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Generation of reactive species in atmospheric pressure dielectric barrier discharge with liquid water

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Abstract

Atmospheric pressure helium/water dielectric barrier discharge (DBD) plasma is used to investigate the generation of reactive species in a gas–liquid interface and in a liquid. The emission intensity of the reactive species is measured by optical emission spectroscopy (OES) with different discharge powers at the gas–liquid interface. Spectrophotometry is used to analyze the reactive species induced by the plasma in the liquid. The concentration of OH radicals reaches 2.2 μm after 3 min of discharge treatment. In addition, the concentration of primary long-lived reactive species such as H_2O_2, NO_3^- and O_3 are measured based on plasma treatment time. After 5 min of discharge treatment, the concentration of H_2O_2, NO_3^-, and O_3 increased from 0 mg $\cdot$ L^{-1} to 96 mg $\cdot$ L^{-1}, 19.5 mg $\cdot$ L^{-1}, and 3.5 mg $\cdot$ L^{-1}, respectively. The water treated by plasma still contained a considerable concentration of reactive species after 6 h of storage. The results will contribute to optimizing the DBD plasma system for biological decontamination.

Keywords: atmosphere pressure dielectric barrier discharge plasma, gas–liquid discharge, electrical characteristics, reactive species

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric pressure plasma has recently attracted increasing attention due to their broad range of applications such as in the fundamental investigation of plasma sterilization [1–9], cell treatment [10, 11], polymer treatments [12, 13] as well as the degradation of organic pollutants in water [14, 15]. Previously, the research was mainly related to the electrical characteristics of plasma discharge in dry environments. Optical emission spectroscopy (OES) and mass spectroscopy (MS) were used to detect the formation of reactive species. However , in many cases, water will be involved in the discharge process. In practical biomedical and environmental applications, such as the inactivation of microorganisms and the degradation of organic pollutants in liquid, the presence of water will affect the discharge process. The reactions of the reactive species induced by plasma at the gas–liquid interface will finally determine their production in liquid. Particularly, reactive species such as, OH, O radicals, H_2O_2, NO_3^-, and NO_2^- in an acid environment induced by plasma in liquid are generally considered to have an important relationship to the mechanisms involved. Lukes *et al* demonstrated that an electrical discharge plasma at the gas–liquid

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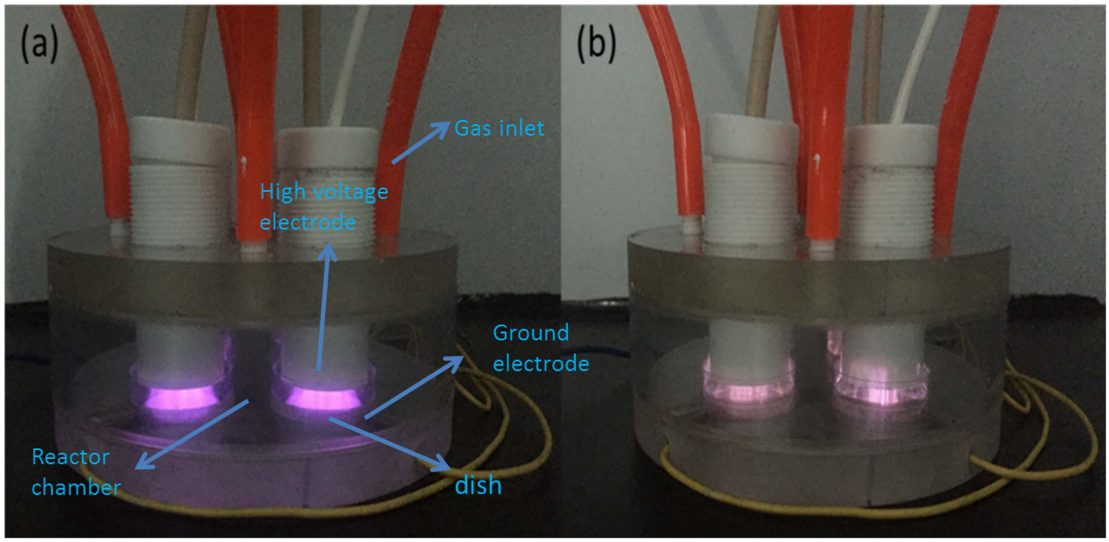

Figure 1. (a) Image of the DBD helium discharge and (b) the DBD helium/water discharge.

interface induced reactive species such as OH, H_2O_2, NO_3^-, and O_3 in the liquid, which has potent effects on microorganisms [16]. Liu *et al* revealed that a surface air discharge can induce aqueous reactive species mainly including H^+, nitrate, nitrite, H_2O_2, and O_3 in liquid via computational and experimental methods [17].

Despite the process of gas–liquid discharge and the generation of reactive species in liquid having been explored, the interaction of gas discharge plasma with liquid is a complex physicochemical process. The kinds and concentrations of reactive species in the gas and liquid phase are key issues, which are closely related to better sterilization and treatment efficiency.

In this paper, a self-made multi-electrode DBD plasma device was used to explore the generation of reactive species in the gas–liquid discharge process. The different properties of pure helium and helium/water plasma discharge were analyzed by the oscilloscope. The emission intensity of a variety of reactive species in the gas phase is determined by OES. The short-lived hydroxyl concentration was detected using the fluorescent probe method. The concentration of reactive species in water (NO_3^-, O_3, and H_2O_2) was analyzed by spectrophotometer analysis.

2. Experimental set-up

2.1. Atmospheric pressure DBD plasma source

An image of the set-up used in the study is presented in figure 1 together with the images of the helium discharge and helium/water discharge. There are four DBD plasma reactors in a hollow plexi-glass cylinder (reactor chamber) and four stainless steel cylinders (diameter 32 mm) are used as the high voltage electrode. Quartz glass (with a thickness of 1 mm), as the insulating dielectric barrier, was used to cover the high voltage electrode. A stainless steel cylinder (diameter 37 mm) served as the grounded electrode. Working helium (99.99% pure) gas at a flow rate of 80 standard liters per hour (SLH) was introduced through a gas inlet. The reactor chamber was purged with helium for 5 min to eliminate air from the reactor chamber as much as possible before the experiment. In the case of helium discharge, empty dishes were placed on the grounded electrode, and in the case of the helium/water discharge, 3 ml of deionized water were added into the dishes. The applied voltage and discharge current in the atmospheric pressure helium DBD plasma were recorded by a Tektronix MSO 5104 digital oscilloscope. The waveforms of the applied voltage and discharge current were measured via a 1000:1 high voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021) respectively.

2.2. Monitoring of reactive species at gas–liquid interface and in deionized water induced by plasma

The reactive species at the gas–liquid interface induced by DBD plasma were diagnosed by a AvaSpec-2048-8-RM spectrometer with a grating of 2400 grooves/mm, and the wavelength ranged from 200–900 nm. The helium/water discharge plasma induced the short-lived and long-lived reactive species. In this paper, terephthalic acid (TA) was used to measure the concentration of the short-lived OH radical based on reference [18]. The TA was dissolved in an NaOH-containing deionized aqueous solution. Briefly, the initial concentrations of the TA and NaOH were 0.2 mm and 1.4 mm, respectively. Additionally, TA is a known OH scavenger which does not react with O_2^-, or O_3, HO_2, and H_2O_2 [19, 20]. TA will react with an OH radical to produce 2-hydroxyterephthalic acid (HTA), which can be detected by a fluorescence spectrometer (Cary Eclipse, Varian, USA) with the excitation/emission wavelength of 310 nm and 425 nm, respectively.

The four main long-lived reactive species, such as hydrogen peroxide, ozone, and nitrite were measured in the DBD plasma-treated deionized water. The four relevant test kits 18 789, 00 607, 09 713, and 00 609 were added into the plasma-treated water, respectively. The water treated with the kits was measured spectrophotometrically by the PhotoLab 6100 (WTW, Germany). The measured methods were guided by the manufacturer's manual and had been used successfully before to measure the concentration of reactive species [21, 22].

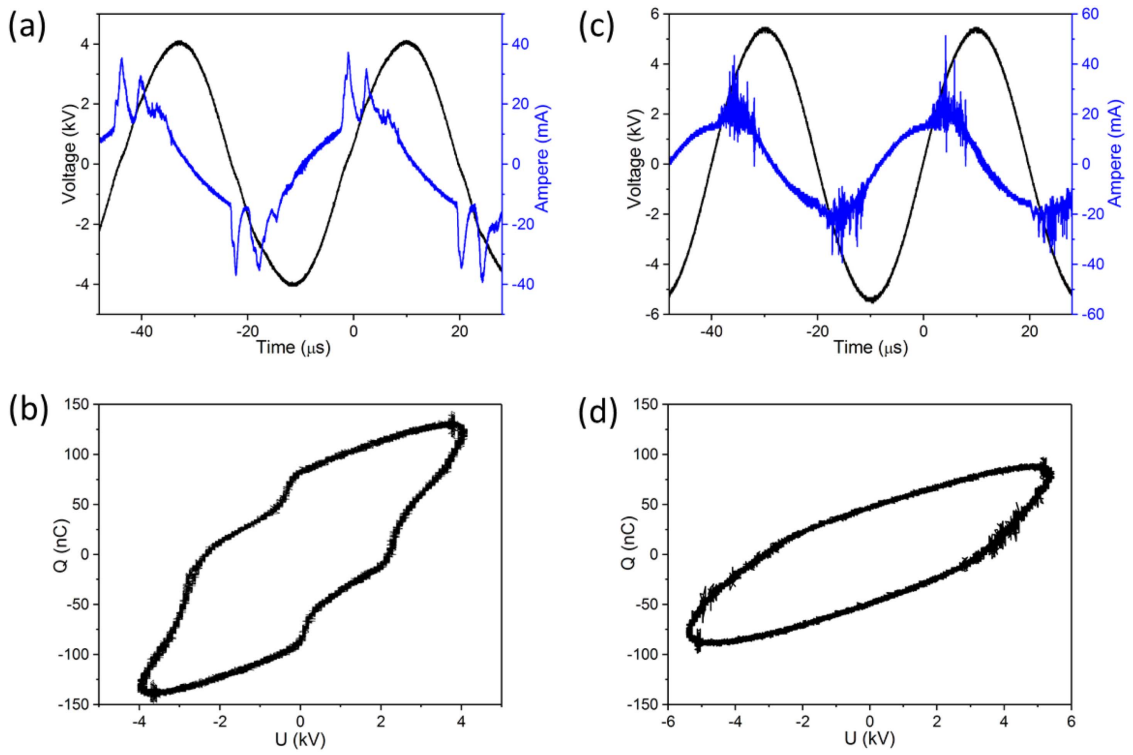

Figure 2. Voltage and current waveforms and the Lissajous figure of the helium discharge and helium/water discharge in the case of the same power.

3. Results and discussion

3.1. Electrical characteristics

In order to distinguish the characteristics of the helium discharge and the helium/water discharge, an oscilloscope combined with the Lissajous method was used to monitor the DBD plasma discharge. From the discharge images displayed in figure 1, it can be observed that the helium discharge is homogeneous, whereas the helium/water discharge is obviously filamentous. Correspondingly, it can also be seen that the current and voltage waveforms of the helium discharge are different from those of the helium/water discharge (figure 2). Two obvious peaks appear on the current waveform with a duration of about 3.5 μs in the helium discharge. By comparison, the discharge at the helium/water gas–liquid interface results in more narrow current filaments [12]. Correspondingly, this difference is also shown in the image of the Lissajous figure in figures 2(b) and (d). The current peak corresponds to the charge transfer process in the Lissajous figure. The Lissajous figure of the helium discharge shows big steps, whereas the helium/water discharge exhibits an approximate standard parallelogram. This difference is mainly due to the fact that the greater the current filament peaks are, the smaller step is as shown by the Lissajous figure [23, 24]. Therefore, the Lissajous figure of the helium/water discharge is mostly a standard parallelogram.

As shown in figure 3, the minimum discharge power reaches 11.2 W in pure helium with a peak to peak voltage of 6.4 kV. The discharge power increases with the applied voltage and finally the power reached up to 37 W (the peak to peak voltage is 11 kV). In contrast, the discharge at the helium/water gas–liquid interface leads to a decrease in the discharge power, and the main reason is the contraction of the discharge current [25]. It also can be observed that the voltage under the helium/water discharge condition is higher at the same power. The result is due to the presence of water, so a higher breakdown voltage is required between the two electrodes at the same power.

3.2. OES

The optical spectra of the DBD in the helium with water were acquired to investigate the reactive species generated in the gas–liquid interface during the discharge process. As shown in figure 4(a), many active species lines are plotted by the optical emission spectrum, such as OH (309 nm), main He lines (501 nm, 587.6 nm, 667.8 nm, 706.6 nm), H lines (H_β 486.1 nm and H_α 656.3 nm) and atomic oxygen O line (777.2 nm). Additionally, under the helium/water discharge condition, the optical spectral emission intensity is also measured with the change in the discharge power. From figure 4(b), the intensity of the emission lines firstly increases with the power. More energy is provided to the gas–liquid discharge reaction with the increasing power, thereby the intensity of emission line of the reactive species increases with the discharge power. With the increase in the discharge power from 30–35 W, the concentration of water vapor in the reactor chamber increases due to the increase in discharge power intensity. When the concentration of the water vapor reaches a high level, a substantial part of the electron energy will transfer to the water vapor and decrease the electron temperature due to the collision between the electron and water in the discharge process. The decrease in electron

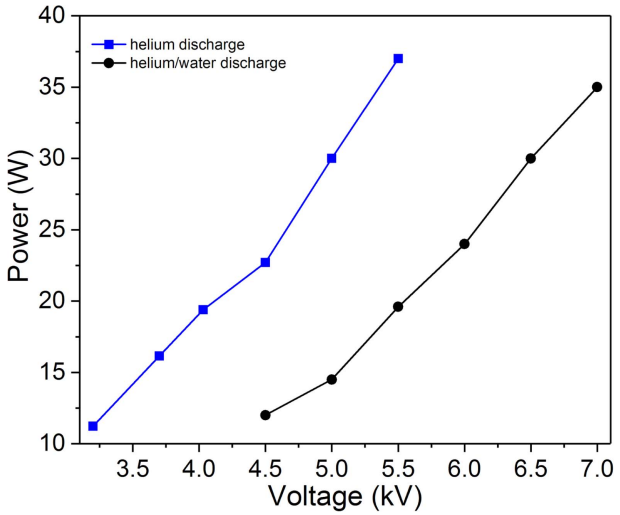

Figure 3. The discharge power as a function of the applied voltage.

temperature will inhibit the generation of reactive species [25, 26]. These active species induced by plasma will result in some continuous reactions with other particles to produce more reactive species in the liquid. The maximum intensity of the reactive species can contribute to improved plasma efficiency for sterilization or water treatment by adjusting the discharge parameters.

3.3. Formation of reactive species in liquid

In many studies, reactive species such as hydroxyl radical, hydrogen peroxide, nitric acid, and ozone have been shown to play an important role in the inactivation of microorganisms [27, 28].

The OH radical has a strong oxidation potential of 2.8 V, which is greater than the oxidation potential of 2.4 V of oxygen atoms [29]. The OH radical can act directly with the microorganisms in the water. The mechanisms of the generation of the OH radical are as follows [26]:

$$e^- + He \rightarrow e^- + He^* \quad (1)$$

$$He^* + H_2O \rightarrow He + OH(A) + H \quad (2)$$

$$e^- + H_2O \rightarrow H + OH(A) + e^- \quad (3)$$

$$OH(X) + e^- \rightarrow OH(A) + e^- \quad (4)$$

$$O + H_2O \rightarrow OH\cdot \quad (5)$$

Figure 5 reflects the change in the concentration of the OH radical. The concentration of the OH radical increases with plasma treatment time when the discharge time reaches 3 min, the concentration of the OH radical reaches the maximum, and then the concentration decreases. However, the measured pH of the solution is lower than 6 at this time and exceeds the test range (the pH test range is 6–11). Therefore, the concentration of OH at 5 min can only be used as a reference value. Additionally, although H_2O_2 will be produced in the plasma discharge process, whose effect on the measurement of OH concentration is weak. In reference [20], Shiraki *et al* analyzed the effect of H_2O_2 formation on the concentration of OH. It was confirmed that the influence of the formation of H_2O_2 on the measurement of the OH radical

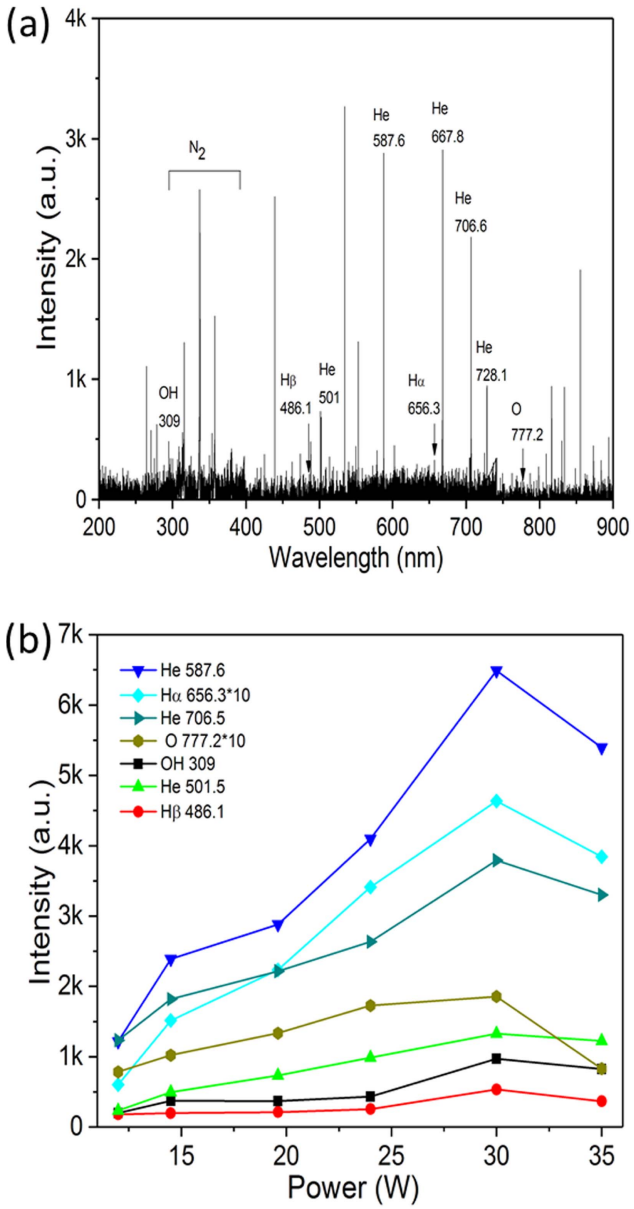

Figure 4. (a) OES under the condition of DBD helium/water discharge (the power is about 20 W), (b) The intensity of emission lines of the excited species as a function of discharge power.

concentration can be almost ignored and the reaction of the TA with the OH radicals played a dominant role.

The pH value and the concentration of NO_3^- are shown in figure 6. The concentration of NO_3^- increased with plasma treatment and finally reaches 19.5 mg · L^{-1}. The NO_3^- generates an acidic environment in the liquid and correspondingly leads to a decrease in the pH value [30, 31]. The NO_3^- in the liquid can be generated by the following series of reactions [8, 32].

$$N_2 + e^- \rightarrow 2N + e^- \quad (6)$$

$$N + O \rightarrow NO \quad (7)$$

$$NO + O \rightarrow NO_2 \quad (8)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (9)$$

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \quad (10)$$

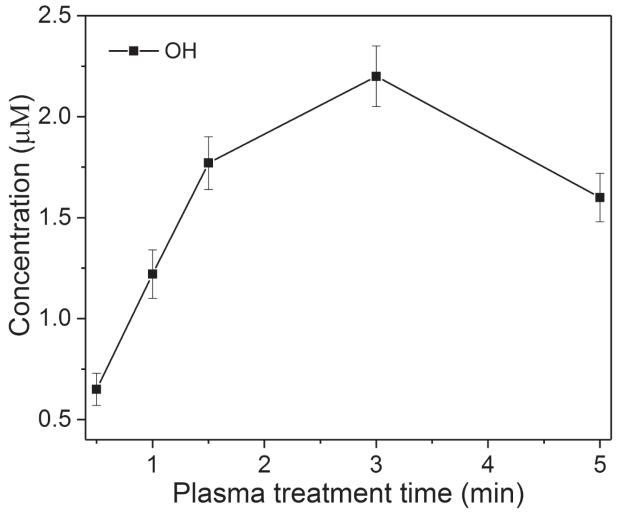

Figure 5. The concentration of OH radicals as a function of plasma treatment time.

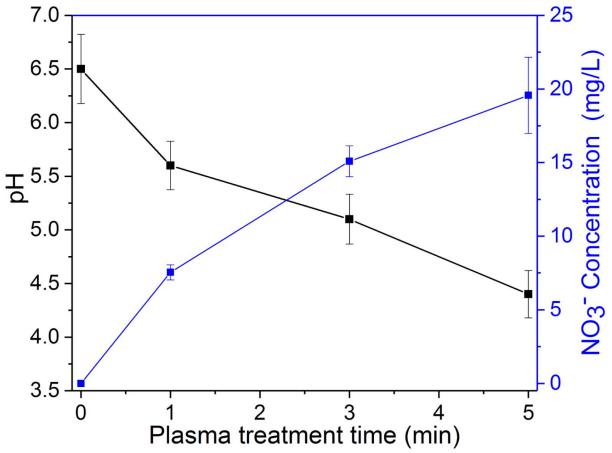

Figure 6. The concentration of NO_3^- and pH value as a function of plasma treatment time.

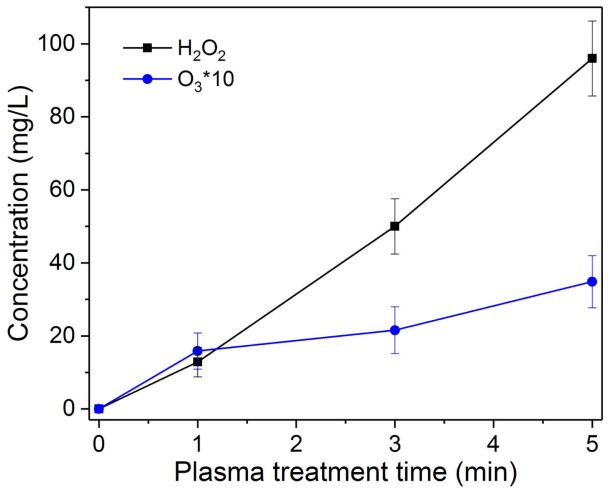

Figure 7. The concentration of H_2O_2 and O_3 as a function of plasma treatment time.

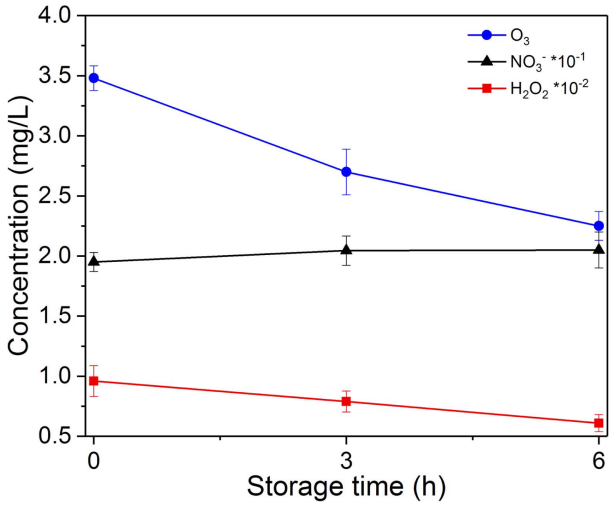

Figure 8. The concentration of the reactive species corresponding to storage time.

$$N_2^+ + H_2O \rightarrow NO + H \quad (11)$$

$$N_2O + H_2O \rightarrow HNO_3 \quad (12)$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3. \quad (13)$$

Besides NO_3^-, O_3, and H_2O_2 are also detected in liquid. The varieties of the concentrations with discharge time are shown in figure 7. After 5 min of plasma treatment, the concentration of hydrogen peroxide increased from 0–96 mg $\cdot$ L^{-1} and the ozone concentration increased from 0–3.5 mg $\cdot$ L^{-1}. At the gas–liquid discharge interface, the reactions of the generation of ozone and hydrogen peroxide are as follows [33–36]:

$$O_2 + e^- \rightarrow 2O + e^- \quad (14)$$

$$e^- + H_2O \rightarrow 2H + O + e^- \quad (15)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (16)$$

$$H_2O + e^- \rightarrow H_2O^+ + 2e^- \quad (17)$$

$$H_2O^+ + H_2O \rightarrow OH + H_3O^+ \quad (18)$$

$$OH + OH \rightarrow H_2O_2 \quad (19)$$

$$O + H_2O \rightarrow H_2O_2 \quad (20)$$

It has been reported that plasma-treated liquid has continuous effects on the inactivation of microorganisms [37]. To determine the content of residual reactive species in the liquid, the 5 min plasma-treated liquid is kept for 6 h and the changes in the concentrations are displayed in figure 8. The concentrations of H_2O_2 and O_3 has an obvious decrease. The concentration of H_2O_2 reduced from 96–61 mg L^{-1} and the concentration of O_3 reduced from 23–3.5 mg $\cdot$ L^{-1}. When the water treated by plasma was stored for 6 h, some decomposition reactions occurred that led the concentration of O_3 and H_2O_2 in the liquid to decrease. The produced O_3 in the liquid occurred in some reactions and led to decomposition [36, 38, 39].

$$O_3 + H_2O_2 + OH^- \rightarrow OH \cdot + HO_2 \cdot + O_2 + OH^-. \quad (21)$$

The decomposition of hydrogen peroxide can lead to the formation of molecular O_2 [36].

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2. \quad (22)$$

Additionally, O_3 and H_2O_2 also react with other reactive species in the liquid, such as NO_2^-. This will contribute to increasing the concentration of NO_3^- [38].

$$H_2O_2 + NO_2^- \rightarrow NO_3^- + H_2O \quad (23)$$

$$O_3 + NO_2^- \rightarrow O_2 + NO_3^-. \quad (24)$$

It can be observed from figure 8 that the concentration of NO_3^- represents a weak increase, which is from the oxidation of NO_2^-.

4. Conclusion

The electrical characteristics and reactive species in the gas–liquid and liquid phase of atmospheric pressure gas–liquid DBD plasma are investigated. The use of an oscilloscope and the Lissajous method are combined to show the difference between the characteristics of helium/water and pure helium discharge. The optical emission spectral lines confirm the presence of some reactive species during the discharge process. Furthermore, it is observed that the water concentration in the reaction device increases with the increase in discharge power, and the intensity of the reactive species exhibits a tendency to decrease after increasing. In addition, the concentrations of the reactive species in the liquid are detected by a spectrophotometer and fluorescence spectrometer in this paper. The plasma-treated water still contains a considerable concentration of reactive species after 6 h of storage. The obtained results are helpful in the optimization of the DBD plasma system for biological decontamination.

Acknowledgments

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