formed in the solution if surrounding gas contains oxygen. Plasma does not need to contact with liquid in plasma-induced chemical processing.

## References

[1] 北野勝久、応用物理学会誌、77(4), pp. 383 (2008).
[2] 北野勝久、日本国特許第 4677530 号.
[3] 北野勝久、現代化学，7 月号，p25，(2009).
[4] S. Ikawa, Plasma Process. Polym., 7, pp.33, (2010).
[5] 井川聡、日本国特許第 4408957 号.
[6] E. Takai, Plasma Processes and Polymers. in press.
[7] M. Kamibayashi, Free Rad. Res. 40, 1166, (2006).
[8] A. Tani K. Kitano, K. Mizotani, S. Ikawa, S. Hamaguchi, Proc. of Int. Interdisciplinary -Symposium on Gaseous and Liquid Plasmas, (ISGLP, Sep. 5-6, Sendai, Japan), p263, (2008).
[9] K. Kitano, Proc. of ISPC-20 (The 20th International Symposium on Plasma Chemistry), Philadelphia, July, (2011).