The Spectra Study on Degradation of Sarin Simulant Diisopropyl Fluorophosphate by Plasma Coupled with Ozone

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Abstract: The diagnosis of irradiance particles produced in the plasma degradation of diisopropyl fluorophosphates (DFP) was studied by spectral method. The characteristic peaks of [O], [O+], [O2+], and [O3+], were obtained by analyzing spectra intensity changes in condition of different discharge parameters. As a result, it is found that the intensity of [O] peaks disappear when DFP is involved in the reaction. Moreover, for [O+], peaks, the intensity drop of 398.69 nm was 70.1%, and other three peaks disappeared, and for [O2+], peaks, the intensity drops of 226.49 nm and 231.19 nm were 95.3% and 94.5%, and 216.92 nm peak disappeared, which means [O], [O+] and [O2+] play important roles in the degradation of DFP by plasma.

1 INTRODUCTION

It is well known that dielectric barrier discharge plasma is mainly high-energy electrons and free radicals for the degradation of pollutants (Yu et al., 2015). In order to diagnose the active particles in plasma system, a characteristic peak set of emission spectra is established for several common active particles to determine the type and concentration of the produced active particles, and the concentration change of the active particles is used to assist in confirming the mechanism of plasma degradation of pollutants. Currently, probe, wave interference (Chang et al., 2007), mass spectrum (Jasmine et al., 2018) and spectrum technologies have been used to spectra diagnosis of plasma. Among these technologies, spectra diagnosis is a common and simple measuring technology (Bibhuti et al., 2017; Saeed et al., 2014). Much spectra researches of plasma have been reported and more about the pure gas, such as the pure oxygen (Zlatko et al., 2011) and nitrogen (Yan, 2004). But the spectral research of mixed gases (Andriy et al., 2016) is more difficult, because there are too many spectral lines to distinguish. There is few spectral analysis to the process of disinfection reaction, so a set of principles for spectral analysis has been formulated and applied to plasma reaction to confirm the active particles involved in the reaction. So, spectral analysis is used to assist the analysis of plasma reaction.

2 EXPERIMENT

2.1 Experimental Setup

Reactor: The outer electrode of non-thermal DBD plasma reactor is ground electrode (outer diameter 45 mm, wall thickness 15 mm), and coaxial inner aluminium electrode is used as the high voltage electrode (diagram 10 mm). The medium media is a quartz glass tube (outer diameter 15 mm, wall thickness 1 mm) is used as dielectric and fixed between inner and outer electrode, and the gap between high voltage electrode and quartz glass tube is 1.5 mm. The discharged gas enters the reactor through the inner electrode, and then exhausts from the gap between inner electrode and quartz glass tube. The reactor is put in the spectrum measuring cavity to avoid the interference of outside. The fiber probe of spectrometer is put 1 cm from the electrode in the quartz glass tube of reactor.

Power: High frequency power is employed that based on the atmospheric DBD plasma, and the power parameters is adjustable continuously. The range of pulse voltage peak value: 0-20 KV; the range of pulse current peak value: 0-200 mA; the
range of pulse frequency: 0-15 MHz; the range of average export power: 0-500 W. These parameters are detected by oscillograph (TDS1012B-type, fitted P6015A-1000X-type high voltage detector and A621-type current detector, America Tektronix Company) in real time.

2.2 Analysis Method

The quantitative analysis of DFP is operated by GC (7890A-type, fitted FPD detector, Agilent Company). The analysis of active particles is operated by spectrometer (AvanSpec-2048 type, fitted fiber probe, Avantes Company).

The plasma reactor and the spectral probe are placed in the spectral detection chamber, and the fiber probe is fixed in the plasma reactor quartz medium tube. The analysis process is as follows. Firstly, open the AvanSpec-2048 spectrometer and perform parameter setting (integration time, etc.). Secondly, the pure gas spectrum is detected. Thirdly, the air discharge spectrum is detected, thus the type and amount of the active particles are determined. Finally, spectral detection was performed before and after the air plasma degradation reaction.

3 RESULTS AND DISCUSSION

3.1 Analysis of Spectra

To study the spectral changes of active particles during plasma degradation of DFP, this study intends to determine the characteristic peaks of several common active particles such as [O],[O^+],[O_2^+] by the emission spectrum experiments and literature review of pure gas (N_2, O_2, Ar) and environment. Due to the plasma reaction, particle level structure and interference between particles, the paper believes that the selection of characteristic peaks of active particles should meet the following principles:

Firstly, the peaks are stably present in the plasma of different background gases, which is the basis for determining the characteristic peaks of the active particles; Secondly, the intensity of the peak is sensitive to the discharge power. The amount of active particles is closely related to the input energy. The active particles may have dozens of lines. Some of the lines may vary with energy, and the intensity changes are not obvious. Therefore, it is necessary to select those spectral lines that are more sensitive to energy (power) as characteristic peaks; Thirdly, the spectral intensity is high and easy to distinguish; Fourthly, the spectral peak is away from characteristic peaks of other active particles. Overlapping peaks may exist because of many spectrum lines from different active particles. If the location of two peaks is nearer, they may overlap affected by resolution ratio.

Take [O] for example, according to spectrum data comparison between literatures (Xie, 2008; Zhang et al., 2002) and this research, approximative wavelength peaks were searched. The principles were also used to treat these peaks.

(1) The spectrum character of [O] in discharging condition of pure oxygen

The spectrum of pure oxygen (gas flow 100 L/h) with the DBD plasma was detected in three different power of 74.4 W, 119.2 W and 154.8 W. comparing with literature, 15 rather apparent peaks of [O] (394.75 nm,395.38 nm,543.50 nm,700.19 nm,700.77 nm,700.82 nm,725.17 nm,725.39 nm,747.64 nm,777.28 nm,778.11 nm,795.63 nm,822.53 nm,844.73 nm,845.08 nm) were discovered. 5 spectrum peaks (543.50 nm,700.77 nm,700.82 nm,822.53 nm,844.73 nm) that its intensity is stronger with the power rising were selected by comparing the spectrum intensity of different power, as is shown in Table 1.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Level</th>
<th>74.4 W</th>
<th>119.2 W</th>
<th>154.8 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>543.50</td>
<td>O^+</td>
<td>78.4</td>
<td>101.6</td>
<td>135.8</td>
</tr>
<tr>
<td>700.77</td>
<td>O^-</td>
<td>172.6</td>
<td>194.4</td>
<td>198.4</td>
</tr>
<tr>
<td>700.82</td>
<td>O^-</td>
<td>164.2</td>
<td>113.8</td>
<td>133.0</td>
</tr>
<tr>
<td>822.53</td>
<td>O^-</td>
<td>107.2</td>
<td>72.8</td>
<td>103.4</td>
</tr>
<tr>
<td>844.73</td>
<td>O^-</td>
<td>47.4</td>
<td>66.6</td>
<td>140.6</td>
</tr>
</tbody>
</table>

Note: Regarding the spectrum intensity value of the lowest power as basis, and divided by all spectra intensity value of different power of each wavelength. This is the calculation method of spectra intensity ratio. Take 543.5 nm, for example, 78.4/78.4=1.0; 101.6/78.4=1.3; 135.8/78.4=1.7. The style of level is low level-high level.

The 5 peaks are sensitive to the power and stronger with the power rising. The energy gap of excited state and ground state is different. After eradiated transition, peaks of different wavelength are emitted. Spectrum intensity of 700.77 nm is insensitive to power, while the intensity of other four peaks is stronger with the power rising. The energy requirement of excited state is different with different energy levels. Jump to the lower level S^3,S^1, the intensity ratio of 543.50 nm and 844.73 nm peaks is 1.0:1.3:1.7 and 1.0:1.4:3.0 when the power ratio is 1.0:1.6:2.1. So the intensity change is obvious. The reason for the difference of spectrum intensity ratio of different peaks is the quantum
yield of eradiated transition between different excited state and ground state different, which leads to the intensity change of spectrums.

(2) The spectrum character of [O] in discharging condition of Ar.

In order to confirm the stable existence of characteristic peaks of [O] in different conditions, the discharging experiment of pure Ar+1.8%O₂ (gas flow 100 L/h) with the DBD plasma was made in condition of three different power 41.2W, 65.5W, 120.0W.

(3) The spectrum character in discharging condition of air.

The spectrum of air (gas flow 100L/h) with the DBD plasma was detected in condition of three different power 107W, 136W, 198W. The spectrum intensity ratio of 5 peaks (detected from pure oxygen spectrum) in discharging condition of air was calculated.

In conclusion, 543.50nm, 700.77nm, 844.7nm were selected as the characteristic spectrum peaks of [O]. According to the principles of characteristic peaks, the characteristic peaks of [O⁺], [O₂⁻] were 398.69nm, 410.49nm, 476.68nm, 494.10nm and 216.92nm, 226.49nm, 231.19nm.

3.2 Analysis of the Roles for Active Particles in the Degradation of DFP

O₃ is a strong oxidant. But the active particles of O₃ produced in plasma play a more important role, rather than the strong oxidability of itself. The molecule iron of O₃ was not reported and this paper also did not find the molecule iron in O₃ spectrum experiment. So we infer that the active particles of O₃ is similar to O₂.

To confirm the active particles that participate in DFP degradation, the spectrum of air +O₃ discharging plasma and air+O₃+DFP discharging plasma was detected. The spectrum before and after degradation was compared and analyzed in condition of O₃ concentration 500 mg/m³, initial concentration of DFP 19.5 mg/m³, flow 400 L/h, power 105 W.

(1) Effects of [O]

[O] can be produced by the following process:

\[ \text{e} + \text{O}_3 \rightarrow \text{O}_2 + \text{O} + e \]
\[ \text{e} + \text{O}_2 \rightarrow 2\text{O} + e \] (1)
\[ \text{e} + \text{O} \rightarrow \text{O} + \text{O} + e \] (2)

According to the comparison of spectrum before and after DFP degradation, it is found that the spectrum peaks of [O] existed in the spectrum of plasma without DFP degradation (the magnifying part of Figure 1) obviously, while the peaks was not detected in the spectrum of plasma with DFP degradation reaction (the magnifying part of Figure 2). Which means [O] did not exist or its concentration was under the limit of detection (LOD) of spectrometer. The only changed factor of experiment was the addition of DFP, and its concentration reduced, so the strong oxidizing [O] was consumed in process of DFP degradation.

(2) Effects of [O⁺]

[O⁺] can be produced by the following process:

\[ \text{e} + \text{O}_2 \rightarrow \text{O}_2 + \text{e} \]
\[ \text{e} + \text{O}_2 \rightarrow \text{O} + \text{O}^+ + 2e \] (3)
\[ \text{e} + \text{O} \rightarrow \text{O}^+ + 2e \] (4)

Figure 1: The spectrum of [O] by plasma coupled with O₃.

Figure 2: The spectrum of [O⁺] from DFP degradation by plasma coupled with O₃.

Figure 3: The spectrum of [O⁺] from plasma coupled with O₃.

Figure 4: The spectrum of [O⁺] from DFP degradation by plasma coupled with O₃.
The spectrum before and after the DFP degradation was shown in Figure 3 and Figure 4. According to the contrast of 4 spectrum peaks of [O⁺], the intensity drop of 398.69 nm was 70.1%, and other three peaks disappeared. The concentration of [O⁺] reduced apparently. So [O⁺] was one of main particles in DFP degradation.

(3) Effects of [O₂⁺]

[O₂⁺] can be produced by the following process:

$$e + O_2 \rightarrow O_2^+ + 2e \quad O^+ + O_2 \rightarrow O_2^+ + O \quad (5)$$

Figure 5: The spectrum of [O₂⁺] from plasma coupled with O₂.

Moreover, for [O⁺] peaks, the intensity drop of 398.69 nm was 70.1%, and other three peaks disappeared, and for [O₂⁺] peaks, the intensity drops of 226.49 nm and 231.19 nm were 95.3% and 94.5%, and 216.92 nm peak disappeared, which means [O], [O⁺] and [O₂⁺] play important roles in the degradation of DFP by plasma.

4 CONCLUSIONS

This paper put forward a basic principle for selecting characteristic peaks based on theory study and experimental data analysis. The diagnosis of irradiance particles produced in the plasma degradation of DFP was studied by spectral method. The characteristic peaks of [O], [O⁺], [O₂⁺] were obtained by analyzing spectra intensity changes in condition of different discharge parameters. As a result, it is found that the intensity of [O] peaks disappear when DFP is involved in the reaction. Moreover, [O₂⁺] peaks, the intensity drop of 398.69 nm was 70.1%, and other three peaks disappeared, and for [O₂⁺] peaks, the intensity drops of 226.49 nm and 231.19 nm were 95.3% and 94.5%, and 216.92 nm peak disappeared, which means [O], [O⁺] and [O₂⁺] play important roles in the degradation of DFP by plasma.

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