3D Integrated Micro-solution Plasma for The Treatment of Water - Effects of Discharge Gases -

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Methylene blue molecules in aqueous solution have been decomposed by using a novel 3D integrated micro-solution plasma reactor operated with Ar and He gases. Energy efficiency for methylene-blue decomposition in the case of Ar is relatively higher than that in the case of He. This result suggests that cheaper Ar gas has brought about superior performance in water purification. In both cases of Ar and He, methylene-blue decomposition efficiency is one order of magnitude higher than that of conventional solution plasma.

Keywords: helium, argon, bubble, plasma, liquid, water, purification

1 Introduction

Recently, electrical discharges in aqueous solution (solution plasma (SP)) are examined as methods for eliminating toxic organics in aqueous solution [1]. One of the reasons is that it can generate OH radicals. These radicals are highly reactive and can decompose organic materials in water.

In our previous works, we have developed 3D integrated micro-solution plasma (3D IMSP) [2], in which a large amount of tiny plasma (microplasma [3]) is generated in a porous dielectric material being filled with a gas/liquid mixed medium. Although 3D IMSP requires external gas (Ar) supply, the gas can be recycled by using an appropriate reactor combined with a gas circulation system. 3D IMSP can be applied to gold nanoparticles synthesis [4] and decomposition methylene blue (MB) molecules in water [2]. Moreover, 3D IMSP has shown superior performance in the case of decomposition of MB molecules in comparison to conventional SP.

However, in our previous reports, we have examined only Ar gas for operating 3D IMSP because its metastable excited species (Ar $^3P_2$, $^3P_0$) have a capability to decompose H_2O to produce reactive OH radicals. On the other hand, He gas is also commonly used for various plasma treatments. He atoms can be excited to metastable excited states ($^1S_0$, $^3S_1$), which are at higher-energy levels than those of Ar atoms. Thus, we have investigated characteristics of 3D IMSP with He gas and compared its performance in MB decomposition with that of 3D IMSP with Ar gas. We have also compared both with the performance of conventional SP [2, 3].

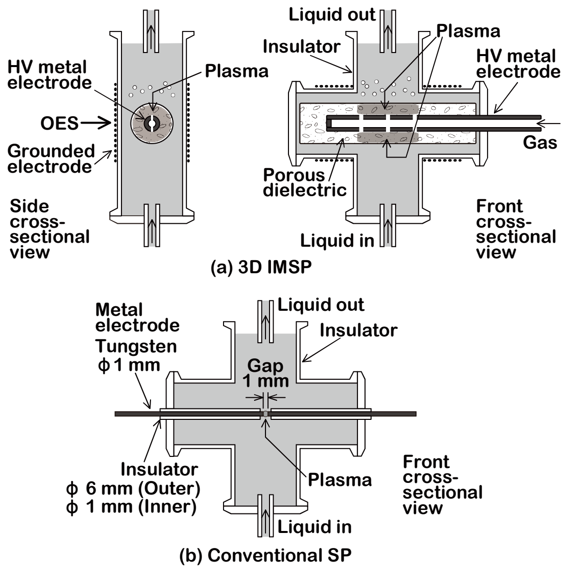

Fig. 1: Schematic illustration of (a) a 3D IMSP reactor and (b) a conventional SP reactor

2 EXPERIMENTAL

Figures 1(a) and 1(b) show schematic illustrations of 3D IMSP and conventional SP reactors. The porous dielectric material is a rod-shaped silica pumice (diameter 20 mm), which is inserted in a glass tube (inner diameter 30 mm). The average diameter of the pores is approximately 0.5 mm. A metal electrode (SUS 304: outer diameter, 1/4 in.), to which a high-voltage pulse is applied, is inserted in the central axis of the pumice rod. It has five holes (diameter, 2 mm) for feeding gas into the po-

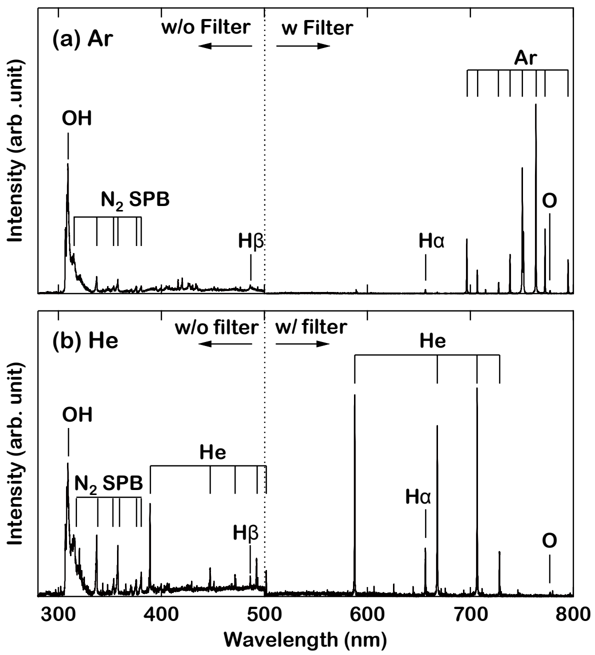

Fig. 2: OES of 3D IMSP operated with (a) Ar and (b) He gases

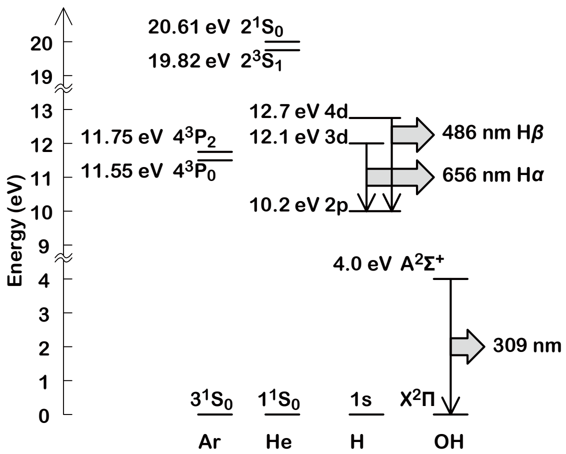

Fig. 3: Energy diagram of Ar, He, H and OH

rous dielectric material filled with the aqueous solution to be treated. The grounded electrode (metal mesh, SUS 304; wire diameter, 0.29 mm; aperture, 0.98 mm) is attached to the outer surface of the glass tube. The voltage is supplied from a bipolar high voltage power source (Haiden, SBP-5K-HK2). Voltage form is a square-wave pulse with amplitude of 5 kV, a frequency of 20 kHz, and a pulse width of 2.0 μs. The gas supplied through the central electrode is He or Ar, and their flow rate is 1.1 L/min. No external gas is supplied in the case of conventional SP. Sample to be treated is aqueous solution (150 mL) containing MB (0.65±0.08 mg), of which electrical conductiv-

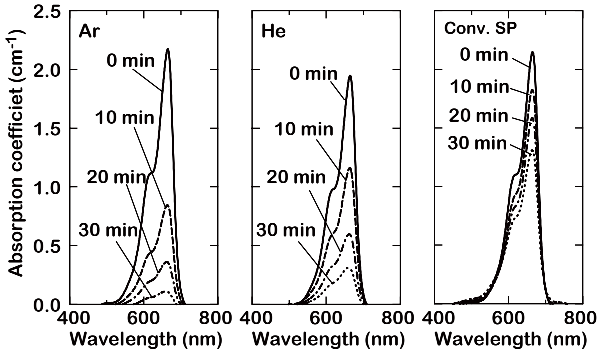

Fig. 4: UV-VIS spectra of MB aqueous solution treated with (a) 3D IMSP (with Ar), (b) 3D IMSP (with He), and (c) conventional SP

ity is 7.4±0.9 μS/cm. The liquid temperature is controlled to 30°C by circulating and cooling the liquid in order to prevent the condensation of MB due to vaporization of water. The maximum treatment time is 30 min.

3 RESULTS AND DISCUSSION

3.1 OES

Before performing MB decomposition experiments, we have measured OES of 3D IMSP operated with Ar and He in order to investigate differences in the chemical species in the microplasma in the 3D IMSP reactor. Figure 2(a) and 2(b) show OES of 3D IMSP operated with Ar and He gases, respectively. In both cases, emission lines from H, O, and OH are observed, which means that H_2O vapor is supplied into gas bubbles from the inner surface of the gas bubbles and are dissociated in the plasma in both cases. Appearance of the 2nd positive system band of N_2 is due to parasitic discharge ignited in isolated pores, which are included in the porous dielectric material during its fabrication process, and/or due to air discharge in a small gap between the metal mesh and glass tube.

A difference in the OES is found in the intensity of Hα and Hβ relative to OH intensity. In the case of He, Hα and Hβ intensity is higher than those in the case of Ar. This is due to the fact that the energy levels (approx. 20 eV) of metastable He atoms are high enough to have H (3d; 12.1 eV) atoms, which are able to emit 656 nm photons as shown in Fig. 3. This means that, in the case of He, higher-energy electrons and/or metastable excited species

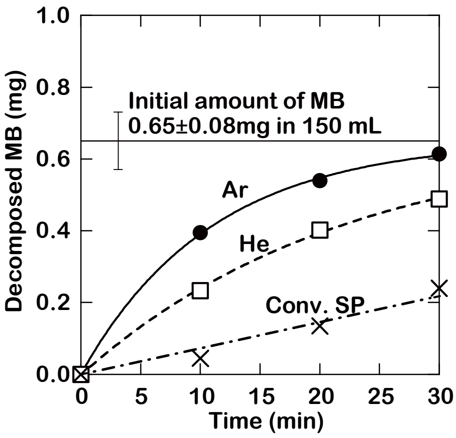

Fig. 5: Amount of decomposed MB molecules as a function of duration of treatment by 3D IMSPs operated using Ar and He, and conventional SP

(He $^1S_0$, $^3S_1$) are working for decomposing H_2O molecules to produce H and OH. Thus, we have investigated effects of this difference on the performance of MB decomposition.

3.2 MB DECOLORIZATION

Figures 4(a)-4(c) show UV-VIS spectra of MB aqueous solution as a function of time of treatment with 3D IMSP using Ar and He gases, and with conventional SP, respectively. In all cases, we can see a reduction in the absorption band centered at 665 nm, which corresponds to a MB absorption band. To investigate reduction rate quantitatively, we have converted the reduction in the absorption coefficient to the amount of decomposed MB molecules. The results are shown in Fig. 5. We can see almost 100% of MB molecules are decomposed for 30 min in the case of Ar, while slightly longer time is required to accomplish the decomposition in the case of He. Since this is not so marked difference, we are now examining reproducibility of this difference. However, the both results obtained with 3D IMSP show superior performance than that with conventional SP.

To investigate power efficiency for the MB decomposition, we have calculated energy efficiency η using following equation,

$$\eta\ (\text{mg/Wh}) = \frac{\Delta \text{MB}_{10\text{min}}\ (\text{mg})}{E\ (\text{Wh})}, \qquad (1)$$

where ΔMB_{10min} is the quantity of decomposed MB for the first 10 min, and E is consumed electrical energy which is calculated from voltage and current waveform. Calculated results are summarized in Table I together with the result for conventional SP. In both cases of Ar and He, their energy efficiency is superior than that of conventional SP. Since He gas is more expensive and is poor in its availability, we can conclude that 3D IMSP with Ar gas is better than that with He gas. Regarding the result that 3D IMSP with Ar gas shows higher decomposition rate than that with He, we are now examining its reproducibility.

Table I: Energy efficiency of the decomposition of MB molecules for the first 10 min treatment with 3D IMSP using Ar and He, and conventional SP

	Ar	He	Conv. SP
$\Delta MB_{10\ min}$ (mg)	0.40	0.23	0.048
E (Wh)	5.4	5.6	15
η (mg/Wh)	0.073	0.042	0.0032

4 CONCLUSION

We have demonstrated MB decomposition using a novel 3D IMSP reactor with Ar and He gases, and compared their energy efficiency to conventional SP. In both cases of 3D-IMSP treatments of MB aqueous solution with Ar and He gases, their energy efficiencies are approximately one order of magnitude higher than that of conventional SP treatment. Comparing 3D IMSP with Ar and He gases, 3D IMSP with Ar gas has shown slightly superior performance, although we must check its reproducibility.

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