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Mechanism of pH variation and H_2O_2 generation in water exposed to pulsed discharge plasma

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Abstract—Positive and negative pulsed discharge plasma is generated above test liquid containing NaCl in Ar atmosphere, and the spatiotemporal variation of pH value in the liquid is visualized by a colorimetric method using bromothymol blue. Furthermore, polarity effects on H_2O_2 generation are examined by electrochemical calculation and a colorimetric method using titanium sulfate. When the positive pulsed discharge plasma is generated, the pH value of the liquid is decreased by H^+ generation through the dissociation of H_2O^+, formed by the charge exchange reaction between Ar^+ and H_2O, while the pH value of the vicinity of an earthed electrode is increased by OH^- generation through the electrolysis of water. When the negative pulsed discharge plasma is generated, the pH value of the liquid is increased by OH^- generation and H^+ reduction respectively through the reaction of hydrated electrons with H_2O and H^+, while the pH value in the vicinity of the earthed electrode is decreased by H^+ generation through the electrolysis of water. The generation of H_2O_2 is found to be promoted when the positive pulsed discharge plasma is generated, and this increase rate of H_2O_2 is in approximate agreement with calculated generation rate of H_2O_2, which is produced from OH generated by electrolysis.

Index Terms—Plasma applications, Colorimetric method, Pulsed discharge plasma, pH measurement.

I. INTRODUCTION

NON-THERMAL atmospheric pressure plasma in contact with water has been widely studied for realizing a variety of plasma applications such as agriculture [1], [2], sterilization [3], [4], medicine [5], [6], food processing [7], nanoparticle fabrication [8], *etc*. In general, many kinds of reactive oxygen species (ROS), such as H_2O_2, OH, and HO_2 radicals, are produced in water by discharge plasma exposure, and these species have high oxidation potential; therefore, the water containing ROS contributes to disinfecting microorganisms [9] and decomposing organic dye [10], [11]. Furthermore, many kinds of reactive nitrogen species (RNS), such as NO_2^-, NO_3^-,and ONOOH, are produced in the water when the discharge plasma is generated in air. RNS have the effects of improving a plant growth rate [1], [12] and maintaining the flavor of food [7]. Since the efficiency of those applications is strongly affected by the kinds and the concentrations of ROS/RNS, these must be properly controlled.

In recent years, Ikawa *et al.* [13] and Lukes *et al.* [14] reported the bactericidal effects of water containing ROS/RNS and the production process of ROS/RNS by plasma exposure. Ikawa *et al.* exposed a low-frequency plasma jet to an aqueous solution containing *Escherichia coli*, and reported that the time to achieve one order reduction of *E. coli* colony number is reduced to one-tenth by decreasing the pH value of the solution from 5.2 to 3.7. It is also reported that the bactericidal effects may be caused by HO_2 radical in the solutions. Lukes *et al.* reported that an acidic aqueous solution enhances bactericidal

effects by ONOOH produced through the reaction of H_2O_2 with NO_2^-. Therefore, it is important to control pH value of water for improving bactericidal effects. Several groups reported the variation of pH value induced by plasma exposure to water. Shimizu *et al.* [15] generated discharge plasma above a methyl red aqueous solution in air, and reported that the decrease of pH value in the solution is caused by the production of H^+ through the dissolution of NO_x. Further, Tian and Kushner [16] computationally predicted that H^+ can be produced in water through the charge exchange reaction between positive ions, generated in plasma, and water molecules; however, the variation of pH value caused by the charge exchange reaction has not been demonstrated experimentally as far as we know.

In this work, pulsed discharge plasma with positive and negative polarities was generated above aqueous solutions in Ar atmosphere, and the spatiotemporal variations of pH value in the solutions were observed by a colorimetric method. Then, the process of the pH variation in the solutions was discussed on the basis of the observations. Furthermore, polarity effects on the concentration of H_2O_2 were examined using a colorimetric method and electrochemical calculation.

II. EXPERIMENTAL SETUP AND PROCEDURE

Figure 1 shows a schematic diagram of the experimental apparatus. A discharge chamber to generate the pulsed
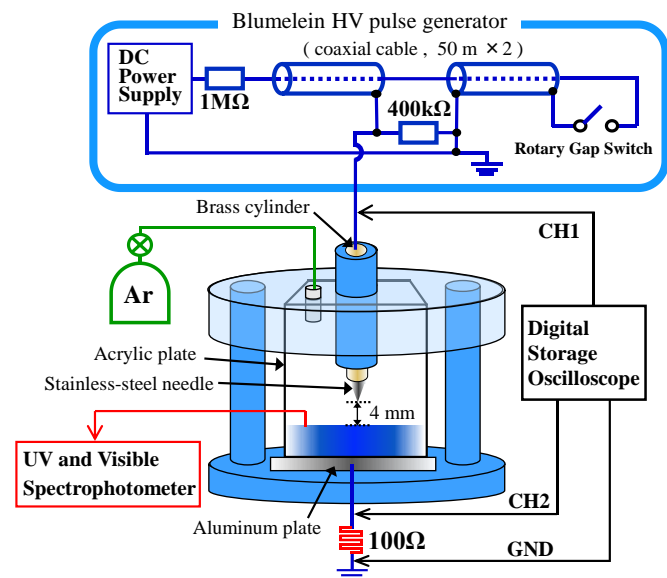

Fig. 1. Schematic diagram of experimental apparatus.

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discharge plasma consisted of a needle electrode and a liquid container. The needle electrode was made of stainless steel and had 4.0 mm in diameter and 30 mm in length. The liquid container consisted of a bottom planar electrode and four sidewalls. The bottom electrode was an aluminum square plate of 85 mm in width, which is earthed, and the sidewalls were made of acrylic resin with 85 mm in width and 90 mm in height. Test liquid was 200 mL of NaCl aqueous solution. The test liquid was poured into the liquid container, and the distance between the tip of the needle electrode and the liquid surface was fixed at 4 mm. To remove dissolved air in the liquid and prevent pH decrease due to the generation of nitrogen oxide from the air by plasma exposure, Ar gas, the purity of which is 99.99%, was sparged into the test liquid from a gas tube immersed in the test liquid, which is not illustrated in Fig. 1. After the sparging, Ar gas was fed into the liquid container at a constant flow rate of 1 L/min as an atmospheric gas, as shown in Fig. 1. A pulsed high voltage with a pulse width of 500 ns generated by a Blumelein pulse generator, which has two coaxial transmission lines (Fujikura 8D-2V) with a length of 50 m and capacitance of 5 nF, was applied to the needle electrode to generate the pulsed discharge above the test liquid. The coaxial transmission lines were charged to a negative and positive voltage of 14.14 kV, and the pulse repetition rate was 20 pulses per second, which corresponds to a duty cycle of 1.0×10^{-5}. The applied voltage was measured using a four-channel digital storage oscilloscope (Iwatsu DS-5524A) through a high-voltage probe (Iwatsu Test Instruments HV-P30). A discharge current was obtained by measuring the voltage drop across a non-inductive resistor connected in series between the bottom electrode and the earth, and the voltage drop was measured using the digital storage oscilloscope. The input power was calculated by multiplying the voltage across the gap and the discharge current, and the input energy was obtained from the time integration of the input power. The variation of pH value was visualized by bromothymol blue (BTB). BTB assumes greenish blue in a neutral aqueous solution, and the color changes to yellow bellow pH 6.0 and blue above pH 7.6. Titanium sulfate was used to visualize and determine H_2O_2 concentration. Titanium sulfate is in the form of titanium and sulfate ions in water, and titanium ions react with H_2O_2 to form peroxotitanium complex [17], which has peak absorption at 510 nm and assumes yellow. BTB of 3.84 µmol and 0.624 mmol of titanium sulfate were added to the test liquid to show color changes due to the variation of pH value and H_2O_2 production, respectively. The conductivity of the test liquid with BTB and titanium sulfate was set to 17 mS/cm by varying NaCl concentration. Titanium sulfate dissolved in the test liquid may be decomposed by the pulsed discharge plasma exposure, and this interferes with the accurate measurement of H_2O_2 concentration. Therefore, only the test liquid, the conductivity of which is 17 mS/cm, was exposed to the pulsed discharge plasma, and then titanium sulfate was added to the test liquid to measure H_2O_2 concentration. The absorbance of the test liquid was measured using UV/Vis spectrophotometer (SHIMADZU UV-1800), and the H_2O_2 concentration was deduced according to the Lambert-Beer's law. The color changes of the test liquid containing BTB and titanium sulfate were recorded from the front side of the liquid container using
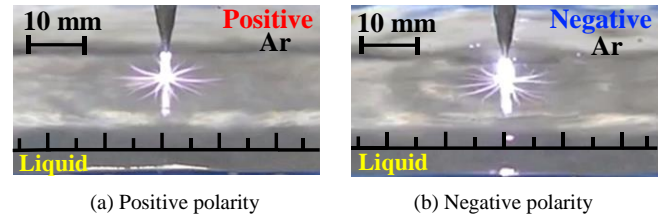

(a) Positive polarity   (b) Negative polarity

Fig. 2. Photographs of single pulsed discharge propagation.

(a) Positive polarity   (b) Negative polarity
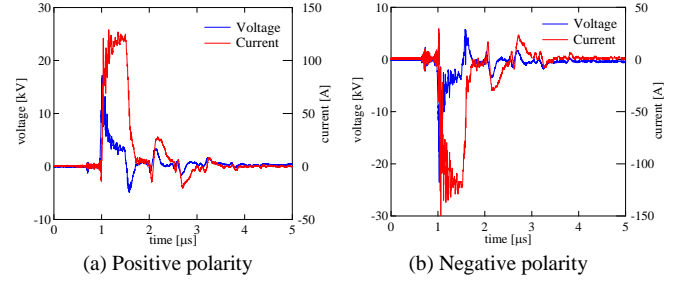
Fig. 3. Waveforms of discharge voltage and discharge current.

a digital camera (Canon EOS-Kiss X7) with an exposure time of 1/60 s and a flame rate of 30 fps.

III. CHARACTERISTICS OF PULSED DISCHARGE PLASMA

Figure 2 shows the representative photographs of a single pulsed discharge above the test liquid when the positive and negative pulsed voltages are applied, taken by the digital camera with an exposure time of 50 ms. The discharge plasma reaches the liquid surface, and then radially spreads approximately 10 mm over the liquid in both the polarities. No significant difference is observed in the branch length and the diameter of the discharges between the positive and negative pulsed discharge plasma. Figure 3 shows the typical waveforms of the discharge voltage and current when the positive and negative pulsed discharge plasma is generated. Input energies of the positive and negative pulsed discharge are 0.253 and 0.238 J/pulse, respectively. Therefore, the electrical characteristics of the positive and negative pulsed discharge are regarded as almost the same.

IV. VISUALIZATION OF PH IN TEST LIQUID

Figure 4 shows the color change in the test liquid containing BTB by the pulsed discharge plasma exposure. When the positive pulsed discharge plasma is generated, the color of the liquid below the discharge area turns yellow, and the colored area propagates downward at 2 s. The coloration indicates the decrease of pH value, namely, the generation of H^+. Tien and Kushner [16] predicted that H_2O^+ is produced by the charge exchange between positive ions in plasma and water molecules, and that H_2O^+ is dissociated into H^+ and OH in water. In the pulsed plasma generated here, argon atoms can be ionized by the collision with high-energy electrons, and then produced argon ions are transported to the test liquid surface, exchanging the charge with water molecule as follows:

$$e_{fast} + Ar \rightarrow 2e_{slow} + Ar^+ \qquad (1)$$

$$Ar^+ + H_2O_{aq} \rightarrow Ar + H_2O^+_{aq} \qquad (2)$$
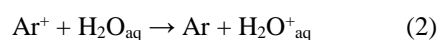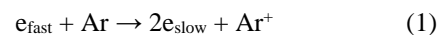
where the subscript $_{aq}$ denotes an aqueous species. Since $H_2O^+_{aq}$ is unstable in water, it is immediately dissociated into H^+_{aq} and OH_{aq} as shown in (3), resulting in the decrease of pH value.

$$H_2O^+_{aq} \rightarrow H^+_{aq} + OH_{aq} \qquad (3)$$

At 10 s, H^+_{aq} flowing downward penetrates to the earthed electrode, and then diffuses horizontally along the earthed electrode. At 30 s, the colored area expands by a vortex flow in the liquid, and the color of the liquid is widely changed to yellow by consecutive H^+_{aq} generation. At 300 s, most of the liquid color assumes yellow, while the liquid color in the vicinity of the earthed electrode assumes blue, indicating the pH value over 7.6. Considering the continuity of electric current, the current flows through the gas-liquid boundary and the liquid-electrode boundary simultaneously and equivalency; therefore, electron transfer may occur from the earthed electrode to the liquid, corresponding to positive ion transfer from the gas phase to the liquid phase as shown in (2). The electrolysis of water at the cathode, as shown in (4), can take place, and OH^-_{aq} can be generated.

$$e + H_2O_{aq} \rightarrow OH^-_{aq} + 1/2H_{2aq} \qquad (4)$$
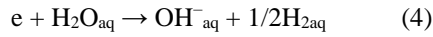
When the negative pulsed discharge plasma is generated, the color of the test liquid below the discharge area turns blue, and the colored area propagates downward at 2 s. This coloration indicates the increase of pH value, namely, the generation of OH^-_{aq}. Electrons, produced in the discharge plasma and transported to the liquid surface, dissolve into the liquid to form hydrated electrons e_{aq} as shown in (5) [18].

$$e \rightarrow e_{aq} \qquad (5)$$

Since the hydrated electrons have high reduction potential, the electrons induce the reduction reactions, as shown in (6) and (7), contributing to pH value increase [19], [20].

$$e_{aq} + H_2O_{aq} \rightarrow H_{aq} + OH^-_{aq} \qquad (6)$$
$$e_{aq} + H^+_{aq} \rightarrow H_{aq} \qquad (7)$$
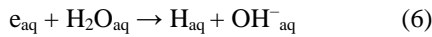
After 10 s, OH^-_{aq} behaves similarly to H^+_{aq} in the positive pulsed plasma exposure. Finally, most of the liquid color assumes blue, while the liquid color in the vicinity of the earthed electrode assumes yellow at 300 s. As shown in the case of positive pulse discharge, the electrolysis of water can take place at the anode, as shown in (8), and H^+_{aq} can be generated.

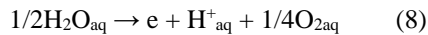$$1/2H_2O_{aq} \rightarrow e + H^+_{aq} + 1/4O_{2aq} \qquad (8)$$

Figure 5 shows the color change of the test liquid with BTB after 300 s of plasma exposure before and after stirring. The colors of the test liquid return to greenish blue after stirring, namely, the liquid become neutrality; therefore, the amounts of H^+_{aq} and OH^-_{aq} generated in the test liquid are found to be equal in both the polarities. It is found that the equal amounts of H^+_{aq} and OH^-_{aq}, as shown in the reactions (2)-(4) and (5)-(8) by positive and negative pulsed discharge, respectively, are generated to satisfy the continuity of electric current through the gas-liquid and liquid-electrode boundaries.

V. VISUALIZATION AND GENERATION OF H_2O_2

Figure 6 shows the color change of the test liquid containing titanium sulfate by the pulsed discharge plasma exposure.

Before discharge plasma initiation

At 2 s after discharge plasma initiation

At 10 s after discharge plasma initiation

At 30 s after discharge plasma initiation

At 300 s after the discharge plasma initiation

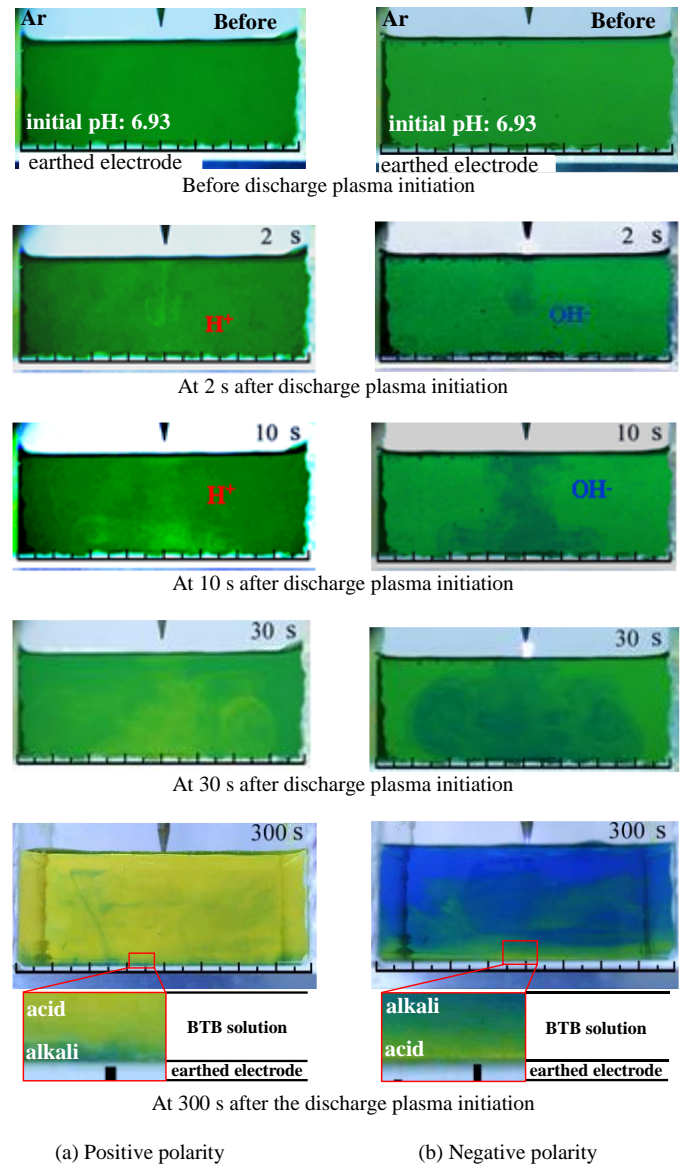(a) Positive polarity   (b) Negative polarity

Fig. 4. Color change of test liquid containing BTB by pulsed discharge plasma exposure.

Before stirring (after 300 s plasma exposure)

After stirring

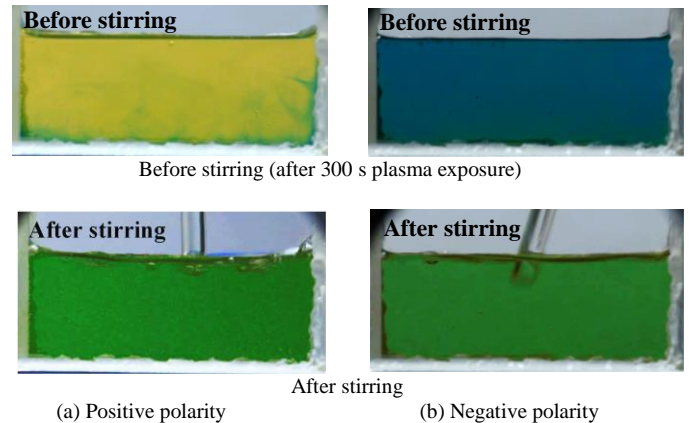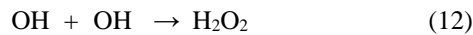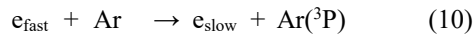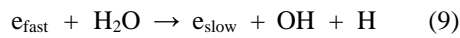(a) Positive polarity   (b) Negative polarity

Fig. 5. Color change of test liquid with BTB after 300 s of plasma exposure before and after stirring.

When the pulsed discharge plasma is generated, the color near the liquid surface turns slightly yellow at 30 s, and the color and its area tend to be thicker and wider at 120 s. Therefore, H_2O_{2aq} is found to be generated in the liquid surface. The colored area spreads horizontally near the liquid surface by consecutive H_2O_2 generation with the exposure time, but the color just under the needle electrode, where the discharge plasma develops, seems to be light. This is probably due to the decomposition of peroxotitanium complex by the pulsed discharge plasma. When the negative pulsed discharge plasmas is generated, the color is lighter than that in the positive pulsed discharge plasma exposure. Therefore, the H_2O_2 generation is found to be promoted in the positive polarity. When water is exposed to plasma, vaporized water molecules can be dissociated by the collision with high-energy electrons and metastable excited Ar atoms ($Ar(^3P)$) in the discharge plasma, as shown in (9) and (11) [21], [22]. H_2O_2 can be generated from OH by reaction (12), and dissolves into the liquid [23], [24].

$$e_{fast} + H_2O \rightarrow e_{slow} + OH + H \qquad (9)$$

$$e_{fast} + Ar \rightarrow e_{slow} + Ar(^3P) \qquad (10)$$

$$Ar(^3P) + H_2O \rightarrow Ar + H + OH \qquad (11)$$

$$OH + OH \rightarrow H_2O_2 \qquad (12)$$

$$H_2O_2 \rightarrow H_2O_{2aq} \qquad (13)$$

As mentioned above, the electrical characteristics of the discharge are almost the same between the positive and negative polarities, so that the amounts of H_2O_2 generated in gas phase, as shown in (12), may be equivalent in both the polarities. In addition to the above H_2O_2 generation, H_2O_{2aq} may be generated from OH_{aq}, which is generated by the reaction (3) when the positive pulsed discharge plasma is generated. This results in the deeper color shown in color change at 120 s after the positive discharge plasma initiation in Fig. 6.
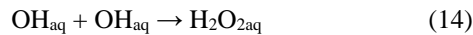
$$OH_{aq} + OH_{aq} \rightarrow H_2O_{2aq} \qquad (14)$$

Figure 7 shows the H_2O_2 concentration in the test liquid as a function of plasma-exposure time. The H_2O_2 concentration increases in proportion to the exposure time, and the H_2O_2 concentration in the positive polarity is higher than that in the negative polarity. The difference of H_2O_2 generation rates between the positive and negative polarities is obtained to be 41.7 nmol/(L·s). Assuming that H_2O_{2aq} is generated from OH_{aq} through the reactions (1)-(3), the generation rate of H_2O_{2aq} can be obtained from the electrochemical calculation. The electric charge transfer from the gas phase to the liquid phase is obtained to be 1.53 mC/s from the time integration of the discharge current as shown in Fig. 3(a), so that the generation rate of $H_2O_{aq}^+$ is calculated to be 15.9 nmol/s on the basis of Faraday's first law; therefore, the generation rate of H_2O_{2aq} is stoichiometrically obtained to be 7.95 nmol/s. This rate is equivalent to 39.8 nmol/(L·s) of H_2O_{2aq} generation rate in 200 mL of the test liquid. The calculated H_2O_{2aq} generation rate is in approximate agreement with the measured H_2O_2 generation rate. This confirms the validity of the H_2O_{2aq} generation process from OH_{aq}, produced by the electrolysis of water, when the positive pulsed discharge plasma is generated.

Before discharge plasma initiation

At 30 s after discharge plasma initiation

At 120 s after discharge plasma initiation

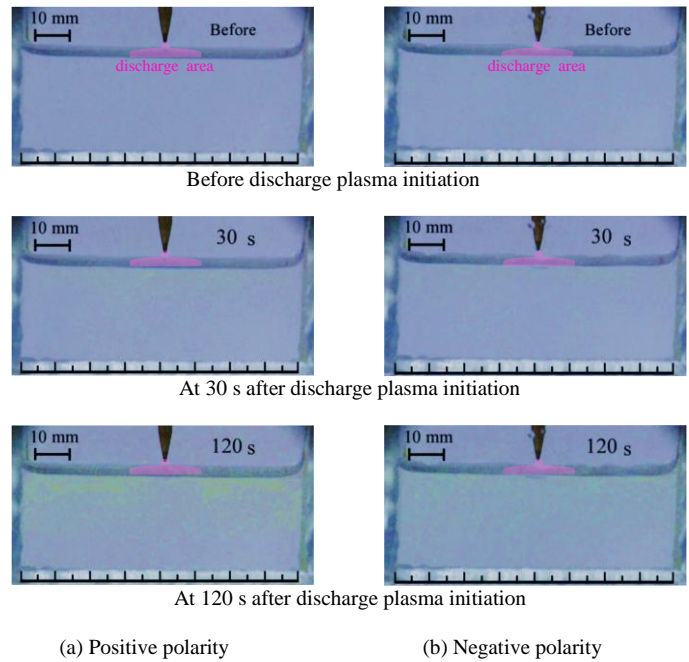(a) Positive polarity   (b) Negative polarity

Fig. 6. Color change of test liquid containing titanium sulfate by pulsed discharge plasma exposure. (The figures is adjusted to -20% brightness, +20% contrast and 200% colorfulness.)
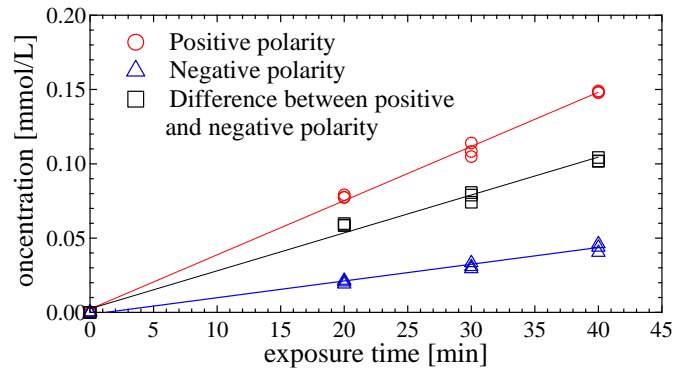

Fig. 7. H_2O_2 concentration in test liquid as a function of plasma-exposure time.

VI. CONCLUSION

The variations of pH value and H_2O_2 concentration in the test liquid, exposed to pulsed discharge plasma with positive and negative polarities in Ar atmosphere, were visualized by a colorimetric method. It was found that the charge exchange reaction and the reaction of hydrated electron play important roles in the variation of pH value and H_2O_{2aq} generation. When the positive pulsed discharge plasma was generated, the pH value of the liquid began to decrease by H_{aq}^+ generation through the charge exchange reaction. At the same time, OH_{aq}^- generation by the electrolysis of water at the cathode occurred, resulting in the increase of pH value in the vicinity of the earthed electrode. When the negative pulsed discharge plasma was generated, the pH value of the liquid began to increase by OH_{aq}^- generation and H_{aq}^+ reduction respectively through the reaction of hydrated electron with H_2O_{aq} and H_{aq}^+, while the pH value was simultaneously decreased in the vicinity of the earthed electrode by H_{aq}^+ generation through the electrolysis of water at the anode. Furthermore, H_2O_2 generation was found to be promoted when the positive pulsed discharge plasma was

generated, and this increase rate was in approximate agreement with the calculated generation rate of H_2O_{2aq}, which is produced from OH_{aq} generated by the electrolysis of water. This confirmed that the pH variation induced by the charge exchange reaction as well as the electrolysis of water takes place to satisfy electrical current continuity when the pulsed discharge plasma is generated.

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