Nitrogen Fixation in Water Using Air Phase Gliding Arc Plasma

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Treatment of irrigation water using plasma involves a series of electrochemical reactions that forms NOx− in water working as a fertilizer in plant cultivation. Here we report the results of an experimental study of the effects of different discharge conditions especially discharge frequency on air phase gliding arc discharge. The results show that, the low-frequency system consumed nearly three times more energy than the high-frequency system while generating the same NOx− production rate in water; gas flow rate has strong influence on the low-frequency system while slight influence on the high-frequency system; high-frequency discharge can generate much larger plasma area to promote electrochemical reactions resulting more NOx− produced in water. Frequency from 5 kHz to 80 kHz does not significantly influence on the nitrogen fixation of gliding arc.

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Nitrogen is an essential element in chlorophyll, DNA, RNA, and amino acids of plants. Nitrogen fertilizer, a much needed nutrient for growing crops, is made from ammonia produced by the Haber-Bosch ammonia synthesis process. Nitrogen fixation via the traditional Haber-Bosch method represents an energy-intensive and environmental-destructive process, and ammonia has been identified as one of the 18 chemical compounds contributing to 75% of greenhouse gas (GHG) emissions. To reduce negative environment footprints by the traditional Haber-Bosch process, the fertilizer industry has been long looking for alternative options of producing ammonia as nitrogen fertilizers in agriculture application. Industrial plasma processing is one novel method demonstrating a great potential to be developed as an alternative technique for nitrogen fixation. In more recent years, generation of nitrogen in aqueous solution has been demonstrated with various discharges, including spark, gliding arc, glow, corona, and dielectric barrier discharge. Oxygen nitrogen water mixture used in irrigation significantly influences plant growth phase working as a fertilizer in plant cultivation. Takaki et al. applied a magnetic pulse power generator with 250 pps repetition rate as the power supply and found the growth rate of Chinese cabbage increased significantly by treating drainage water with underwater discharge. Alex Lindsay et al. developed a unique low-voltage large-volume glow discharge with 162 MHz frequency power supply. The method was capable of generating plasma activated water, demonstrating statistically significant positive effects on plant height, sprouts per pot, leaf span and shoot mass on the growth of radishes, marigolds, and tomatoes. Park et al. compared three discharge methods: submerged spark discharge at an average frequency of 5 Hz; transferred gliding arc discharge and gliding arc plasmatron powered with DC supply. Their results showed that most plants grew better with the non-thermal gliding arc plasmatron discharge than submerged spark discharge and transferred gliding arc discharge. However, considering limited pressure and power levels, conventional glow discharge seems to represent potential weaknesses for large scale agricultural applications. Characterized with operating at atmospheric pressure and high dissipated power (up to 75–80%) at non-equilibrium conditions, particularly with low cost and simplicity, gliding arc discharge shows a prior in nitrogen fixation comparing with the above-mentioned techniques. In agreement with superiority of gliding arc discharge, a series of experiments were carried out using air phase gliding arc discharge in this study. While the literature for plasma treatment of aqueous phase with gliding arc discharge is extensive, there are few reports on the influence of power frequency on NOx− production. In this paper, a wide range of power supply frequencies from 50 Hz to 80 kHz influence on NOx− production in plasma treated water and arc characteristics were investigated. Therefore, the objective of the study is to provide an experimental basis for improving efficiency of the gliding arc plasma nitrogen fixation by controlling discharge conditions.

Experimental

Plasma experiment system.—The gliding arc reactor, fabricated of acrylic material, was cylinder with a diameter of 105 mm and a height of 150 mm. As the raw material for nitrogen fixation reactions, dry air with 39% relative humidity was continuously supplied from the bottom of the reactor using an intake pump. The electrodes consisted of a pair of stainless steel diverging knives (120 mm long, 30 mm wide and 4 mm thick) which were fixed on a base plate. During the discharge, arc is firstly ignited at the shortest gap between the electrodes, then glides up and stretches to break up under the air blowing. The gliding arc is a non-thermal plasma, which produces reactive oxygen (O3) and reactive nitrogen species (NO, NO2). The plasma was extracted out from the top of the reactor by another pump and injected into the gas absorber containing 150 mL deionized water in a conical flask. This pump was aimed at increasing nitrogenous gas dissolution in water. An experimental system of gliding arc discharge was designed as illustrated in Figure 1. The low-frequency gliding arc discharge system generated a 50 Hz voltage using an adjustable transformer (0.22/50 kV) connecting with a current limiting resistor (40 kΩ, 600 W) providing protection for the transformer. The high-frequency gliding arc system was powered by a high frequency high voltage generator (f: 5–90 kHZ, Pk-Pk voltage: 0–40 kV,C.TP-2000K PLASMA GENERATOR, Nanjing Suman Plasma Technology Co., Ltd) with a built-in current limiting inductor.

Experimental method and design.—Experiments were designed to investigate the primary factors in gliding arc nitrogen fixation process: (1) to compare digital waveforms of gliding arc discharge between 50 kHz and 50 Hz; (2) to compare discharge phenomena by capturing images among 50 Hz, 10 kHz and 50 kHz; (3) to analyze the influence of NOx− production with different power supplies (power supply of high frequency: 21.30–77.77 W, power supply of low frequency: 231.39–505.68 W), gas flow rate (1.2–3.2 L/min) and frequency (5–80 kHz). In the third part, the transport time of single gliding arc was defined as the period starting from its ignition to extinction. And it was measured with different gas flow rates. A power meter was employed to measure the total input power of plasma systems. An in-line glass rotameter with a maximum range of 5 L/min was applied to monitor the gas flow rate.

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The applied voltages were monitored by a high voltage probe (Tektronix P6015A); the currents were measured according to the voltages across a very low resistance (1 ohm, non-inductive) by oscilloscope probe. All the waveforms were sampled by a digital oscilloscope (Tektronix TPS2024B). The temperature contour maps of electrodes were captured by a Thermal Imager (Agilent U5855A True IR) 10 minutes after each discharge. Other discharge images were taken with the NIKON D7000 digital camera on a black background. NO$_x$ production was measured under different input powers, gas flow rates, and frequencies, respectively. In order to investigate which frequency of the power supply would be more efficient, the production rate per watt was defined as the quotient of production divided by input power, and its unit was mg/L/watt. A high-speed video camera (iPhone 5s, 120 fps) was used to record the transport time of arc, and the precision is 5%. The plasma gas absorption time in deionized water was set as 10 minutes. Ultraviolet spectrophotometer (UV2450, SHIMADZU) was used to measure the concentration (mg/L) of the NO$_x$ in plasma treated water; the resolution of concentration was less than 0.1 μg/L. It should be noted that all experiments were repeated three times and the data averaged.

Results and Discussion

Discharge waveforms differed significantly between high frequency and low frequency. Figure 2a shows the typical voltage and current waveforms in the high frequency powered discharge process (50 kHz, 100 W, and 3.2 L/min). The amplitude of voltage across the electrodes constantly changed within the scope, where the minimum value corresponded to the firstly ignited arc, and the maximum value indicated the extinction of arc. The current (RMS value: 0.91 A) of Figure 2a were non-sinusoidal waveforms superposed by pulsed peaks. However, in Figure 2b, powered by low-frequency supply (50 Hz, 350 W, 3.2 L/min), the voltage varied significantly from 50 kHz AC waveforms when the discharge occurred. Instead, each discharge aroused a pulsed voltage peak, which was superposed on the AC voltage; the current (RMS value: 0.06 A) was nearly in phase with the voltage, and contained pulsed current peaks as well. The voltage across the resistor was very close to that of the power supply, which indicated that the current limiting resistor consumed the majority energy of the plasma generation system, resulting in a very low efficiency. Since discharge currents were low under both types of power supply, gliding arc was considered as non-thermal plasma.

Three groups of images are presented in Figure 3, and each group in column includes a snapshot of gliding arc at a shutter speed of 1/100 second, a gliding arc area image captured with long exposure time of 2 seconds, and a temperature contour map of electrodes. The left group (Figure 3a) was with 50 Hz power supply (350 W, 3.2 L/min); the middle (Figure 3b) was with 10 kHz power supply (100 W, 3.2 L/min); and the right group (Figure 3c) was with 50 kHz power supply (100 W, 3.2 L/min). It was found that the discharge phenomena with low-frequency power supply apparently differed from that with high-frequency power supply. The low-frequency gliding arc only
concentrated in the lower half of the air gap between the electrodes, while the high-frequency gliding arc covered the entire air gap. Therefore, it denoted that high-frequency gliding arc has relatively larger reaction region than that in low-frequency gliding arc. The maximum temperature with 50 Hz, 10 kHz and 50 kHz power supply was 82.2 °C, 98.9 °C, 88.8 °C after a 10-minute discharge, respectively, which were all based on the same initial temperature of 20.7 °C. High-frequency gliding arc showed a slightly higher maximum temperature than low-frequency gliding arc, because the current of the high-frequency discharge was greater than that of low frequency, resulting in more energy dissipated in electrodes as denoted in Figure 2. Besides, the maximum temperature of 10 kHz was somewhat higher than that of 50 kHz, because the former case offered a greater current resulting from its lower reactance ($X = 2\pi fL$) of the built-in inductor. The maximum temperature positions were different depending on the frequency. For example, a hottest spot of 50 Hz gliding arc was at the middle edge of each electrode, while for the high-frequency gliding arc, the hottest spot shifted to the tip of each electrode. The phenomena present an instructive significance for the electrodes heat dissipation design.

**Influence factors for the NOx$^-$ production in water.**—When gliding arc discharge occurred, NO and NO$_2$ were formed via the reactions of energetic electrons with gaseous N$_2$ and O$_2$ in the gas phase:13

$$N_2 + e \rightarrow 2N + e \quad [1]$$

$$O_2 + e \rightarrow 2O^* + e \quad [2]$$

$$N + O^* \rightarrow NO \quad [3]$$

$$NO + O^* \rightarrow NO_2 \quad [4]$$

Then NO$_3^-$ and NO$_2^-$ ions could be generated from the dissolution of NO$_2$ and NO into the liquid phase. Once ions (NO$_3^-$ and NO$_2^-$) reacted with H$_2$O, then HNO$_3$ and HNO$_2$ were formed,14 as shown in Equations 5–8:

$$3NO_2 + H_2O \rightarrow 2H^+ + 2NO_3^- + NO \quad [5]$$

$$2NO_2(g) \rightarrow 2N_2O_4 + H_2O(l) \rightarrow HNO_3 + HNO_2(l) \quad [6]$$

$$NO_2(g) + NO(g) + 2H_2O \rightarrow 2HNO_3(l) \quad [7]$$

$$3HNO_2(l) \rightarrow HNO_3 + 2N_2O_3(g) + H_2O(l) \quad [8]$$

Table I gives experimental data of NOx$^-$ production in water under 50 Hz and 5 kHz with different power supplies. All the gas flow rates were fixed at 3.2 L/min. In general, the NOx$^-$ production increased with the increase of input power under both frequencies. The two maximum productions were measured as 5.328 mg/L with 77.77 W, 5 kHz and 3.211 mg/L with 505.68 W, 50 Hz respectively. Figure 4 shows the two trends of production rate per watt. The trends were unlike that of the NOx$^-$ production shown in Table I; there existed a maximum value with the specific power. Therefore, to get the highest efficiency of nitrogen fixation, input power should be adjusted to the maximum value with the maximum production rate per watt. High-frequency plasma system had significantly higher production rate per watt than low-frequency system, because of the existing of the current limiting resistor installed in the low-frequency system, which consumed the majority of energy and resulted in lower production efficiency. In addition, the high-frequency gliding arc showed a larger discharge region than low-frequency gliding arc, contributing to gliding arc more thoroughly exposed to air, and producing more energetic electrons.

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**Table I. Experimental data of NOx$^-$ production with different powers and frequencies.**

| No. (#) | Power (W) | Production (mg/L) |
|---------|-----------|--------------------|
| 5 kHz   | 50 Hz     |                    |
| 1       | 21.30     | 0.216              |
| 2       | 34.86     | 1.455              |
| 3       | 48.47     | 3.724              |
| 4       | 58.63     | 5.105              |
| 5       | 69.77     | 5.200              |
| 6       | 77.77     | 5.328              |
| 50 Hz   |           |                    |
| 1       | 231.39    | 0.985              |
| 2       | 286.64    | 1.730              |
| 3       | 340.28    | 2.621              |
| 4       | 372.58    | 3.159              |
| 5       | 449.26    | 3.544              |
| 6       | 505.68    | 3.211              |
which were apt to the positive reaction (Equations 1–8). Replacing the resistor with an inductor in the low-frequency system for current limiting may greatly reduce the waste of energy, but the employment of inductor may inevitably increase the weight and volume of the apparatus. Hence, high-frequency plasma system represents relatively higher energy efficiency and compact structure.

On the conditions of different gas flow rates of the pumped-in air, NO$_x$ productions in plasma treated water and transport time were measured with high frequency (5 kHz, 100 W) and low frequency (50 Hz, 350 W) groups (Figure 5). The arc could not be blown out when the gas flow rate was lower than 1.2 L/min, because a continuous short-circuits between electrodes caused the failure of expected arc gliding motion. Figure 5a shows that gas flow rate had slight influence on the production rate in the high-frequency system, and this production ranged from 5.105 mg/L to 5.501 mg/L, with the highest production of 5.501 mg/L as the gas flow rate was 3.2 L/min. Conversely, gas flow rate affected the production rate considerably in low-frequency system. The production apparently reduced with the flow rate increasing. In Figure 5a, there was a broad range of production from 2.448 to 5.182 mg/L with the 1.2 to 3.2 L/min gas flow rate. Figure 5b indicates that gliding arc under high-frequency case had a longer transport time than the low-frequency case, thus a longer reacting time with the ambient air, which accounts for the higher productivity of NO$_x$ of high-frequency system. With the increasing of the gas flow rate, the transport time gets shorter under both frequency cases.

Figure 6 shows the influence of different frequency conditions on NO$_x$ production using high-frequency system (100 W, 3.2 L/min). There were no significant changes in NO$_x$ production rate when the frequency increased from 5 kHz to 80 kHz, indicating frequency does not significantly influence on the production of nitrogen fixation in this case. On the other hand, since the high-frequency system has the built-in current limiting inductor in plasma generator, higher frequency apparatus may bring another benefit in reducing the volume.

Experimental phenomena in this study are consistent with the mechanism of arc formation. Arc extinguishes instantaneously when its current reaches zero crossing point, and re-striking may occur immediately if the recovery voltage rises faster than the insulation level of air gap, otherwise, arc column will not appear again. For low-frequency arc, its interval time between extinction and re-striking is relatively longer than that of high frequency, therefore it is more easily blown out by air flow. Conversely, high-frequency arc readily sustains its column because of the shorter interval time. The mechanism may explain why high-frequency arc gets a larger discharge region. Furthermore, as the frequency rises to high value region, in which the difference in the interval time will contribute little to the features of high-frequency gliding arc, such as 5–80 kHz in our experiments. As a result, it is observed nearly identical experimental phenomena with high frequency cases. However, the process from quantitative changes to qualitative changes. The critical frequency will be necessarily investigated in the future.
Operating at atmospheric pressure and ambient temperature, gliding arc discharge is easy to be applied to agriculture. Power consumption of high-frequency gliding arc nitrogen fixation system is relatively low, hence it may be supplied by solar energy, which is green and environmental friendly. High-frequency gliding arc nitrogen fixation with solar panels is potentially expected to provide fertilizers for remote places and/or small farms in the near future. The solubility of gas products in the water was low which resulted that most gas products escape from liquid to atmosphere. For this reason, we are improving the absorption device to increase the production of NO$_3^-$ in water. The growth promoting effects for plants with plasma treated irradiation water will be verified in the following study.

**Conclusions**

Significant differences between low-frequency and high-frequency system were observed. High-frequency system is prior to the low frequency in the following aspects: low energy consumption, small volume, high efficiency of reaction, and insensitivity to gas flow rate. To generate the same NO$_3^-$ production in water, the low-frequency system consumed nearly three times more energy than the high-frequency system. It is found that frequency from 5 kHz to 80 kHz does not significantly influence on the nitrogen fixation based on air phase plasma method of gliding arc. The NO$_3^-$ production increased with the input power in either high-frequency or low-frequency system. Gas flow rate has a strong influence on the low-frequency system while little influence on the high-frequency system. The discharge images illustrate that high-frequency discharge can generate much larger plasma area to promote adequate reaction.

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