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Atmospheric Pressure Humid Argon DBD Plasma for the Application of Sterilization - Measurement and Simulation of Hydrogen, Oxygen, and Hydrogen Peroxide Formation

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Abstract—Hydrogen, oxygen, and hydrogen peroxide have been measured downstream of an atmospheric pressure humid argon dielectric barrier discharge. The yield of the three species was studied as a function of the discharge power and gas flow rate. Hydrogen peroxide was measured after dissolution into water downstream of the discharge, while hydrogen and oxygen were measured in the gas phase. The production rates of both hydrogen and oxygen were found to be at least one order of magnitude greater than that of hydrogen peroxide. In all cases, the molar rate of molecular hydrogen production was more than twice that of molecular oxygen. At various total gas flow rate, and over a range of energy density of 0 to 1500 J/L, the concentration of hydrogen found at the reactor outlet varied from 0 to 1000 ppm, while oxygen reached a maximum concentration of about 400 ppm. The corresponding concentration of hydrogen peroxide that was calculated to have been in the reactor outlet gas did not exceed 11 ppm. Mechanisms for this system based on experiments and a numerical model are presented. The results of experiments on the use of post-discharge effluent gas of humid argon plasma for sterilization purposes (inactivation of *E. Coli*) bacteria are also presented and discussed in relation to the results of the chemical measurements and simulations.

Keywords—Non-thermal plasma, hydrogen, oxygen, hydrogen peroxide, sterilization

I. INTRODUCTION

Non-thermal plasma technology at atmospheric pressure using oxygen-nitrogen mixtures has been shown to be effective for sterilization purposes [1], and dielectric barrier discharge (DBD) in humid argon at atmospheric pressure has been shown to produce hydrogen peroxide [2]. Here, the application of humid argon plasma effluent gas for sterilization is investigated. In order to better understand the chemical pathways involved not only in the production of hydrogen peroxide, but that lead to the inactivation of bacteria, measurements of two other stable species produced in humid argon plasma, hydrogen, and oxygen have been made and a mathematical simulation of the system has been developed.

The application of atmospheric pressure non-thermal argon plasma produced by a variety of techniques has recently begun to receive attention for the application of sterilization of surfaces associated with the medical industry [1,3-7]; investigation of argon plasma 'cleaning' of surfaces has also been made [8-9]. In addition, there is considerable work on atmospheric pressure plasma sterilization processes using other working gases [10-13]. A major advantage of non-thermal plasma technology is its ability to operate at or near room temperature, thereby allowing treatment of polymer surfaces which cannot be subjected to conventional dry or wet heat treatment. Here it is important to note that any use of plasma technology in the application of sterilization must consider the requirement of not doing major physical damage to the material(s) underlying the bacteria. In addition, since plasma treatment of polymer surfaces is well-known to increase surface hydrophilicity, thereby increasing the

future capacity of surfaces to support bacterial growth [14], this issue should be carefully considered.

One investigation of humid argon plasma sought to measure OH radical concentration and to develop numerical simulations of the chemical kinetics in such a system [15]. Other work on electrical discharges in water has shown that that type of discharge leads to the formation of hydrogen, oxygen, and hydrogen peroxide in a roughly 4:2:1 ratio [16]. The results of these two studies will be shown to have similarities with the results presented here.

II. EXPERIMENTAL METHODS

The plasma was generated at atmospheric pressure and room temperature by a dielectric barrier discharge in a reactor with a cylindrical geometry using a Pyrex tube as the dielectric. The high voltage electrode was a stainless steel rod with a 2 mm diameter while the counter-electrode was a copper sheet wrapped around the exterior of the Pyrex tube, which had an inner diameter of 3 mm. The counter-electrode was 4 cm in length, giving a plasma volume of 0.157cm³. Electrical measurements were made using either a Tektronix TDS 544A 500MHz oscilloscope or a LeCroy LC374A 500MHz oscilloscope. Voltage measurements were made using a LeCroy PPE20kV 1:1000 voltage probe and current measurements were made by measuring the voltage across a 25 Ω resistor (actually two 50 Ω resistors in parallel) which was placed between the 'grounded' electrode and ground. The high voltage transformer and signal generators used for the generation of the discharge were homemade at Supélec.

Gas phase chemical measurements of hydrogen and oxygen were made using an Agilent 6890A gas

chromatograph (GC) with a Restek 100/120 Shincarbon-ST 2m×1mm column with a thermal conductivity detector. Simultaneous measurement of hydrogen and oxygen in the gas phase was accomplished by the use of argon as the GC carrier gas. In certain cases, especially at the lower flow rates, it was necessary to subtract a 'background' level of oxygen from the chromatograms. The origin of this oxygen was found to be diffusion through the Teflon-PFA tubing that was used to carry the sample gas from the reactor to the GC [17]. Hydrogen peroxide was collected by bubbling the reactor effluent through a volume of water, typically 5ml, just after the plasma zone and a small length of Teflon tubing. A simple experiment with a second 'bubbler' downstream of the first showed that at least 95% of the hydrogen peroxide was captured by the first water trap. Liquid phase measurement of hydrogen peroxide was done using absorption spectroscopy of hydrogen peroxide-vanadate complex at ~430 nm with a Perkin Elmer Lambda 15 spectrometer. Gas flow was controlled using Brooks 5850S series mass flow controllers and/or Brooks Sho-rate rotameters. Arcal 1 grade Argon from Air Liquide was used ($O_2 < 0.5\text{ppm}$, $N_2 < 1\text{ppm}$, $H_2O < 1\text{ppm}$) in all experiments. The gas was humidified by bubbling through distilled water in a gas sparging bottle at room temperature and the relative humidity was measured to be greater than 95% in all cases.

Measurement of bacteria (*Escherichia Coli*) was done using a direct plate-counting method. The initial bacteria solution contained 10^9 bacteria/mL. For each experiment five slides were prepared: four were then treated and one used as a control. The bacteria were treated in $10\mu\text{L}$ distilled water droplets on each slide, giving a total of 10^7 initial bacteria suspended in each droplet. After treatment the droplets were collected in 2mL of distilled water and then serially diluted. Next, $100\mu\text{L}$ of this solution was plated out on agar nutrient in Petri dishes, and the colonies were then directly counted after about 12 hours of incubation at 37°C . The serial dilutions were made so that a statistically significant level of colony forming units (CFU) i.e. 30-300 bacteria was obtained. Of course, the appropriate level of dilution was not knowable *a priori*, however after a level of experience had been gained, the procedure was followed on the basis of an expected level of bacterial inactivation for the particular experimental conditions applied.

III. RESULTS

A. Experimental Results - Chemical

Fig. 1 shows the results obtained for both hydrogen and oxygen production as a function of the plasma energy density and at three different gas flow rates. The concentrations of both hydrogen and oxygen increase roughly linearly with increasing energy density for all three gas flow rates, but with different slopes for the different flow rates.

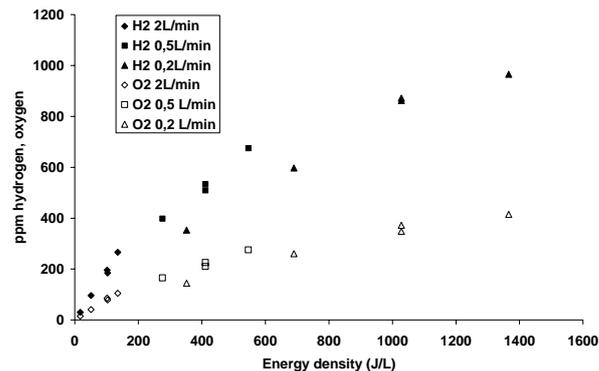


Figure 1. Hydrogen and oxygen concentration in the effluent gas as a function of energy density and gas flow rate.

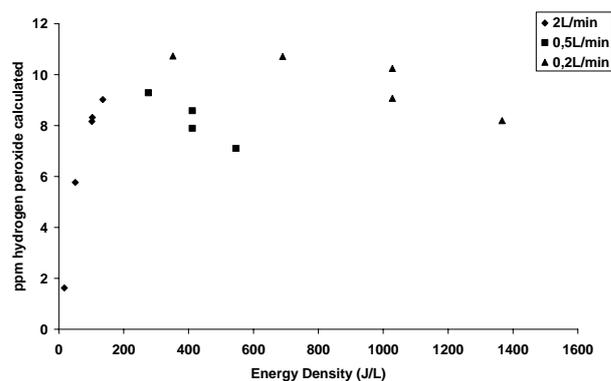


Figure 2. Hydrogen peroxide production calculated to have been in the effluent gas as a function of energy density and gas flow rate.

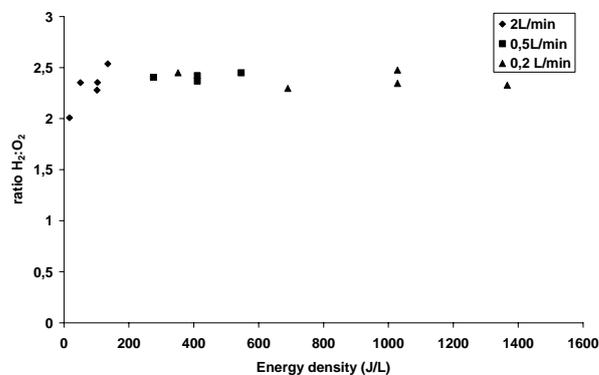


Figure 3. Ratio of hydrogen to oxygen production as a function of energy density.

The production rates of both hydrogen and oxygen appear to be reduced slightly at a given energy density by a reduction in flow rate (which implies a reduction in discharge power). This effect will not be discussed here as a satisfactory explanation has not been found.

The concentration that was calculated to have been in the gas from the measurement of liquid phase hydrogen peroxide as a function of plasma energy density is presented in Fig. 2. The gas phase concentration increases at low energy densities, then stabilizes, and even begins to decrease at very high energy density. By comparing Figs. 1&2, it can be seen that the production rates of both hydrogen and oxygen are roughly two orders

of magnitude greater than that of hydrogen peroxide. The fact that the gas phase concentration of hydrogen peroxide never exceeds roughly 10 ppm turned out to be very important in the development of the numerical simulation, and will be discussed further in that section.

Overall, the experimental results show that a dielectric barrier electrical discharge in humid argon results in the production of hydrogen and oxygen in quantities considerably larger than that of hydrogen peroxide. Another basic result is that the ratio of hydrogen to oxygen production is roughly 2.

Fig. 3 shows the ratio of hydrogen to oxygen concentration. The ratio appears stable at about 2.0-2.5 over the range of energy densities considered. If the concentration of hydrogen peroxide were zero, the ratio of observed hydrogen: oxygen would necessarily be exactly 2. However, the observed amount of hydrogen peroxide is not sufficient to explain the seemingly high ratio of hydrogen to oxygen, which implies that there is 'missing' oxygen. While it is possible that some of the oxygen may have dissolved ($K_{\text{Henry}} = 1.3 \cdot 10^{-3} \text{ M/atm}$) into the water, the level of dissolved oxygen has not been measured (the water was degassed).

B. Kinetic Simulation

A kinetic simulation was developed using reaction rate constants from the atmospheric chemistry literature. The simulation was spatially independent and was therefore easily done using Matlab 7 and its ode23s routine. A reaction list has been provided in the appendix showing all the reactions used in the simulation except the initiation and hydrogen peroxide dissociation reactions to be discussed later. The simulation consisted of two basic parts: a plasma zone portion and a post-plasma or 'relaxation' portion. Residence time in the two zones was determined by the residence time that was utilized in experiments for both chemical and biological measurements.

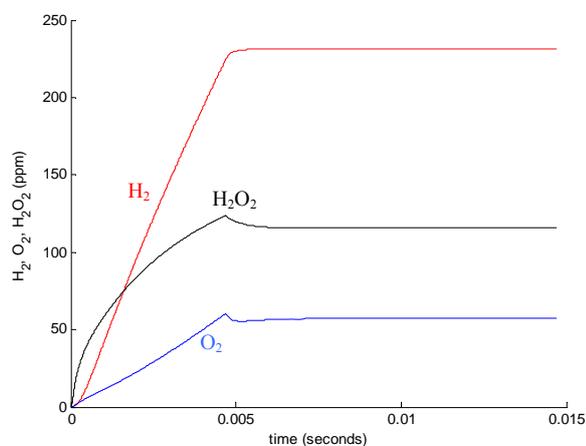


Figure 4. Result of simulation without dissociation of hydrogen peroxide in the plasma zone.

An initiation reaction (1) was used in the plasma zone portion of the simulation.



For this system, reaction (1) represents the net production of hydrogen and hydroxyl radicals which are in reality produced by a combination of the direct electron impact reaction (2) and the reaction of water with excited argon (reaction (3)) which of course is itself excited by electron impact.



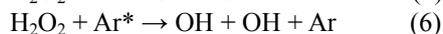
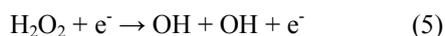
The rate constant for reaction (1) in this simulation was not calculated but used as an adjustable parameter and can be thought of as $k_1 \sim k_2 + k_3[\text{Ar}^*]$, k_2 being a function of the electron energy distribution and the water vapor dissociation cross-section for this system. While the use of an adjustable parameter can be used to 'fit' the experimental data, in this case, there are three measurements to be simulated, namely the concentrations of hydrogen, oxygen, and hydrogen peroxide in the gas downstream of the plasma discharge. It can be noted here that the 'post-discharge' portion of the model does not contain any adjustable parameters, thereby limiting the amount of 'fitting' that can be done since the measured values correspond to the end result of the 'post-discharge' zone. So, if the rate constant for reaction (1) is adjusted so that the simulation returns a concentration of hydrogen that is in agreement with the measured result, and the simulation then also returns the correct values for both oxygen and hydrogen peroxide, this result may be seen as a verification of the simulation. The residence time of the gas in the plasma zone for this simulation was 4.7ms, corresponding to a flow rate of 2L/min and reactor volume of 0.157cm^3 , which was a typical case in the experiments. The post-plasma simulation was carried on for another 10ms, corresponding roughly to the time for the gas to traverse from the plasma zone to either the water film that was used to collect hydrogen peroxide or the water droplets containing bacteria.

However, as seen in Fig. 4, the simulation using only reaction (1) and the set of pertinent reactions in the appendix produced a result contrary to the results obtained by experimentation. In Fig. 4, initiation reaction rate constant (1) was adjusted to an arbitrary value which gave a concentration of hydrogen that would have corresponded to the hydrogen level at an energy density of about 120 J/L; this was done to facilitate an easy comparison with the next simulation. However, the major result of this simulation is that the concentration of hydrogen peroxide is far higher than it should be, and the ratio of hydrogen to oxygen production was significantly greater than observed in experiments. Clearly, the simulation in this form does not succeed in replicating the results measured experimentally. However it does

strongly suggest that hydrogen peroxide is dissociated in the plasma zone (if the simulation is generally speaking valid except for failing to include some mechanism that reduces hydrogen peroxide production and increases oxygen production). Therefore, another reaction was added to the simulation, reaction (4).



Again, like reaction (1), and since the temperature is too low for gas phase thermal dissociation of hydrogen peroxide, reaction 4 is representative of the net effect of two reactions that act to dissociate hydrogen peroxide in the plasma zone, reactions (5) & (6).



Similar to the case with reactions 1-3, the rate constant for reaction (4) in this simulation was not calculated but used as an adjustable parameter and can be thought of as $k_4 \sim k_5 + k_6[\text{Ar}^*]$, k_5 being a function of the electron energy distribution and the hydrogen peroxide dissociation cross-section for this system (it can be noted here that reactions 2,3,5&6 and all the three body reactions in the appendix should in fact follow a more complex, pressure dependant mechanism but this simple formulation is valid for high pressure). With the addition of another adjustable parameter, the data may be 'fitted' for two of the three experimental results. Now the two reactions and their effect on the simulation results are coupled, and an iterative procedure was used: first adjusting k_1 to give approximately the correct result for hydrogen, then adjusting k_4 to give the correct value for hydrogen peroxide, then readjusting k_1 and so on. Also, as will be seen, the flexibility of k_4 as an adjustable parameter is limited because it only affects the plasma zone, and a significant portion of the hydroxyl radicals remaining from the plasma zone are converted into hydrogen peroxide in the post-discharge zone.

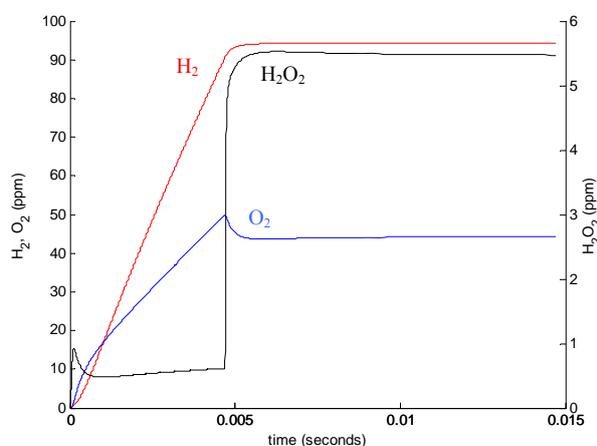


Figure 5. Result of simulation with dissociation of hydrogen peroxide in the plasma zone for the case of 2L/min and 50J/L.

If, after this iteration, the simulation then returns the correct value for the concentration of oxygen, not only is the simulation shown to be valid, but the addition of reaction (4) is shown to be justified, indicating that this reaction is indeed important in this system.

It is perhaps worthy of note here that the result of the first simulation is very similar to the result observed experimentally for pulsed electrical discharge in water [16]. This suggests that in discharge in water, where for each pulse the hydrogen peroxide is lost from the plasma zone into the surrounding water, and therefore not available to be dissociated in the next pulse discharge, that the underlying process in the streamer channels may be similar to the gas phase system under discussion here, with the caveats of higher local temperatures and that the third body in many of the pertinent reactions would be water and not argon.

Fig. 5 shows the result of the simulation when using reaction rate constant (1) to fit the data for hydrogen and reaction rate constant (4) to fit the hydrogen peroxide data; the gas residence time and hydrogen and hydrogen peroxide levels used for this simulation correspond to the experimental case for 2L/min and approximately 50J/L as seen in Figs. 1&2. This relatively low energy density condition was used so that any possible thermal effects could be ignored - the temperature in both plasma and post-plasma zone was 298K in the simulation (and also so that the possibility of a third adjustable parameter, namely temperature in the plasma zone, could be avoided). As can be seen, the simulation predicts a concentration of oxygen slightly less than half that of hydrogen, exactly the result that was obtained experimentally. The simulation implies that for this case, the majority of hydrogen peroxide is quickly formed in the post-discharge region after the gas exits the plasma zone, although significant amounts of the hydroxyl radicals existing at the reactor outlet go to form not hydrogen peroxide but water.

Another implication of this simulation is that hydroxyl radicals formed by the dissociation of hydrogen peroxide (reaction 4) act to reduce the production of hydrogen and to a lesser extent, oxygen. This is deduced from the fact that for the two simulations (Figs. 4&5), the same value for reaction rate constant (1) was used, and as can be seen by comparing the two figures, the concentrations of hydrogen and oxygen are reduced significantly by the inclusion of reaction (4). This result led to the idea of what the model would predict if extra hydrogen peroxide were added to the inlet gas. The simulation predicts that for increasing amounts of hydrogen peroxide vapor added to the inlet gas, increasing amounts of oxygen, decreasing amounts of hydrogen and about the same amount of hydrogen peroxide (~ 5-10 ppm) should be detected at the reactor outlet. All three of these predictions have been verified experimentally.

Another significant result of the simulation is that it predicts a significant lifetime downstream of the discharge of hundreds of part-per-billion levels of

hydroperoxyl radical and tens of parts-per-billion levels of oxygen atom and hydroxyl radical, as shown in Fig. 6 (the scale of the figure is too large to see the final concentration of hydroxyl radical, which is about 10 ppb). It is possible that these are the species responsible for the observed bacterial inactivation discussed in the following section. It can also be noted that the maximum concentration of OH at early time was about 30 ppm, almost exactly that found in the calculations of [15].

C. Experimental Results - Biological

Fig. 7 shows the results of bacteria (*Escherichia Coli*) subjected to treatment by the effluent gas from atmospheric pressure humid argon plasma. The bacteria were suspended in 10 μ L water droplets placed 3cm from the reactor outlet. As can be seen, with increasing exposure time to the effluent gas, the number of survivors is reduced by up to 5 orders of magnitude from 10⁷ to 10² bacteria/mL. It should be emphasized here that the bacteria are not contacted by the plasma but only the effluent gas, thereby minimizing damage to the underlying material. The control sample was exposed to the same conditions as the treated samples except that the discharge was not turned on.

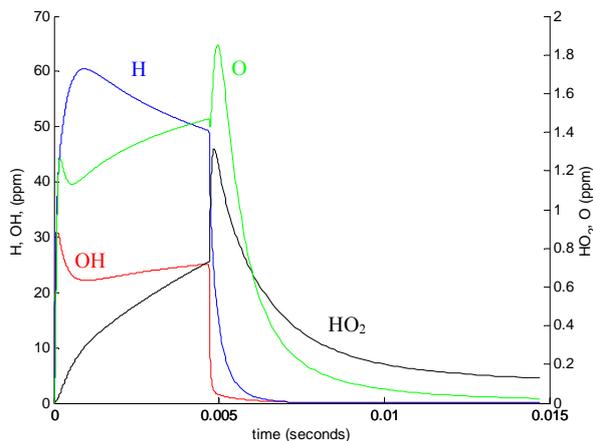


Figure 6. Radical levels in simulation with the inclusion of dissociation of hydrogen peroxide in the plasma zone.

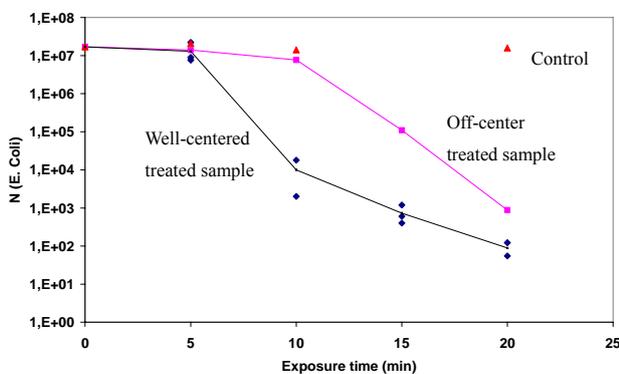


Figure 7. Colony forming units of *E. Coli* vs. treatment time by humid argon plasma effluent gas; 0.7 L/min; 2.2 W; 199 J/L.

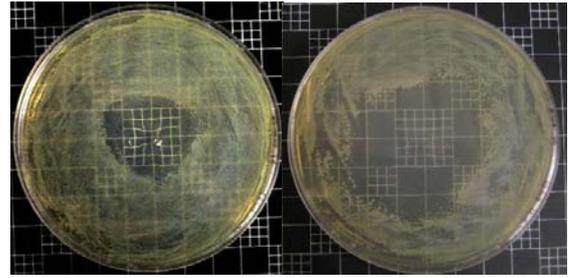


Figure 8. Photographs of Petri dishes with agar gel covered with 10⁶ bacteria and then subjected to 20 min of treatment at 2.2W. The only difference between the two photographs was the flow rate, 0.7L/min (left) and 1.4L/min (right).

Another experiment was done to investigate whether the sterilization effect was simply due to the exposure of the bacteria to hydrogen peroxide. No effect of hydrogen peroxide on bacteria viability was observed even at 300 ppm of hydrogen peroxide which is much higher than the experimentally measured concentration.

For comparison to the chemical data above, the experimental conditions in the experiment shown in Fig. 7 was flow rate: 0.7L/min, power 2.2W, giving an energy density of 188J/L. The difference between the two curves in Fig. 7 with the discharge turned on was that in one case the sample container was placed off-center from the reactor outlet. This leads to the idea that the gas residence time between the reactor outlet and the sample plays an important role in sterilization. This idea is further enforced by the result shown by photographs in Fig. 8. A different experimental procedure than explained in Section 2 was used to obtain these photographs. Instead of treating the bacteria in droplets, the bacteria (100 μ l of 10⁸ mL⁻¹, giving 10⁷ total bacteria) were first plated in Petri dishes with agar nutrient, and then subjected to the reactor effluent gas. The difference between the two photographs was the flow rate: 0.7 L/min and 1.4L/min for left and right, respectively, using the same discharge power (2.2W). As can be seen in the photographs, the bacteria in the center of the Petri dishes were killed while the outlying bacteria survived.

IV. CONCLUSIONS

New measurements were made of both hydrogen and oxygen formation in atmospheric pressure humid argon DBD plasma. The experimental results were that under the conditions studied, hydrogen and oxygen are produced in quantities at least one order of magnitude greater than that of hydrogen peroxide. With this result in combination with a kinetic simulation, it is shown that this is the result of hydrogen peroxide dissociation in the plasma zone. It was also noted that for a simulation disregarding the dissociation of hydrogen peroxide in the plasma zone, a very similar result to that found in electrical discharge in water [16] was found, suggesting that the two seemingly disparate systems may have some similar basic mechanisms in common. Another result of the simulation is the implication that 10 ms downstream

of the discharge, that hydroperoxyl radical persists in hundreds of ppb and oxygen atom and hydroxyl radical in tens of part-per-billion, suggesting a possible role of these species for the purpose of surface sterilization. The results

of experiments for sterilization were that up to 5 orders of magnitude of *E. Coli* inactivation were observed within a 20 minute treatment time and that this sterilization was spatially dependant.

APPENDIX. CHEMICAL REACTIONS AND RATE CONSTANTS

N ^o	Reaction	k(T)	E _a /R(K), T _r (K)	A	a	T(K)	form
1	OH + OH + Ar → H ₂ O ₂ + Ar	9.7*10 ⁻³¹	na	na	na	298	na
2	OH + H ₂ O ₂ → HO ₂ + H ₂ O		160	2.9*10 ⁻¹²	0	240-460	1
3a	2HO ₂ → H ₂ O ₂ + O ₂		-620	2.2*10 ⁻¹³	0	230-420	1
3b	2HO ₂ + Ar → H ₂ O ₂ + O ₂ + Ar	3.69*10 ⁻³²	na	na	na	298	na
4	H + H ₂ O ₂ → HO + H ₂ O		1801	1.69*10 ⁻¹¹	0	300-1000	1
5	H + H ₂ O ₂ → HO ₂ + H ₂		1892	2.81*10 ⁻¹²	0	300-1000	1
6	2OH → H ₂ O + O		-945, 298	6.2*10 ⁻¹⁴	2.6	200-350	1
7	OH + HO ₂ → O ₂ + H ₂ O		-250	4.8*10 ⁻¹¹	0	250-400	1
9	O + OH → O ₂ + H		-110	2.4*10 ⁻¹¹	0	150-500	1
10	O + H ₂ O ₂ → HO ₂ + OH		2000	1.4*10 ⁻¹²	0	280-390	1
11	O + HO ₂ → O ₂ + OH		-224	2.7*10 ⁻¹¹	0	220-400	1
12	H + HO ₂ → O ₂ + H ₂		710	7.11*10 ⁻¹¹	0	300-1000	1
13	H + HO ₂ → 2OH		440.2	2.81*10 ⁻¹⁰	0	300-1000	1
14	H + HO ₂ → H ₂ O + O		866	5.0*10 ⁻¹¹	0	300-1000	1
15a	H + OH + Ar → H ₂ O + Ar		312, 298	1.48*10 ⁻³⁰	-1.18	200-6000	1
15b	H + OH + H ₂ O → H ₂ O + H ₂ O		na, 298	9.26*10 ⁻³²	-2	300-3000	2
16	H + OH → H ₂ + O		1952, 298	6.86*10 ⁻¹⁴	2.8	300-2500	1
17	H + H ₂ O → H ₂ + OH		9721, 298	6.82*10 ⁻¹²	1.6	300-2500	1
18a	2H + Ar → H ₂ + Ar		na, 298	6.04*10 ⁻³³	-1	300-2500	2
18b	2H + H ₂ O → H ₂ + H ₂ O		na, 298	9.26*10 ⁻³²	-1	300-2000	2
18c	2H + H ₂ → H ₂ + H ₂		na, 298	8.85*10 ⁻³³	-0.6	100-5000	2
19	H ₂ + O → OH + H		3160, 298	3.44*10 ⁻¹³	2.67	300-2500	1
20a	2O + Ar → O ₂ + Ar		na, 298	9.26*10 ⁻³⁴	-1	300-5000	2
20b	2O + O ₂ → 2O ₂	1*10 ⁻³²	na	na	na	298	na
20c	2O + H ₂ → O ₂ + H ₂	2.21*10 ⁻³²	na	na	na	298	na
21	H + O ₂ + M [§] → HO ₂ + M [§]		na, 300	5.4*10 ⁻³²	-1.8	200-600	2
22	OH + H ₂ → H ₂ O + H		2100	7.7*10 ⁻¹²	0	200-450	3

form 1: $k = A*(T/T_r)^a * e^{-E_a/RT}$

form 2: $k = A*(T/T_r)^a$

form 3: $k = A*(T/T_r)^a$

Reaction table for humid argon system: (molecule/cm³s) for 2nd order reactions, (molecule²/cm³s) for 3rd order reactions; all values were found on the NIST "chemical kinetics database on the web" (<http://kinetics.nist.gov/index.php>). § For reaction 21 M=N₂, however rate constants for argon as the third body are always similar to the case for nitrogen.

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