GAS-LIQUID INTERFACIAL DISCHARGE WITH A POROUS GLASS MEMBRANE

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ABSTRACT

An underwater plasma source with a porous glass membrane which functioned in bubble supply and formation of micro-discharges was proposed. We first observed behaviour of bubbles and discharge emission on the surface of the membrane using a high-speed camera and a fiber spectroscope. Additionally, decomposition of acetic acid using an underwater plasma was evaluated. Compared with an ozone bubbling method, there was remarkable decrease in the acetic acid concentration. The results showed that our proposed underwater plasma could generate radicals and effectively decompose recalcitrant organic matter.

1. INTRODUCTION

Environmental purification technology using plasma has drawn much attention, and various studies have now been carried out energetically. Among them, advanced oxidation process (AOP) with hydroxyl radicals (OH) produced by the effective use of plasma is considered to be useful for water purification through oxidation. The OH radical is a powerful oxidizing agent, and high efficient process is expected.

We proposed an underwater plasma [1-2] with a porous glass membrane which functioned in bubble supply and formation of micro-discharges, i.e. gas-liquid interfacial discharges are generated inside bubbles formed at the surface of the porous glass membrane arranged in water. The discharges are in direct contact with liquid; therefore, OH radicals are easily formed.

There are some techniques to generate OH radicals by applying high electric field. The electrode surface is set parallel to the liquid surface and the generated discharge produces OH radicals by being in direct contact with water. Instead of the electrode, a plasma jet is possible to be used. For the case of setting a pair of electrodes in water, discharges are produced in bubbles in water. The bubbles are supplied by a membrane filter or a cavitation phenomenon. In addition, there are reports for bacterial inactivating examinations.

In contrast, a porous glass membrane supplies minute air bubbles in water for our proposed underwater plasma source, and the discharges are generated in pores and bubbles at the surface of the porous glass membrane. The following characteristics are expected,
(1) Discharges are in direct contact with water; therefore, OH radicals are easily formed.
(2) Transportation of generated O_3 is unnecessary, and then the downsizing of a plasma source is possible.
(3) Plural air bubbles can be supplied at the same time by using a porous glass membrane with a mean pore diameter of several tens μm, and then a large amount of OH radicals are produced.

In this study, we first observed bubbles and discharge emissions on the surface of a porous glass membrane using a high-speed camera and a fiber spectroscope. Additionally, dependence of gas pressure on generation of OH radical and decomposition of recalcitrant organic matter were examined.

2. EXPERIMENTAL SETUP

Figure 1 shows the experimental setup which consists of a reactor, a capacitor for measuring discharge power, a resistor, and a high frequency power source with FWHM of 3.2 μs of positive and negative pulses with frequency of 6 kHz.

The discharge voltage and the current were measured by a high voltage probe and a CT sensor, respectively. The discharge power was obtained by a *V*-*Q* curve, and unconsumed O_3 concentration from water was measured by an ozone monitor.

A reactor is composed from a porous glass membrane with a mean pore diameter of 20 μm and needle electrodes for applying high voltage. The needle electrodes allow us to be in closely contact with the porous glass membrane and to apply the operation gas. Discharges are formed in not only bubbles on the surface of the membrane but also pores of the membrane by applying high voltage to the needle electrodes; therefore, O_3 and radicals are generated. Figure 2 shows the cross section of a porous glass membrane with a mean pore diameter of about 20 μm, obtained with scanning electron microscopy (SEM). Pores with a diameter of 20 μm distribute uniformly. The diameter of our used membrane was 20 mm and the thickness was 0.6 mm. Bubble is generated when O_2 pressure is higher than a certain pressure defined as bubble point pressure (P_b). P_b is in inverse proportion to the pore diameter (D_m). For D_m = 20 μm, P_b is calculated as 110 kPa.

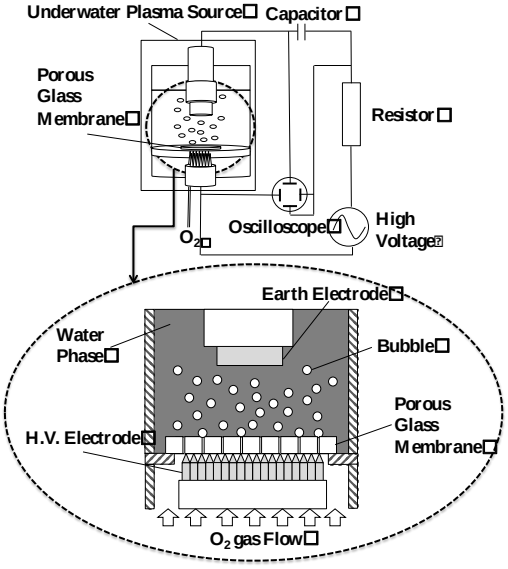


Fig. 1 Schematic diagram of experimental setup

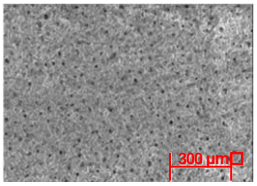


Fig. 2 SEM image of a porous glass membrane

Conductivity of treated water was set at 60μS/cm. Operating gas was O_2 or Ar. Bubble and water discharge were observed by a high speed camera (FASTCAM MC2.1) with a shutter speed of 500 fps (exposure time of 1998.2 μs), and optical emission was also observed by a fiber spectroscope (Ocean Optics Inc, USB4000).

For the examination of decomposition of acetic acid, 50 ml – solution of acetic acid (CH_3COOH) with a concentration of 1 ppm was used. The required oxidation potential to decompose acetic acid is more than 2.4 V; therefore, OH and O radicals can be expected to decompose the acetic acid. Here, not only OH and O radicals but also O_3 with a concentration of 200 ppm was supplied to the solution of acetic acid by generating plasma in the solution of acetic acid. As a parallel experiment to probe contribution of radicals, O_3 bubbles with 200 ppm generated by another ozonizer was supplied to the solution of acetic acid through a porous glass membrane. Additionally, to investigate contribution of OH radicals produced by an underwater plasma on the decomposition, we used Ar as the operating gas for plasma formation. The gas pressure was set to 118 kPa, and the applied voltage was adjusted to a certain value which could make the discharge current the same as that in the case where O_2 was used as the operating gas. Treated solution was evaluated with a total organic carbon meter (Shimazu, TOC-500). Radicals which may contribute on the decomposition are obtained through the following reactions.

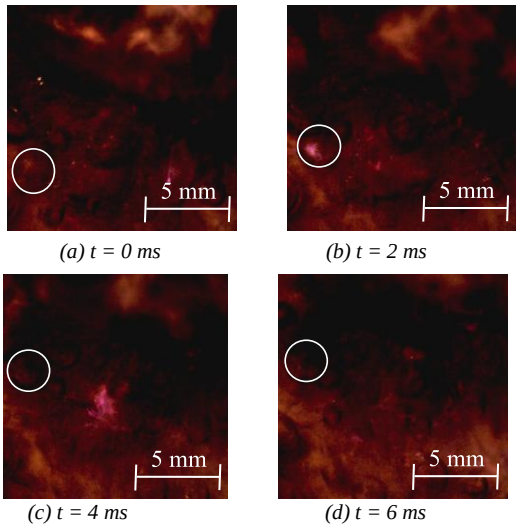
$$H_2O + e\ (> 6.4\ eV) \rightarrow H + OH + e \quad (1)$$
$$O + H_2O \rightarrow OH + OH \quad (2)$$
$$OH + OH \rightarrow H_2O_2 \quad (3)$$
$$Ar + H_2O \rightarrow Ar + H + OH \quad (4)$$

3. RESULTS AND DISCUUSSIONS

Figure 3 shows the underwater plasma observed by a high speed camera. The operating gas was Ar, which allowed us to make the observation of discharge easy. Circles in Fig. 3 denote the outlines of bubbles, and the bubbles at t = 0 ms, 2 ms, 4 ms, and 6 ms are the same ones. The diameter was about 1.5 mm. An obvious discharge is seen at t = 2 ms while that isn't seen at t = 0 ms. The discharge is disappeared; thereafter, another discharge can be confirmed at t = 4 ms. Thus, discharge, which is produced inside a bubble formed at the surface of the

porous glass membrane, is repeatedly generated inside the same bubble within several ms. Such discharges are observed at whole area of the porous glass membrane. The exposure time of our used high speed camera was 1998.2 μs while frequency of voltage source was 6 kHz (166.7μs). Assuming discharge is repeatedly formed more than 2 times in the same bubble as shown in Fig. 3, discharge emissions due to 24 times-discharges must be observed per flame.

Figure 4 shows discharge emission spectra. As can be seen from this figure, OH band spectra ($A^2\Sigma \rightarrow X^2\Pi$) at around 309 nm and O at 777.4 nm and 844.6 nm, H_α at 656.3 nm, and H_β at 486.1 nm are remarkable. Thus, not only OH band spectra but also spectra due to H_α, H_β are observed; therefore, it can be concluded that a reaction through Eq. (1) is achieved and that our proposed discharge source can produce OH radical by gas – liquid interfacial discharge.



(a) t = 0 ms *(b) t = 2 ms*

(c) t = 4 ms *(d) t = 6 ms*

Fig. 3 Appearance of discharge inside bubble generated by Ar gas

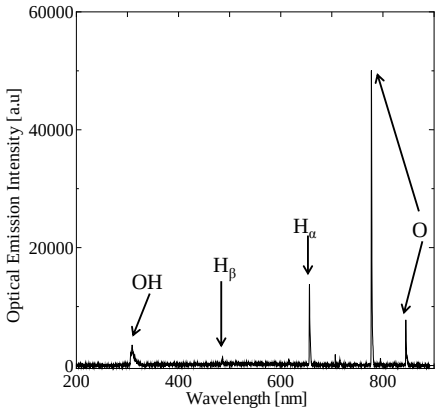


Fig. 4 Emission spectra from discharges in bubbles

Figure 5 shows relationship between discharge power and spectral intensity due to OH in the case where the applied voltage was kept at about 1.8 kV. Even though discharge power decreases with the increase of gas pressure, the spectral intensity increases. Waveforms of discharge voltage and current are shown in Fig. 6. Because the discharge voltage was kept, the number of discharge times at 118 kPa might become smaller than that at 112 kPa. Additionally, the discharge current becomes small because the reduced electric field becomes small. Thus, the electric power becomes small with the increase of gas pressure. However, the spectral intensity increases in spite of decreasing of electric power. This is probably due to pore distribution of a porous glass membrane. Pore diameter distributes in a range of 10 μm to 30 μm. P_b is in inverse proportion to pore diameter; therefore, bubbles from pores whose diameter are less than 20 μm begin to form by setting the gas pressure at higher than P_b. Then, the whole area of the surface of a porous glass membrane is almost covered with plasma.

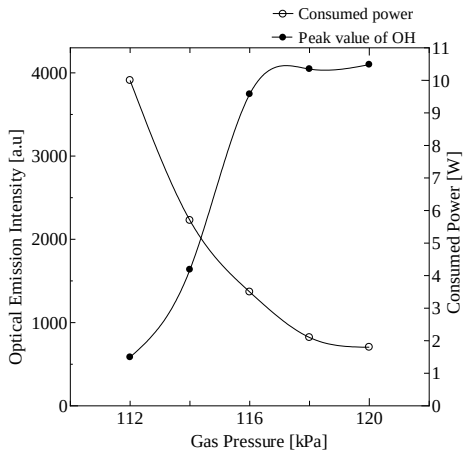
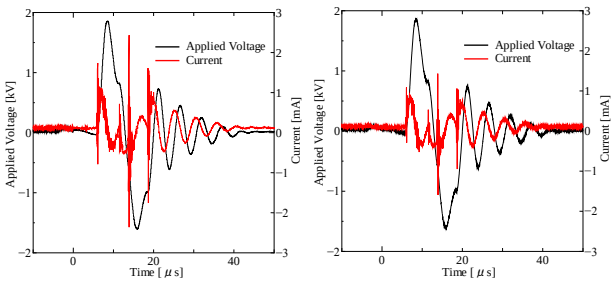


Fig. 5 Gas pressure dependence on OH intensity and electric power



(a)112 kPa *(b)118 kPa*

Fig. 6. Waveforms of voltage and current for 112 and 118kPa

As mentioned above, the reduced electric field and the electric power become low with increasing gas pressure; however, the area where discharges generated inside bubbles becomes large. The discharge emission at the area with a diameter of 5 mm on the surface of a porous glass membrane was integrated for measuring so that the increase in bubbles with discharges causes the increase of OH spectral intensity. There was not remarkable change in forming bubble more than 116 kPa. As the result, the spectral intensity of OH seems to reach a saturation value. Thus, effective generation of OH radical is expected by setting optimal gas pressure, which can carry out a OH-based-process for decomposing recalcitrant organic matter.

Figure 8 shows variation in concentration of acetic acid. ● and ▲ denote variations obtained by an O_3 bubbling and an underwater plasma with operating gas of O_2, respectively. ■ was obtained by an underwater plasma with operating gas of Ar. It can be seen that an O_3 bubbling method can't decompose acetic acid even for 60 min. The increase in H_2O_2 concentration for an O_3 bubbling method couldn't confirm while that for an underwater plasma treatment with Ar or O_2 increased to 2 ppm for 40 min. This indicates that O radical produced through decomposition of O_3 and OH radical produced through reaction between O and H_2O don't largely contribute to decomposition of acetic acid. On the other hand, the residual ratio after 30 min for an underwater plasma with operating gas of O_2 is about 60%. The decomposition is probable due to O and OH radicals produced by gas-liquid interfacial discharge. Also, the residual ratio after 40 min for an underwater plasma with operating gas of Ar is about 70%. Thus, it is indicated that contribution of OH radicals produced by electron – H_2O collision on the decomposition is large.

The decomposition efficiency was also evaluated. The required time for the decomposition when O_2 was used is shorter than that when Ar was used. However, the efficiencies for the cases of O_2 and Ar are 0.17 g/kWh and 0.23 g/kWh, respectively. For O_2 use, O_3 is generated as well as OH radical, i.e. decomposition efficiency becomes smaller than that for Ar use because energy from external electric field is also distributed to O_3 formation.

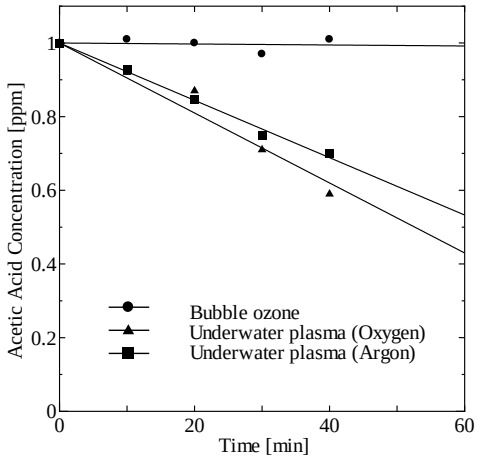


Fig. 8 Decomposition of acetic acid by an underwater plasma and an O_3 bubbling

4. CONCLUSIONS

To make the superiority of our proposed underwater plasma with a porous glass membrane clear, observations of bubble formation at the porous glass membrane surface and the discharges inside the bubbles were carried out. In addition, the influence of gas pressure on generation of OH radical and the decomposition of acetic acid were examined.

The observation results showed that gas-liquid interfacial discharges were formed inside bubbles formed at the surface of the glass membrane arranged in water and that OH radicals were generated by the discharges. The spectral intensity of OH depended on the gas pressure. Additionally, it was investigated that the decomposition of acetic acid due to OH radicals was effectively achieved by gas-liquid interfacial discharges.

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