Reaction Kinetics of Active Species from an Atmospheric Pressure Plasma Jet Irradiated on the Flowing Water Surface — Effect of Gas-drag by the Sliding Water Surface —

Tatsuru Shirafuji* and Jun-Seok Oh

Department of Physical Electronics and Informatics, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
*shirafuji@osaka-cu.ac.jp

We performed numerical simulations for investigating atmospheric pressure humid air chemistry triggered by metastable argon atoms fed from an atmospheric pressure plasma jet (APPJ) irradiated on a flowing water surface. We discuss the gas-drag effect caused by the flow of water surface. The gas-drag effect may alter spatial profiles of gas-phase species around the APPJ. It may alter also spatial profiles of the flux of active species impinging on the water surface. The numerical simulations have revealed that the flux profile of OH radicals is surely altered by the gas-drag effect and its flux on the surface is reduced to 1/6 of that on the static surface.

Keywords: Atmospheric pressure plasma jet, Argon, Metastable, Water surface, Flow, Gas-drag, OH radical, Atomic oxygen

1. Introduction

Recently, extensive works have been reported on the application of an atmospheric pressure plasma (APP) and APP jet (APPJ) for surface treatments since the APP can treat not only inorganic solid-state surface but also living tissues and liquid media because it does not require low-pressure or vacuum environments [1-3].

In the case of industrial applications, however, most of the APPJ are utilized in the roll-to-roll processes for continuous treatment of a target surface. In this case, we must pay attention to the difference between APPJ treatments on a static surface and a sliding surface. The difference is that the gas-drag effect is accompanied with the APPJ treatment when the target surface slides against the APPJ.

Based on these viewpoints, the authors performed a numerical simulation of the situation in which APPJ is irradiated to the sliding solid surface [4]. As a result, it was revealed that the mixed gas of nitrogen and oxygen contained in the atmospheric pressure atmosphere was dragged into the APPJ irradiation area by the gas-drag effect. This phenomenon results in promotion of gas-phase reactions to consume active oxygen species supplied from APPJ and leads reduction in surface-treatment performance.

Such a situation is considered to occur also when the liquid surface is irradiated with APPJ. When we are required to continuously treat the liquid surface with APPJ, the flowing liquid are going to be irradiated with APPJ. In this situation, the liquid...
surface acts as a sliding surface, which is accompanied with the gas-drag effect. In addition to this, the evaporation is accompanied on the surface when the surface is substituted from a solid surface to liquid surface. Therefore, we must pay attention to the fact that the gas-drag effect involves not only atmospheric gases but also the liquid vapor.

Thus, we have conducted numerical simulation for understanding the effect of sliding surface in the case of liquid treatment by APPJ.

2. Model description

Figure 1 shows the schematic diagram of the cross section of the simulation space used in this work, in which an APPJ of Ar gas is irradiated on the flowing water surface. For modeling the primary reactions in front of the APPJ nozzle, we have employed an extremely simplified scheme. In our previous work, we found that the decomposition of H2O is mostly governed by the reaction of H2O with metastable Ar atoms (Ar(3P), hereafter) rather than electron impact dissociation in the highly Ar-diluted environment [5]. In the present model, therefore, we assumed that the active species supplied from the APPJ is only Ar(3P), and that all the primary reactions are triggered by Ar(3P). The species ejected from the APPJ are hence only the ground-state Ar atoms and metastable Ar atoms.

Velocity of the species ejected from the APPJ was 1 m/s. Ambient gases are assumed to be humid air, namely, gas mixture of N2 and O2 containing 1.4% H2O, where the ratio of N2/O2 is 80/20. Sliding velocity of the water surface was 0.5 m/s, where the water surface is assumed to be in the no-slip condition for the gas-phase species on it. Number density of Ar(3P) at the APPJ nozzle was assumed to be 6×10^{14} m^{-3} according to the measured results

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactants</th>
<th>Products</th>
<th>A (cm^3/s)</th>
<th>n</th>
<th>E (kJ/mol)</th>
<th>Refs.</th>
</tr>
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<tbody>
<tr>
<td>R1</td>
<td>Ar(3P)+Ar</td>
<td>2Ar</td>
<td>2.30×10^{-15}</td>
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<td>0</td>
<td>[12,13]</td>
</tr>
<tr>
<td>R2</td>
<td>Ar(3P)+Ar+M</td>
<td>Ar*+M</td>
<td>1.14×10^{-32}*</td>
<td>0</td>
<td>0</td>
<td>[12,14,15]</td>
</tr>
<tr>
<td>R3</td>
<td>Ar*</td>
<td>2Ar</td>
<td>6.20×10^{-7}*</td>
<td>0</td>
<td>0</td>
<td>[14,15]</td>
</tr>
<tr>
<td>R4</td>
<td>Ar(3P)+H2O</td>
<td>Ar+OH(X)+H</td>
<td>2.10×10^{-10}</td>
<td>0</td>
<td>0</td>
<td>[16-18]</td>
</tr>
<tr>
<td>R5</td>
<td>Ar*+H2O</td>
<td>2Ar+OH(X)+H</td>
<td>1.40×10^{-9}</td>
<td>0</td>
<td>0</td>
<td>[16-18]</td>
</tr>
<tr>
<td>R6</td>
<td>Ar(3P)+O2</td>
<td>Ar+O(3P)+O(3P)</td>
<td>9.70×10^{-11}</td>
<td>0</td>
<td>0</td>
<td>[16,19,20]</td>
</tr>
<tr>
<td>R7</td>
<td>Ar*+O2</td>
<td>2Ar+O(3P)+O(3P)</td>
<td>4.60×10^{-11}</td>
<td>0</td>
<td>0</td>
<td>[16,19,20]</td>
</tr>
<tr>
<td>R8</td>
<td>OH(X)+H2O</td>
<td>H2O+HO2</td>
<td>2.90×10^{-12}</td>
<td>0</td>
<td>-1.33</td>
<td>[21-23]</td>
</tr>
<tr>
<td>R9</td>
<td>OH(X)+O3</td>
<td>HO2+O2</td>
<td>1.70×10^{-12}</td>
<td>0</td>
<td>-7.82</td>
<td>[22]</td>
</tr>
<tr>
<td>R10</td>
<td>OH(X)+H2</td>
<td>H+H2O</td>
<td>7.70×10^{-12}</td>
<td>0</td>
<td>-17.46</td>
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<tr>
<td>R11</td>
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<td>H2O+O2</td>
<td>4.80×10^{-11}</td>
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<tr>
<td>R12</td>
<td>OH(X)+OH(X)+M</td>
<td>H2O2+M</td>
<td>6.89×10^{-31}*</td>
<td>-0.8</td>
<td>0</td>
<td>[21-28]</td>
</tr>
<tr>
<td>R13</td>
<td>OH(X)+OH(X)</td>
<td>H2O+O(3P)</td>
<td>1.87×10^{-12}</td>
<td>0</td>
<td>0</td>
<td>[21-28]</td>
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<tr>
<td>R14</td>
<td>O(3P)+O2+M</td>
<td>O3+M</td>
<td>6.01×10^{-34}*</td>
<td>-2.8</td>
<td>0</td>
<td>[29]</td>
</tr>
<tr>
<td>R15</td>
<td>O(3P)+O3</td>
<td>O2+O2</td>
<td>8.00×10^{-12}</td>
<td>0</td>
<td>0</td>
<td>[22]</td>
</tr>
<tr>
<td>R16</td>
<td>O(3P)+H2</td>
<td>H+OH(X)</td>
<td>3.44×10^{-13}</td>
<td>2.67</td>
<td>-26.27</td>
<td>[26]</td>
</tr>
<tr>
<td>R17</td>
<td>O(3P)+H2O</td>
<td>HO2+OH(X)</td>
<td>1.40×10^{-12}</td>
<td>0</td>
<td>-16.63</td>
<td>[21,22]</td>
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<td>R18</td>
<td>O(3P)+OH(X)</td>
<td>O2+H</td>
<td>2.40×10^{-11}</td>
<td>0</td>
<td>0</td>
<td>[22]</td>
</tr>
<tr>
<td>R19</td>
<td>O(3P)+HO2</td>
<td>O2+OH(X)</td>
<td>2.70×10^{-11}</td>
<td>0</td>
<td>0</td>
<td>[22]</td>
</tr>
<tr>
<td>R20</td>
<td>H+O2+M</td>
<td>HO2+M</td>
<td>5.40×10^{-32}*</td>
<td>-1.8</td>
<td>0</td>
<td>[21-23,30]</td>
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<tr>
<td>R21</td>
<td>H+O3</td>
<td>OH(X)+O2</td>
<td>1.40×10^{-10}</td>
<td>0</td>
<td>-3.91</td>
<td>[31,32]</td>
</tr>
<tr>
<td>R22</td>
<td>H+H2O</td>
<td>H2+HO2</td>
<td>8.00×10^{-11}</td>
<td>0</td>
<td>-33.26</td>
<td>[33]</td>
</tr>
<tr>
<td>R23</td>
<td>H+H+M</td>
<td>H2+M</td>
<td>8.85×10^{-33}*</td>
<td>-0.6</td>
<td>0</td>
<td>[26]</td>
</tr>
<tr>
<td>R24</td>
<td>HO+HO2+M</td>
<td>H2O2+O2+M</td>
<td>1.90×10^{-33}*</td>
<td>0</td>
<td>8.150</td>
<td>[30]</td>
</tr>
</tbody>
</table>

Rate constant is given by \( k = A \left( \frac{T}{(298 \text{ K})} \right)^n \exp(-E/(RT)) \), where \( T \) is temperature and \( R \) is gas constant.

*The unit is cm^6/s. **The unit is 1/s.
Temperature and pressure of the whole environment was assumed to be 300 K and 1 atm.

Velocity profiles was calculated by solving Navier-Stokes equations. Number density profiles of the chemical species was calculated by solving convection-diffusion equations coupled with rate equations for gas-phase and surface reactions considered in the present model.

Since the water vapor is supplied from the water surface, we used the following reversible reaction at the water surface for considering the effect of condensation and evaporation of water:

\[
\text{H}_2\text{O (Liq)} \leftrightarrow \text{H}_2\text{O (Gas)}. \quad (1)
\]

The rate of the condensation was calculated using Hertz-Knudsen equation which gives the flux of particles impinging on the surface [7,8]. The rate of the evaporation was obtained through the thermodynamical calculation [7,8] using enthalpy for evaporation of H\(_2\)O at 300 K and 1 atm [9]. For simplicity, the present mode does not involve thermal conduction. Thus, temperature drop due to evaporation, which will be our future work, was not considered.

In this model, 24 gas-phase chemical reactions are involved as shown in Table 1. Most of Ar(\(^3\)P) ejected from the APPJ nozzle firstly collides with Ar to be de-excited to Ar through R1, and also to produce excited dimer Ar\(_2\)\(^*\) through R2. Some of Ar\(_2\)\(^*\) is de-excited spontaneously through R3. The Ar(\(^3\)P) and Ar\(_2\)\(^*\) survived above de-excitation processes play the role of the primary gas-phase reactions R4-R7 to produce active species of ground-state OH radicals (OH(X), hereafter) and ground-state O atoms (O(\(^3\)P), hereafter) together with H atoms of which the behavior is not focused in the present study.

The secondary reactions R8-R24 are selected according to the reports by Herron and Green who selected high-priority plasma reactions in humid air [10]. In the present model, we neglected production of N because dissociation of N\(_2\) by Ar(\(^3\)P) can be neglected although quenching of Ar(\(^3\)P) can occur through collision with N\(_2\) [11]. Thus, nitrogen-related species are not considered in Table 1.

Surface reactions are also considered for active species of Ar(\(^3\)P), Ar\(_2\)\(^*\), OH(X), O(\(^3\)P), H, and HO\(_2\). Reaction rates for the surface reactions are calculated using Hertz-Knudsen equation with sticking probability of unity.

### 3. Results and discussion

#### 3.1. Spatial profile on the static surface

Figure 2 shows the results on the static water
surface, in which Fig. 2(a) shows velocity of gas, of which the length of arrows is proportional to logarithm of the velocity. Figures 2(b), 2(c), 2(d), 2(e), and 2(f) show the number density of Ar, H$_2$O, Ar($^3$P), O($^3$P), and OH(X), respectively. The density of these species is normalized by total number density ($2.44 \times 10^{25} \text{ m}^{-3}$) at 1 atm and 300 K.

Looking at their horizontal spatial profiles, all the spatial profiles in these results shows symmetric characteristics, since we assumed axisymmetric profiles for the gas-ejection velocity and density of ejected chemical species at the nozzle. Vertical spatial profiles of the density of chemical species show different features depending on the species.

The density profiles of the stable species of Ar and H$_2$O has broad spatial profiles as shown in Figs. 2(b) and 2(c), which is due to their low reactivity. These spatial profiles are mostly governed by fluid dynamics rather than reaction kinetics.

Active species shows more steep density profiles. Ar($^3$P) does not spread and is extremely confined in front of the nozzle because Ar($^3$P) encounters immediate reactions with the other molecules just after ejected from the nozzle and quenched to its ground state. The density profile of Ar$_2^*$, which is not shown here, shows almost the same profile, but its density is one order of magnitude less than Ar($^3$P).

O($^3$P) and OH(X), which are responsible for oxidation reaction at the water surface, are generated through the reactions of O$_2$ and H$_2$O with Ar($^3$P) and Ar$_2^*$ near the nozzle. However, they are consumed before reaching the water surface because of secondary reactions R8-R20. Comparing the spatial profiles of O($^3$P) and OH(X), OH(X) travels longer distance. This is owing to lack of consumption reactions with abundant ambient gas of O$_2$ for OH(X), while O($^3$P) encounters the reaction R14 with abundant O$_2$ to produce O$_3$ as indicated in Table 1.

3.2. Spatial on the sliding surface

Figure 3 shows the results on the sliding water surface. Comparing these results to those in Fig. 2, we can recognize that the horizontal spatial profiles are bowing toward the left side corresponding to the direction of water flow. This is due to the gas-drag effect, by which the ambient gases are dragged and the gas composition on the surface is diluted by the dragged ambient gas.

The density of Ar around the nozzle and that on the water surface are relatively lower than that on the static surface, which can be confirmed by comparing Figs. 2(b) and 3(b).

The density profile of H$_2$O is markedly altered by the gas-drag effect. H$_2$O on the static water surface simply spreads toward upper region from the water surface working as an evaporation source as shown in Fig. 2(c). On the other hand, H$_2$O on the sliding surface is pushed toward the left side because of dragged ambient air. The density of H$_2$O in the
upper region on the sliding surface is highly diluted by ambient gases than that on the static surface. Because of this, the density profile of H₂O on the sliding water surface is mostly confined on the water surface as shown in Fig. 3(c), while that on the static water surface fully spread upward except for the jet stream region as shown in Fig. 2(c).

Regarding the density of active species of Ar(3P), O(3P), and OH(X) on the sliding surface shown in Figs. 3(d), 3(e), and 3(f), their spatial profiles are not markedly altered from those on the static surface shown in Figs. 2(d), 2(e), and 2(f). This is due to that production and consumption reactions for these species are mostly confined near the jet nozzle where the gas flow profile is mostly governed by jet flow as can be understood from Figs. 2(a) and 3(a).

Looking at the density of OH(X), however, we can recognize that its density profile is slightly bowing to the left-side. Since the OH(X) is less consumed and survives during their transport toward the water surface as discussed in the previous section, the density profile of OH(X) tends to be altered by the variation of the gas flow profile. Thus, we investigated the flux of OH(X) on the water surface and compared with that of O(3P).

3.3. Flux on the water surface

In this subsection, we discuss the effect of gas-drag on the flux of the active species O(3P) and OH(X) on the water because they are the important oxidation species in the case of water treatment by an APPJ. For this purpose, we calculated the flux of these species on the water surface using their density gradient on the surface. Sticking probability of these species is assumed to be unity in the present model.

Figures 4(a) and 4(b) show the flux of O(3P) and OH(X). Firstly, we can see that marked difference between them. The flux of O(3P) is 11th-order of magnitude less than OH(X). This is due to that O(3P) is almost fully consumed just after the ejection from the nozzle through the secondary reactions R14-R19. Thus, with in our present model, O(3P) has negligible contribution to the oxidation on the water surface. The reduction of O(3P) flux is further pronounced by sliding water surface as shown in Fig. 4(a) with the solid line.

OH(X), which is regarded as the major oxidation species in the present model, shows higher flux of 1.2×10¹¹ m⁻² s⁻¹ than O(3P) on the static surface. In the case of the sliding surface, however, the flux of OH(X) markedly reduced to 2×10¹⁰ m⁻² s⁻¹, which is 1/6 of the flux on the static water surface. According to Herron and Green, the reaction of OH(X) with O₂ show less priority than the other reactions [10], which is the reason why the reaction of OH(X)+O₂ is missing in the Table 1. Thus, OH(X) does not encounter the reactions with abundant O₂ supplied from the ambient air by the gas-drag effect.

Since the density of OH(X) is governed by its production and loss reactions. Its loss reactions are not major reason of the reduction in the density of OH(X) as discussed above. Thus, the reduction in the density of OH(X) is mainly caused by reduction in the production of OH(X), which can be understood from the fact that the maximum value of the density of OH(X) is reduced from 4.7×10⁻¹³ to 2.2×10⁻¹³. The reduction in the production of OH(X) originates in poor supply of H₂O from the water surface. H₂O vapor is pushed away to the left side by the gas-drag effect and the amount of H₂O to produce OH(X) through the reactions R4 and R5 is markedly reduced near the nozzle as can be understood from comparison between Figs. 2(c) and 3(c).
4. Conclusion
We have numerically investigated atmospheric pressure humid air chemistry triggered by metastable Ar atoms fed from a simplified APPJ irradiated on a flowing water surface. We focus on the gas-drag effects caused by the flow of water surface. The gas-drag effect alters spatial profile of gas-phase species near the APPJ. It alters also spatial profiles of the flux of OH(X) on the water surface. The flux of OH(X) is reduced to 1/6 when the water surface slides with the velocity of 0.5 m/s.

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References