22G01

Plasma-Induced Chemical Processing in Solution by LF plasmajet

LFプラズマジェットを用いたプラズマ誘起液中化学プロセス

Katsuhisa Kitano [1], Satoshi Ikawa [2], Atsushi Tani [3], Tsuyoshi Kitamura [4], Ryuichi Arakawa [4], Yusuke Ono [1]

北野勝久 [1]、井川聡 [2]、谷篤史 [3]、北村豪 [4]、荒川隆一 [4]、大野友輔 [1]

[1] *Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.*

[2] *Technology Research Institute of Osaka Prefecture 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan*

[3] *Department of Earth and Space Science, Graduate School of Science, Osaka University 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan*

[4] *Faculty of Chemistry, Materials and Bioengineering, Kansai University 3-3-35 Yamatecho, Suita, Osaka, 564-8680, Japan*

[1] 大阪大学工学研究科　原子分子イオン制御理工学センター　〒565-0871　大阪府吹田市山田丘2-1

[2] 大阪府立産業技術総合研究所、[3] 大阪大学理学研究科、[4] 関西大学化学生命工学部

Atmospheric pressure plasmajet with low gas temperature has been produced by a simple system with a dielectric tube through which He gas flows and a single electrode to which LF (Low Frequency) high-voltage pulses (~10kV, ~10kHz) are applied. Supplied active species from air to liquid induce the chemical reactions in liquid. They were measured by ESR (electron spin resonance) and MS (Mass Spectrometry). The formation of free radicals in liquid is discussed from various perspectives. This attractive reaction fields have been utilized for biomaterial synthesis, surgery treatment and so on.

1. Introduction

Recent development of atmospheric plasmas with low temperature has enabled non-conventional plasma processing [1]. In this paper, formation mechanisms of free radicals inside liquid by non-thermal plasma jet are discussed.

Low gas temperature atmospheric pressure plasmas can be produced by a high-voltage (HV) low-frequency (LF) power supply in the range of kV and kHz in a tube where a discharge gas (typically He or Ar) flows. A schematic illustration of the system is shown in Fig. 1. We call it a LF microplasma jet as the plasma seemingly extends from the tip of the tube into ambient air. Partial discharges between the HV electrode and the electrical ground in the surroundings occur in the He/Ar gas flowing into the air [2]. Due to its low gas temperature, as shown in Fig.2, this type of jets is desirable for plasma processing in liquid.

We have successfully found that efficient bactericidal activity can be achieved if the solution is sufficiently acidic [3]. 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 the bacteria are hardly affected by the plasma application. It has been also found experimentally that the presence of superoxide anion radicals ($O_2^-\cdot$) in the solution is essential for bacterial inactivation by the plasma application. The critical pH value may be associated with pKa of the dissociation equilibrium between $O_2^-\cdot$ and hydroperoxy radicals (HOO·), which is known to be approximately 4.8.

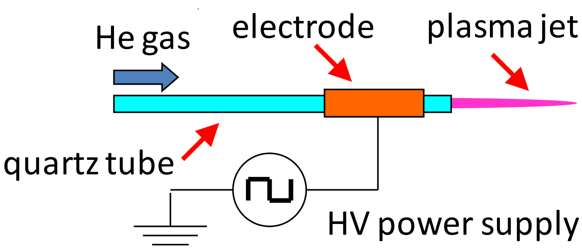

Fig. 1 Schematic diagram of LF micro plasma jet with a single electrode.

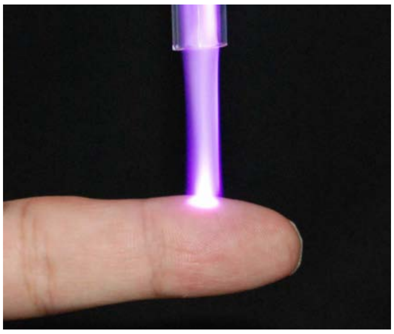

Fig. 2 Plasma jet exhausted to a finger without burning.

The fundamental question regarding such new chemical reaction environments is what kinds of species in plasmas cause these reactions. We have studied free radical formation in water after plasma exposure, using electron spin resonance (ESR) with a spin-trapping method [4]. Some atomic species in the gas phase are converted to free radicals by plasma application. In this paper, we discuss about the formation mechanisms of $O_2^-\cdot$, which plays an important role in the bacterial inactivation in the solution by the plasma application.

2. Experimental Results

It is known that $O_2^-\cdot$ in the solution become extinct by disproportionation reaction and its half life time can be longer in alkaline solution. This means that $O_2^-\cdot$ can be trapped in alkali solution. We applied this alkali-trapping method for ESR measurements, instead of spin-trapping method, for high sensitive measurement. ESR measurement was done at liquid-nitrogen temperature with X-band ESR system (JEOL, JES-FA100).

The plasma exposure experiments were performed against alkali solution (pH14) in the case of contact and non-contact (distance is 30mm) with LF plasmajets. ESR spectra after plasma exposure are shown in Fig. 3. This shows the existence of $O_2^-\cdot$ with clear signals. Unlike the usual chemical spin-trapping method, trapping efficiency with the alkali-trapping method is theoretically almost unity. In addition of the strong signal in the case of contact, weaker signal was seen also in that of non-contact. The fact suggests that the existence of some active species in the air.

To clarify the above experimental results, the air 100mm apart from the tip of the plasma jet was analyzed by MS (Mass Spectrometer) with differential pumping. As seen in Fig.4, the clear peak signal of $O_2^-\cdot$ hydrated with one water molecule is observed at m/z = 50. This shows the existence of $O_2^-\cdot$ in the air. This is a sort of air ion.

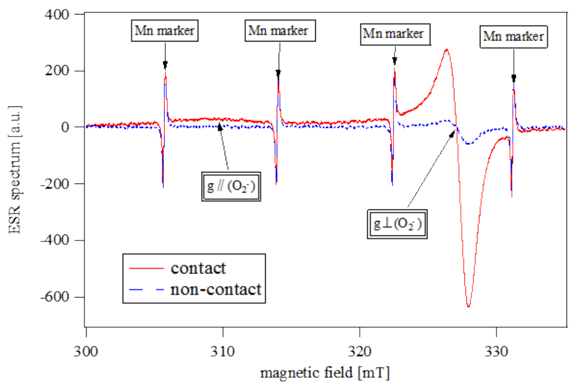

Fig. 3 ESR spectra of the solution samples in the cases of contact and non-contact with the plasma.

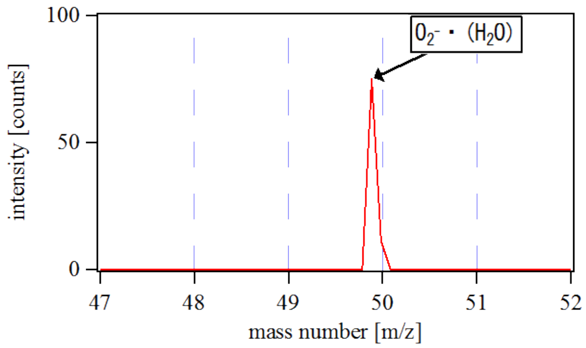

Fig. 4 MS spectrum of the air 100mm apart from LF plasmajet.

3. Summary

We developed the alkali trapping ESR measurement method for $O_2^-\cdot$ formed in the solution by the plasma exposure. Using this high-sensitive method, the $O_2^-\cdot$ was observed even in the solution which is not in contact with the plasma. In the air, the existence of $O_2^-\cdot$ is also confirmed with MS. These experimental results strongly suggest that the air ions of $O_2^-\cdot$ are formed from the air around the plasma and they are transported into the solution.

In this paper, the generation of $O_2^-\cdot$ is focused because of its interesting characteristics concerning about plasma disinfection. Another active species are also generated in gas and supplied to liquid. We conclude that it is important to clarify the key specie(s) for each application and their fundamental reaction, and to optimize their generation.

Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Microplasma" and a Grant-in-Aid for Young Scientists (A) from MEXT, and A-STEP (JST).

References

[1]K. Kitano, H. Furusho, Y. Nagasaki, S. Ikawa, S. Hamaguchi, Proceedings of International Conference on Phenomena in Ionized Gases XXVIII,(Prague, July 2007), p. 1131-1134,(2007).

[2] K. Kitano and S. Hamaguchi, Proc. The 4th International Workshop on Microplasmas, (October 28-31, 2007, Tainan Taiwan), FP-017, 55-56 (2007).

[3] S. Ikawa, K. Kitano, S. Hamaguchi, Plasma Process. Polym., 7, 1, pp.33, (2010).

[4] 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).