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DIRECT WATER TREATMENT BY APGD WITH ROTATING ELECTRODES

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The APGD with rotating star-shaped electrodes was applied directly to the surface of liquid as a counter electrode. It was shown that the rotation of electrodes enables the stabilization of the discharged. A high concentration of H_2O_2 and nitrates were measured. The high level of microbial reduction was shown for inoculated deionized water treated by APGD with rotating electrodes.

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INTRODUCTION

The Atmospheric Pressure Glow Discharge (APGD) is one of the most widely used sources of Low-Temperature Nonequilibrium Plasma, which has found broad industrial applications including gas and water treatment, chemical conversion and materials synthesis, food processing and medicine [1]. Visually APGD divides into two zones: bright – ionization layer and glowing – diffuse/drift zone [2]. Near a sharp electrode, a strong electric field forms a narrow ionization layer, in which enough charged particles are generated for the self-sustaining development of the discharge. The diffuse zone with a relatively low electric field covers the remaining (biggest) part of the discharge gap. The complex plasma-chemical processes, as well as the transportation of charged particles to the electrode, occur in the diffuse zone. APGD has attracted the attention of many researchers [3] because the entire discharge gap operates as a plasma-chemical reactor and provides chemical reactivity at low gas temperature. However, APGD has one significant weakness, it is an uncontrollable transition/contraction of the discharge from the volume discharge mode to the spark mode with a thin hot discharge channel. Such a transition to the spark has a destructive effect on the electrodes, changes the variety of generated reactive species and remains an exceptional challenge both for experimental studies and for many emerging applications.

There are three common practices to control early transition to the spark. They are: (i) ballast resistors in discharge circuit, (ii) high speed gas flow, and (iii) very short pulse duration of applied HV. Ballast resistors are used to prevent sparks by reducing the voltage across the discharge gap when the discharge current exceeds a predetermined limit. Laroussi et al. [4] realized stable APGD by using suitable material with resistivity in the range of $10^9 \ldots 10^{10}\,\Omega$ instead of using dielectric layer normally used in Dielectric Barrier Discharge. The high-speed gas flow has a more complex effect on the discharge. Akishev et al. [5] used point-to-sphere electrode geometry and a fast gas flow to produce APGD by DC negative corona discharge. They studied in detail the effect of the electrode geometry and gas flow velocity on the transition of corona-to-glow and glow-to-spark mode in ambient air. They demonstrated that a high-speed gas flow disperses the charged cloud formed in the discharge gap and reduces its shielding effect; additionally, the gas and the electrode surface are cooled down by the gas flow, helping to keep the ionization rate at its lowest level. Typically, the APGD with high-speed gas flow works for applications requiring large volumes of gas to be treated with a relatively low concentration of active species. The short HV pulse duration (usually a range of nanoseconds) with the short voltage rising time is a relatively new and very effective method to generate APGD, however this technic requires a complex HV pulsed power supply with pulses of nanoseconds range which has a poor power efficiency (usually less than 50%). Moreover, EMI shielding is a challenge for these HV short pulse power generators.

All these three methods for the discharge stabilization are currently being used in a broad range of practical applications. However, as highlighted in the report "The 2022 Plasma Roadmap" [3], novel and expanding fields of applications for low-temperature plasma require the development of new and unique low-temperature plasma sources with high energy efficiency, specifically, capable operated with liquid electrodes and/or in high humidity plasma-forming gases.

In conventional APGD systems, when the electrodes are stationary, upon application of high voltage across the electrodes, the ionization of gases begins in vicinity of the tip of the sharp electrode, and then the ionization front propagates through the discharge gap either in the form of a streamer or in the form of an ionization wave. However, due to the weakness of the electric field at a distance from the sharp electrode, i.e., in the diffuse zone, the electrons begin to attach to molecules and atoms forming a charged cloud that shields the sharp electrode, and the ionization around the sharp electrode comes to the end until the charged cloud disperse and decay, and then the shielding effect comes to the end and the cycle will be repeated again. Because the mobility of ions and charged molecules is low, the next discharge cycle will develop and pass along the same discharge channel that was formed in the previous discharge cycle. The repeated pass through the same channel will heat the channel, the pressure in the channel will drop and ionization will increase, and, as result, the spark breakdown occurs. Although details of the spark breakdown mechanism remain unclear, the above-described mechanism of the thermal instability for a spark is well established. As the transition of APGD to

the spark has unpredictable behavior, a major challenge for many low-temperature plasma applications is to keep the APGD stable and operating at high specific power input.

In this article, the innovative Atmospheric Pressure Glow Discharge with Rotating Electrode will be examined for the direct plasma water treatment. Over the conventional stationary electrode discharge system, the rotating electrode has a significant advantage. The rotation of electrodes allows stabilization of the discharge, shifts the glow-to-spark transition towards higher voltage and increases the specific energy input to the discharge. The physical phenomena behind these advantages can be explained as follows. When the electrode rotation speed is higher than the ion drift velocity, the tips of the sharp electrodes surrounded by the ionization layer will run away from the diffuse zone of the discharge, increasing the electrical resistance of the discharge gap and, therefore, continuing to stabilize the discharge. In addition, the tips movement will elongate and rupture the discharge channel, preventing the formation of a spark. Further, the electrode movement through the gas will lead to cooling down of the electrode tips and mixing of the gas in the discharge gap. Thus, a plasma system with rotating electrodes can potentially be a promising way to suppress thermal instability in a low-temperature plasma-chemical reactor. This is especially relevant for the discharge with liquid electrodes and high humidity plasma-feeding gases.

EXPERIMENTAL SET-UP

To study the effect of direct treatment of water by APGD, a device with rotating electrodes was built. The device includes a shaft with a set of star-like electrodes; reactor housing; overflow bath/tray; water tank; recirculation water pump; an electric motor with gears joined to the shaft and HV power supply unit connected to the rotating shaft. Fig. 1 shows the schematic drawing of the developed device.

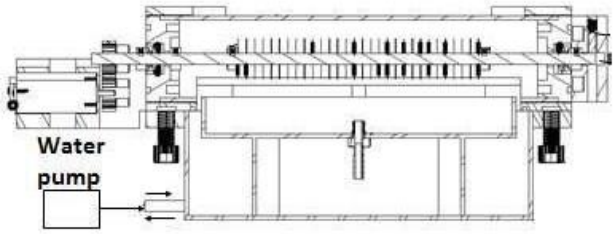

Fig. 1: The schematic of the experimental system with rotating electrodes

The set of star-like electrodes disposed radially along the longitudinal axis of the plasma-chemical reactor and individual star-like electrodes separated with spacer from one another. The shaft with a set of star-like electrodes is rotationally supported in the isolated reactor housing by a pair of bearings, one end of the shaft joined to the electrical motor through a gearbox with 1:1 ratio. The gears are made from insulating material to provide electrical isolation for the motor. The power regulator module sets the rotation speed for star-like electrodes up to 10000 RPM. The bottom part of the reactor housing is open to allow discharge above the water surface of the overflowing bath. The water overflows to the water tank and then the recirculating pump continuously pumps water back to the overflowing bath to keep the water level stable, as well as a distance between tips of rotating electrodes and water surface. The total water volume was 4.4 liters, the rate of recirculating pump is 3 lpm. An electrical contact for a high voltage supply is provided at the other end of the shaft with star-like electrodes. The adjustable DC high voltage power supply (0…20 kV, 0…5 mA) with positive polarity was used to power the plasma-chemical reactor.

The current and voltage signals from the reactor were gathered by the high voltage probe Tektronix P6015A and current probe Tektronix CT2 and were analyzed with oscilloscope Tektronix TDS 3034. The digital power meter KUMAN KW-47 was used to control the total power input to the plasma-chemical reactor. The electrode rotation speed was controlled with the digital laser tachometer EXTECH 461920-NIST, range 2-99.000 RPM. The temperature and humidity were measured by the thermo-hygrometer Michell Instruments MDM25.

To test water parameters the following devices and kits were used: Thermo Scientific Orion Star A211 pH Meter with 9165BNWP Sure-Flow pH electrode and 927007MD ATC probe; Myron L Ultrapen PT1 EC/TDS 1-9999 μS or ppm; Hach Water Quality Test strips: Nitrate 0…50 ppm, Nitrite 0…3.0 ppm; WaterWorks Hydrogen peroxide test strips 0.5…100 ppm (0.5-2-5-10-25-50-100 ppm); Chemetrics Dissolved Ozone Meter with Vacu-vials Kit I-2019 0-5.0ppm.

RESULTS AND DISCUSSION

Plasma-Liquid surface interaction is an emerging and fast-growing topic of the Low Temperature Plasma research because they offer unique conditions that enable decontamination of pathogens, synthesis of nanomaterials, and treat of contaminated water. Plasma-Liquid discharge makes a very complex impact on the water surface such as charged particles, UV photons, electric field, reactive species (O_3, OH, NOx). Result of such interaction is the saturation of interfacial water layer with ozone, reactive oxygen species and reactive nitrogen species, hydrogen peroxide, increasing of acidity and mixing of the water, all this together give a strong effect on water contaminants, including high oxidative stresses on bacteria and other pathogens [6]. But the challenge with keeping a steady Plasma-Liquid Discharge is that the surface of the liquid is extremely unstable due to the electric field and the influence of the ionic wind. Further, the water surface is also unstable due to the water flowing through the reactor. Waves on the water surface lead to fluctuations in the height of the discharge gap and an early transition of the glow-to-spark.

As was mentioned above, one of the new and most promising methods to stabilize the Plasma-Liquid Discharge is the rotation of the electrodes. Let's make the estimation of the threshold velocity which is required to stabilize the discharge. Because the rotation of electrodes should suppress the thermal instability, the rotation speed of electrode pins should be higher compared to the ion drift velocity. The ion mobility in air at atmospheric pressure, μ, is estimated to be in the range of

1.5…2.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$ depending on the humidity [7]. The electric field in the diffusing zone of the discharge is typically in a range 3…5 $kV \cdot cm^{-1}$. Therefore, the estimation for average ion drift velocity is $(5…10) \cdot 10^2$ $cm \cdot s^{-1}$. When the electrode has a diameter of 65 mm, the tips of electrodes get a velocity of $10 \cdot 10^2$ cm/s if the rotation speed is 3000 RPM. For the same electrode with the diameter of 65 mm, at rotation speed 6000 RPM, the velocity of the electrode tips will be $20 \cdot 10^2$ $cm \cdot s^{-1}$, which is greater than the speed of a charged cloud decay in the diffused zone, associated with an ion drift velocity of $(5…10) \cdot 10^2$ $cm \cdot s^{-1}$. New streamers or ionization waves will be formed in the fresh/low ionized air, which should prevent the development of thermal instability that occurs due to the propagation of multiple streamers along the same channel. The stable running APGD with rotating electrodes above the water surface is shown in Fig. 2.

Fig. 2. Prototype reactor with rotary electrode with liquid counter electrode

As mentioned above, the APGD above the water surface is very effective in generating active particles. As an example, the variation in discharge characteristics and water parameters during the treatment of deionized water with a total volume of 4.4 l using positive polarity APGD with a rotating electrode above the water surface is shown in Table 1. The total treatment time was 360 min, measurements and samples were taken after 0, 30, 60, 90, 120, 240, and 360 min.

Table 1

Plasma and water characterization during direct water treatment by APGD with rotating electrodes, rotation speed – 4400 rpm

Treatment time, min	**0**	**30**	**60**	**90**	**120**	**240**	**360**
I, mA	0	2.4	2	2	2	2	2
V, kV	0	15.2	15.3	15.3	15.6	15.6	15.6
Power, W	0	49	47	48	47	47	46
pH	6	6	5.5	5	5	4.5	4.5
EC, uS/cm	40	120	186	240	305	496	740
H_2O_2, ppm	0	1	4	7	10	17	20
NO_3, ppm	0	3	5	10	12	25	30
NO_2, ppm	0	0	0	0	0	0	0
O_3, ppm	0	0	0	<0.5	<0.5	<0.5	<0.5
T_{water}, °C	26	29	32	33	33	36	35

The concentration of the dissolved ozone in the plasma treated water is very low, less than 0.5 ppm (see Table 1), due to the suppression of ozone synthesis under the high humidity condition and low ozone transfer rate through the water surface compared to gas-water mixing system, for example, Venturi injectors. Further, the presence of strong oxidizers (H_2O_2 and O_3) in water makes the nitrite concentration (NO_2-) almost zero.

The concentration of nitrates (NO_3-) and hydrogen peroxide (H_2O_2) in treated water is given in Table 1 and shown in Fig. 3.

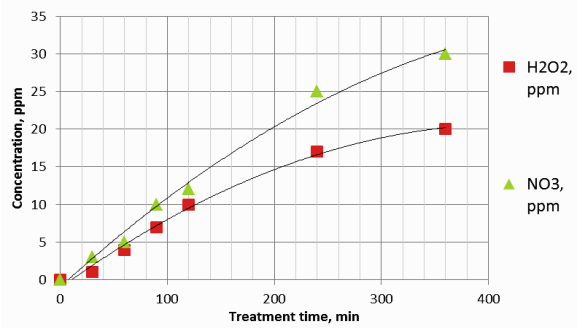

Fig. 3. Variation of concentration H_2O_2 and NO_2 in the deionized water exposed to APGD. Total water volume is 4.4 l. Average discharge power is around 50 W

It was expected that nitrate would accumulate in the water and that the concentration of nitrates (NO_3-) would increase with treatment time, but the concentration of hydrogen peroxide was surprisingly high. This can be explained by the high humidity conditions in the discharge and may indicate the presence of the high concentration of OH-radicals [8].

During treatment, the temperature of the water slowly rises because of the heating from the discharge and submersible recirculation pump. Fig. 4 shows the variation in pH and electrical conductivity EC of the treated water at different treatment time under the APGD with the rotating electrodes.

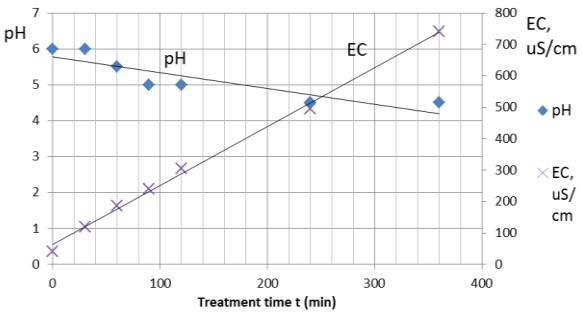

Fig. 4. pH and EC measurement in the deionized water exposed to APGD with the rotating electrodes. Total water volume is 4.4 l. Average discharge power is around 50 W

As expected, the pH level decreases during plasma treatment, and it correlates with an increase of NO_3 concentration. However, the rapid linear increase in electrical conductivity EC of the treated water, which is a function of the accumulation of ions in the water, cannot be explained either by the concentration of nitrate ions NO_3, nor by the concentration of hydrogen peroxide, because for the electrical conductivity EC of 700…800 uS/cm, the concentration of ions must be in 10 times greater compared to the measured concentration of nitrate ions NO3. Perhaps the rapid linear increase in electrical conductivity EC can be explained by the accumulation of hydrogen ions H+ (or hydronium H_3O+) in water, which has high

ion mobility, and many other reactive ions that were not measured in the current tests.

More importantly, these reactive species in plasma-activated water, namely reactive oxygen species and reactive nitrogen species, such as nitric oxide radicals, nitrite, nitrate, atomic oxygen and ozone, can provide the strong antimicrobial effect [9] by inducing high oxidative stress on bacteria and other pathogens.

To examine the microbial reduction ability of APGD with the rotating electrode, 1.5 l of deionized water was inoculated with 1 ml E. coli test cultures. The initial concentration of E. coli in the bulk water averaged between 7.05E5 to 1.88E6 CFU/ml. The water was then circulated through the system without plasma discharge. The 0-minute sample was collected immediately before the start of plasma treatment. The electrode rotation and plasma power supply were then started, and water samples were collected every 15 min thereon. The average power of the plasma was ~50 W, in positive polarity.

The treated water samples were serial diluted (1:10, $1:10^2$, $1:10^3$, $1:10^4$, $1:10^5$), plated and incubated for enumeration. Images of Petri dishes with samples of different dilution after incubation 36 hours are shown in Fig. 5. Table 2 shows the test data of water samples taken from inoculated water treated by APGD for 0, 15, 30, 45, and 60 min.

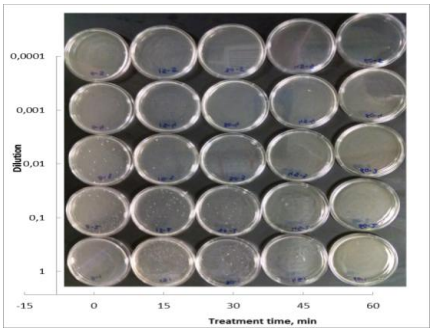

Fig. 5. Images of Petri dishes with water samples treated by APGD for 0, 15-, 30-, 45- and 60-min. Dilution 1:10, $1:10^2$, $1:10^3$, $1:10^4$, $1:10^5$

Table 2

Microbial reduction during direct water treatment by APGD with rotating electrodes (TNC – Too Numerous to Count)

Sample, min		**0**	**15**	**30**	**45**	**60**
pH		6	6	6	5.5	5.5
H_2O_2, ppm		0	1.5	5	5	7
Bacteria counts	1:10	TNC	TNC	400+	8	0
	$1:10^2$	TNC	TNC	387	0	0
	$1:10^3$	400+	385	52	0	0
	$1:10^4$	133	28	1	1	0
	$1:10^5$	19	5	1	0	0

The data presented in Table 2 is a composite of 3 repetition tests. As shown, a greater than 4 log reduction of E. coli was observed after 45 min of APGD treatment of the inoculated deionized water.

CONCLUSIONS

The innovative Atmospheric Pressure Glow Discharge with Rotating Electrode was tested for direct plasma discharge treatment of water. It demonstrated both the high level of microbial reduction and the high concentration of hydrogen peroxide in plasma treated water. Over the conventional stationary electrode discharge system, the rotating electrode enables the improving of the long-term stability of discharge, suppressing thermal instability, and increasing the specific power consumption of the discharge.

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БЕЗПОСЕРЕДНЯ ОБРОБКА ВОДИ APGD З ОБЕРТОВИМИ ЕЛЕКТРОДАМИ

В. Голота, П. Моханті, Л. Завада

Використовувався тліючий розряд атмосферного тиску (APGD) між обертовим зіркоподібним електродом і поверхнею води в якості другого електрода. Показано, що обертання електродів дозволяє стабілізувати розряд. Була зафіксована висока концентрація H_2O_2 та нітратів. Високий рівень мікробного зменшення було показано для інокульованої деіонізованої води, обробленої APGD з обертовими електродами.