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Comparison between the Mechanism of Liquid Plasma Discharge Process in Water and Organic Solution

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"Liquid in Plasma" has been demonstrated as a versatile process with high performance for many applications including nanoparticle synthesis, water purification, organic compound decomposition as well as sterilization. The application of electrical discharge in water has been studied for many years; however, liquid discharge under organic solutions has yet been thoroughly investigated. In this study, a detailed analysis of the fundamental characteristics of plasma discharges under water and benzene were conducted. The solution plasma reactor was connected to a bipolar pulsed power supply with a pair of tungsten electrodes under 280 ml of solution. The discharge voltage and current were in the order of 1 kV and 10 kA, and the characteristics were found to be different between the two liquids. The discharge in water occurred in three different phases: pre-discharge, the initiation and the formation of discharge, whereas the discharge in benzene happened in two main steps: pre-discharging and the formation of discharge. By the observation of optical emission spectrum, significant H radicals were generated in discharge under water, accompanied with the formation of other active species such as O and OH. As for the discharge under benzene, the majority of active species changed to C_2, and followed by CH and H.

1. INTRODUCTION

Liquid phase electrical discharge processes have been recently studied in nanoparticle synthesis [1-5], water treatment [6-7], organic compound decomposition [8-9] as well as sterilization [10-12]. High voltage electrical discharges directly in water (electrohydraulic discharge) initiating both chemical and physical processes. It injects energy directly into an aqueous solution through a plasma channel formed by a high-current/high voltage electrical discharge between two submersed electrodes [6-7]. The liquid plasma is consisted of multiple phases: plasma, gas and liquid phase. Also, the density of the plasma and active species are different from each interface, from plasma to gas and gas to liquid phases. These unique properties and novel reaction kinetics promote fast reaction and high density of radicals. The process generates UV radiation, hydrogen peroxide, hydrogen, oxygen and other radicals and ions [13].

Electrohydraulic discharge can be divided into four different types based on the amount of energy deposited and operating voltage/current ranges in the system: pulsed corona (PCED) and pulsed spark (PSED) type systems use high voltage/ low current discharges around 1 J/pulse and 10J/pulse, respectively, whereas the pulsed arc (PAED) and the pulsed power (PPED) type systems use higher current discharges around 1 kJ/pulse with few kV and larger energy per pulse with higher voltages, respectively [14].

While the application of electrical discharge in water has been studied for many years, liquid discharge under organic solutions has yet been clearly investigated. The plasma aimed to apply to current experiment was belonged to the spark type system: which occurred in the range of discharge voltage and current, respectively, 1-2 kV and 1-20 kA.

In this study, plasma discharges under water and benzene were conducted. Detailed analyses of fundamental characteristics of the discharge were compared between the two liquids. Benzene (C_6H_6) is chosen to be a reference solution of organic solution as it is a simple, non-polar, non-conductive organic solution.

In addition, it is a potential liquid used for the synthesis of carbon nanotube or nanoparticle in electrical plasma discharge [15-16]. The discharge mechanism is expected to be significantly different compared to the water, which is polar and conductive in properties. This fundamental knowledge can provide us information to control the mechanism for future carbon nanoparticle synthesis process.

2. EXPERIMETNAL APPARATUS

The solution plasma reactor was connected to a bipolar pulsed power supply with a pair of tungsten electrodes with diameter of 1 mm. The electrode gap distance was fixed at 0.5mm. The energy input to the plasma reactor was controlled by the primary voltage input in the bipolar power supply with a frequency of 15 kHz. The discharge was conducted in 280 ml of tap water and pure benzene.

Fundamental characteristics (discharge voltage and current) were measured by a digital oscilloscope (Tektronix, TDS 3014B) via high voltage and current probe. An optical fiber/PC computer-based optical spectrometer (Ocean Optics Inst. Co. 200-800nm) was used to measure the time dependent optical emission spectrum through a horizontal Quartz lens window. The window was located less than 1 cm away from the discharge. The schematic of reactor is shown in Fig. 1.

Table 1: Properties of tap water and pure benzene

	Conductivity μS/cm	Boiling Point °C	Polarity
Water	280	100	Polar
Benzene	N/A	80.1	Non-Polar

3. RESULTS

3.1 EFFECT OF VOLTAGE ON WATER PLASMA DISCHARGE

The mechanism of plasma discharge in tap water with a conductivity of 250 μs was served as a reference of basic understanding of the liquid plasma mechanism. In order to fully understand the process of plasma discharge, primary voltage (from power supply), were gradually increased from 30 - 130 V with each increment voltage of 10 V. The relationship between primary voltage, discharge voltage and discharge current was summarized in Fig 2. The primary voltage is the voltage indicated in bipolar power supply, where the discharge voltage and current are the actual value measured at the tungsten electrodes by the oscilloscope. The discharge voltage increased proportional to the increase of primary voltage. The current, on the other hand, was increased in three different stages. When the primary voltage was above 100V, the discharge occurred between the electrode and the plasma channel become conductive, and resulted in a significant rise of current. Detail analyses of water discharge will be carried out in the next section.

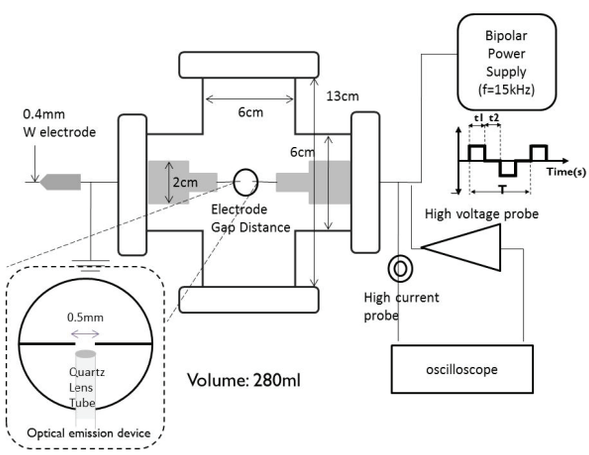

Fig.1 Schematic of solution plasma reactor of 280ml of solution

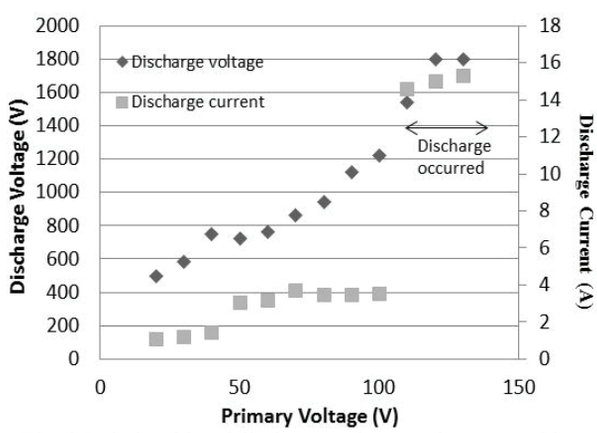

Fig. 2 Relationship of discharge voltage and current with respect to primary voltage (power supply voltage)

3.2 FUNDAMENTAL CHARACTERISTICS OF DISCHARGE UNDER WATER

The discharge under water were observed in three different stages: (I) the pre-discharge, (II) the initiation and (III) the formation of water discharge. These stages were corresponding to different ranges of voltage and current. The summary of the discharge parameters for water in different stages were obtained by 10 sets of experiments and the result was shown in Table 2. The typcial voltage and current waveforms obtained from the pre-discharge, the initation and the formation of liquid discharge are shown, respectively, in Fig.3, Fig.4 and Fig.5.

In stage I, a small current (I < 1A) was flowing between the electrodes since water is conductive. The water was gradually heated by Joule heating, J α I^2Rt where I = conducting current, R = resistance of water and t = time. At this stage, no bubbles, glow corona or spark was observed.

In stage II, when the discharge votlage increased to 0.2 kV, more energy was applied to the liquid media and the heated water started to evaporate. Micro-bubbles were formed around the electrodes. The high electric field of $1x10^5$ V/m (calculated by E ~ V/d, where V is the discharge voltage of 1.5 kV, d is the electrode diameter of 1 mm) first introduced small discharge in micro-bubbles. Thus the micro-gap spark discharge was initiated at the edge of both electrodes in the gas-liquid interface. However, the electric field in current stage is not high enough to cause the electrical breakdown in liquid water. Thus, no glow or spark was fully generated between the electrodes. The physical phenomena observed in this stage included rapid formation of small bubbles. In Fig.4, the current waveform was distored due to the current flow occurred between gas/liquid interface.

At stage III, the spark discharge was initiated when the discharge voltage reached 1kV. The electrical field was higher than $1x\ 10^7$ V/m and was able to cause electrical breakdown of water. In the physical phemomina, the micro-gap spark discharge in bubbles formed in stage 2 growed bigger with increasing the applied volage, and these discharge bridged together and allowed a relative high current (I > 10A) flowed through the plasma/gas interface. In Fig. 5, it is observed that the current rised sharply after voltage breakdown. Ringing of the current was observed due to the specfic properties of the bipolar power supply.

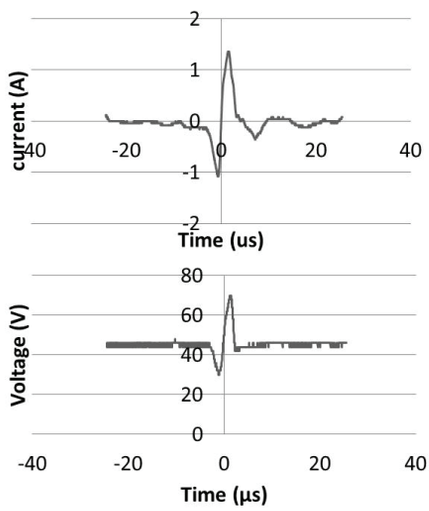

Fig. 3. Discharge curent and voltage waveforms of the pre-discharge under water

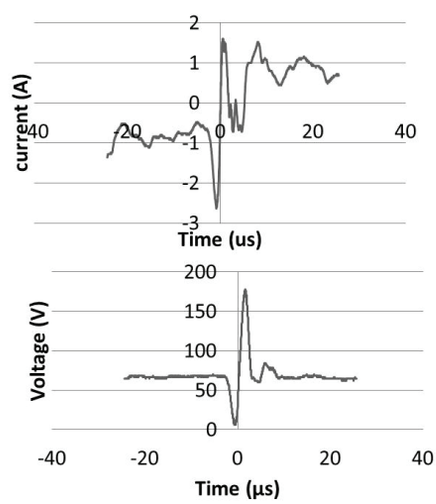

Fig. 4 Discharge curent and voltage waveforms of the initiation of discharge under water

Table 2. Summary of the conditions for three different stages in discharge under water

	Discharge Voltage kV	Discharge Current A
(I) Pre-discharge	0.1 – 0.2	< 1
(II) Initation of the discharge	0.2 - 0.5	1 - 10
(III) Formation of the discharge	0.5 - 1	> 10

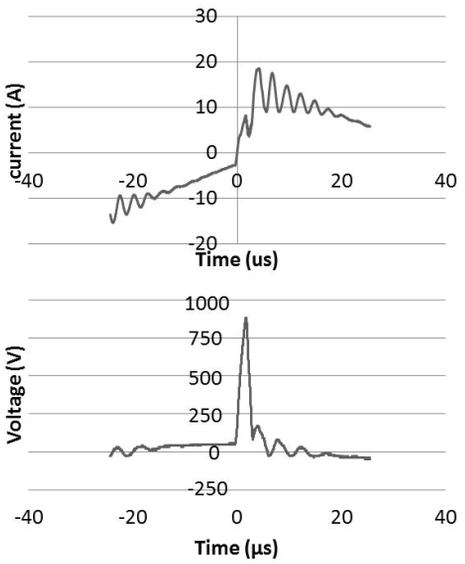

Fig 5. Discharge curent and voltage waveforms of the formation of disharge under water

3.3 OPTICAL EMISSION SPECTRUM FROM WATER DISCHARGE

The optical emission spectrum observed under plasma discharge in water thoroughly investigated by previous studies [10, 17]. However, this experiment was repeated in order to act as a reference spectrum in current reactor for the comparison of the spectrum obtained from benzene in section 3.5. As agreed with previous studies, the active species including OH, H and O were observed during the discharge period. This active species were mostly generated by water dissociations. The major active species were H, followed by atomic O and OH radicals.

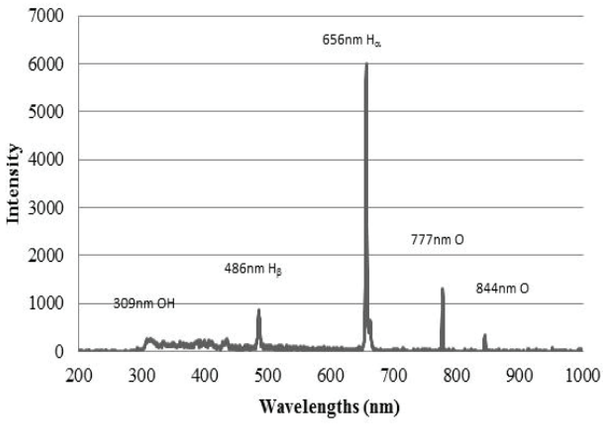

Fig. 6. Typical optical emission spectrum of plasma in water with various discharge gaps

3.4 FUNDAMENTAL CHARACTERISTICS OF PLASMA DISCHARGE UNDER BENZENE LIQUID

The discharge in benzene was considered as a representative of the discharge occurred in a non-polar, non-conductive organic solution. As expected, the discharge mechanism was significant different to water, which has polar and conductive as main properties. The discharge under benzene were observed in two different stages: (I) pre-discharge and (II) formation of the discharge. Typical voltage and current waveforms obtained from the pre-discharge and the formation of benzene discharge are shown, respectively, in Fig.7 and Fig.8. The generation of micro bubbles was not observed between the pre-discharge and the formation of plasma. It is suggested significant difference behavior in discharge is goverend by the conductivity of the solution [6-7, 16]. Since benzene is a non-polar solution, almost no conductivity can be detected. In Fig.7, a correspondingly low conducting current (< 0.05A) was recorded in the pre-discharge stage with primary voltage increased from 30 to 90 V. The discharge started simultaneously when the voltage was above 1.5 kV. With this amplitude of votlage, the electric field is high enough to cause dielectric breakdown of benzene. Dielectric breakdown is defined as a sharp reduction in

electric resistance when the electric field higher than the benzene's dielectric constant (~ 10^6V/m). After the dielectric breakdown of benzene, the liquid become conductive and allow a large current flow of 5 A. Benzene was heated up by the large current (J α I^2Rt) and became gasified. The high electric field of 10^6 V/m (E ~ V/d) initiated the spark discharge intanesouly. The summary of the discharge parameters for benzene in different stages is shown in Table 3.

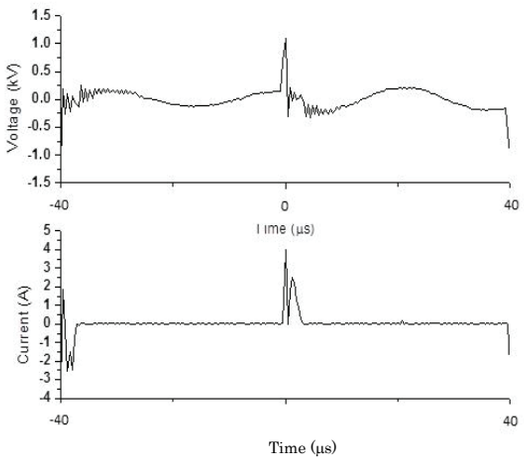

Fig. 7. Curent and voltage waveforms of the pre-discharge under benzene

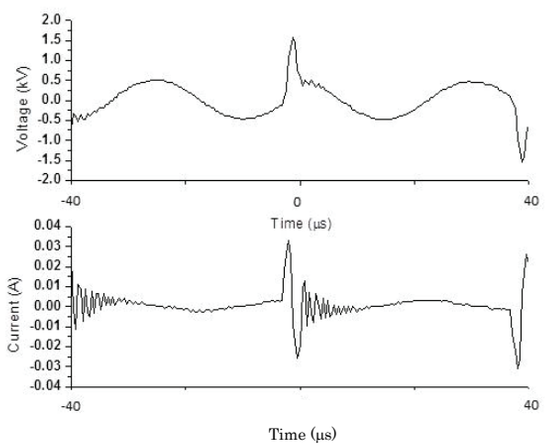

Fig. 8. Curent and voltage waveforms of the formation of liquid discharge under benzene

Table 3. Summary of the conditions for two different stages in discharge under benzene

	Discharge Voltage (kV)	Discharge Current (A)
(I) Pre-discharge	1 – 1.5	< 0.05
(II) Formation of the discharge	~ 1.5	4 - 8

3.5 OPTICAL EMISSION SPECTRUM OF DISCHARGE UNDER BENZENE

The optical emission spectrum observed under plasma discharge in benzene was shown in Fig. 9. Major emitted wavelengths were found in the range of 470 - 480, 510 - 520 and 560 - 565 nm. The spectrum might be corresponded to the excited C_2 emission spectrum obtained from pure methane flame [18]. A weaker intensity of wavelength between 430 and 435 nm were also inspected. It might be generated by the excited CH radicals [19]. The peak of 657 nm was possible contributed by active species of H_α.

It is assumed this intensive energy input is sufficient for the excitation of benzene molecules within the plasma channel [3,13]. When the benzene was gasified and excited, the resonance electron structure was being disturbed and then broken. The open chain structure was further excited and finally, the active species such as C, H, C_2 and CH were generated in the plasma. It is expected that these radicals were created in multiple steps of dissociation and recombination [20].

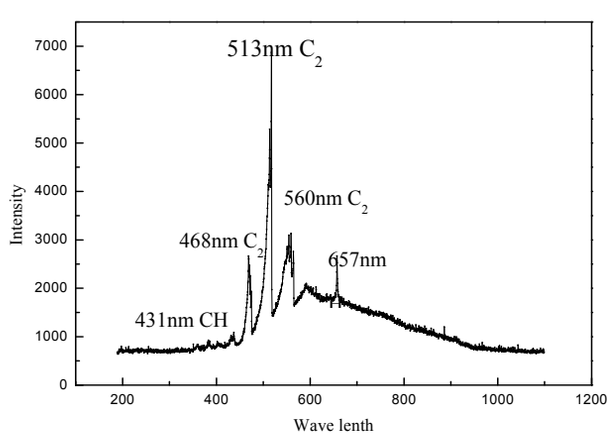

Fig. 9. Optical emission spectrum obtained from liquid discharge under benzene

4. CONCLUSION

A detailed comparison of the fundamental characteristics of discharge under water and benzene was carried out in this study. The discharge mechasnim was governed mainly by the conductivity of the solution. For water which is polar and conductive properties, the liquid is first heated by small conducting current and leads to bubble formation due to evaporation. When increasing the discharge voltage, the high electric field intiated the discharge in bubbles and a full discharge was formed when these bubbles bridged together. For the discharge phenomena in benzene, no conducting current was observed since it is non-polar and non-condcutive liquid. The discharge occurred when dielectric breakdown of benzene occurred with a higher discharge voltage of 1.5kV. The liquid became conductive and allowed large current flow. The current thus heated the liquid media and leads to gasification of benzene. A full discharge was formed simultaneouly since the eletric field was in the range of 10^6 V/m. In optical emission spectrum, major active species was based on the solution property. For the discharge under water, major active species such as H, OH and O were generated based on water dissociation chemistry. As for discharge under benzene, the major active species were C_2, CH and H.

REFERENCES

[1] Takai O.: Solution Plasma Processing. Pure Appl. Chem., 80 (2008) 2003

[2] Hieda, J.; Saito N.; Takai, O.: Exotic shapes of gold nanoparticles synthesized using plasma in aqueous solution. J.Vac. Sci. Technol. A., 26 (2008) 854

[3] Bratescu, M.A.; Cho, S.P.; Takai. O.; Saito N.: Size-controlled gold nanoparticles synthesized in solution plasma. J. Phys. Chem. C, 115 (2011) 24569

[4] Saito, G.; Hosokai, S.; Tsubota M.; Akiyama, T.: Synthesis of copper/copper oxide nanoparticles by solution plasma J. Appl. Phys. 110 (2011) 330

[5] Cho, S.P; Bratescu, M.A.; Saito N.; Takai. O.: Microstructural characterization of gold nanoparticles synthesized by solution plasma processing. Nanotechnology, 22, (2011) 455701

[6] O.L. Li, J.S. Chang and Y. Guo Pulsed Arc Electrohydraulic Discharge Characteristics, Plasma Parameters and optical emission of Sludge-Water IEEE Electrical Insulation (EI) Magazine 27 (2010) 8

[7] O.L. Li, N. Takeuchi, Z. He, Y. Guo, K. Yasuoka, J.S. Chang and N.Saito. Active Species Generated by a Pulsed Arc Electrohydraulic Discharge Plasma Channel in Contaminated Water Treatments. Plasma Chem. Plasma Process. 32 (2012) 343

[8] Angeloni D.M., S.E. Dickson, M.B. Emelko, J.S. Chang: Removal of methyl-tert-butyl ether from water by a pulsed arc electrohydraulic discharge system. J. Journal of App. Phys. 45 (2007) 8290

[9] Chang J.S., K. Urashima, Y. Uchida: Characteristics of pulsed arc electrohydraulic discharges and their application to water treatment. Res. Dep. Tokyo Denki Daigaku 50 (2002) 1

[10] Yamatake A., D.N. Angeloni, S. Dickson, M.B. Emelko, K. Yasuoke and J.S. Chang: UV and optical emissions generated by the pulsed arc electrohydraulic discharge. J. Journal of App. Phys. 45 (2007) 8298

[11] Vel Leitner N.K.V., G. Syoen, H. Romat, K. Urashima, J.S. Chang: Active species generated by a pulsed arc electrohydraulic discharge plasma channel in contaminated water treatments. Water Research 39 (2005) 4705

[12] Sato M., T., Ohgiyama, J.S. Clements: Formation of chemical species and their effects on microorganisms using a pulsed high-voltage discharge in waterIEEE Trans. Ind. Appl. 32 (1996) 106

[13] Locke, B. R.; Sato, M.; Sunka, P.; Hoffmann, M. R.; Chang, J. S: Electrohydraulic discharge and nonthermal plasma for water treatment. Ind. Eng. Chem. Res., 45 (2006) 882

[14] Chang, J.S.: physics and chemistry of plasma pollution control technology. Plasma Sources Sci Tech. 17 (2008) 045004

[15] Nemes-incze. P., N. Daroczi, Z. Sarkozi, A.A. Koos, K.Kertesz, O. Tiprigan, Z.E. Horvath, AL. Darabont, L.P. Biro, 2007. Journal of Optoelectronics and Advanced Materials 9(5): 1526-1529

[16] Sergiienko, E. Shibata, H. Suwa, T. Nakamura, Z.Akase, Y. Murakami, D. Shindo: Synthesis of bamboo-structured multiwalled carbon nanotubes by spray pyrolysis method, using a mixture of benzene and pyridine. Ultrasonics Sonochem. 13 (2006) 6

[17] O.L.Li, Y. Guo, and J.S Chang: Gaseous By-products from Pulsed Arc Electrohydraulic Discharge Treatment of Contaminated Stormwater Ponds. Inter. J. of Plasma Enviro. Sci. and Tech. 6 (2012) 1

[18] Alkemade, C.Th.J., Herrmann, R.,1979. *Fundamentals of Analytical Flame Spectroscopy*, Hilger L.t.d, Bristol, UK.

[19] Mavrodineanu, R., Boiteux, H., 1965. *Flame Spectroscopy*, Wiley, New York.

[20] Yamamoto. T,: On the photochemical formation of CN, C 2, and C 3 radicals in cometary comae. Moon and the Planets. 24 (1981) 453