

Received October 9, 2018, accepted October 29, 2018, date of publication November 9, 2018, date of current version December 19, 2018.

Digital Object Identifier 10.1109/ACCESS.2018.2879157

Study on Degradation of SF₆ in the Presence of H₂O and O₂ Using Dielectric Barrier Discharge

XIAOXING ZHANG¹, ZHAOLUN CUI¹, YALONG LI¹, HANYAN XIAO², YI LI¹, AND JU TANG¹

¹School of Electrical Engineering, Wuhan University, Wuhan 430072, China

²Electric Power Research Institute, State Grid Jiangsu Electric Power Co., Ltd., Nanjing 210008, China

Corresponding author: Xiaoxing Zhang (xiaoxing.zhang@outlook.com)

This was supported by the National Natural Science Foundation of China (NSFC), under Grant 51777144.

ABSTRACT In this paper, a method using dielectric barrier discharge for SF₆ abatement is investigated. The destruction and removal efficiencies (DRE) of plasma abatement of 2% SF₆ in the presence of H₂O and O₂ were studied. The addition of H₂O and O₂ effectively promoted the decomposition process of the SF₆. With the participation of 0.5% H₂O and 2% O₂, the DRE reached 98.2% at 50mL/min flow rate and the energy efficiency reached 5.73 g/kWh. By emission spectra and products composition analysis, we found that the addition of H₂O can generate a large amount of H and OH radicals in plasma region, making SF₆ tend to degrade to produce SO₂. The addition of O₂ can generate a large amount of O radicals, which promotes the production of SO₂F₂. The addition gas not only affects the type of products, but also determines the selectivity of each degradation product. The results in this paper provide experimental support for the treatment of SF₆ tail gas using low temperature plasma.

INDEX TERMS SF₆, DBD, H₂O, O₂, emission spectra, products analysis.

I. INTRODUCTION

As a colorless, odourless and non-toxic gas, SF₆ is widely used in the power industry as the insulating gas because of its excellent insulation properties. However, SF₆ has a very strong greenhouse effect with a global warming potential up to 23,500 and a stable atmospheric presence of 3,200 years [1]. It was one of the six greenhouse gases listed in the 1997 Kyoto Protocol [2]. In recent years, with the development of the power industry, the demand for SF₆ has been increasing. The electrical field accounts for about 80% of the total demand of SF₆ [3]. In the past five years, the content of SF₆ in the global atmosphere has increased to the order of ~10⁵ tons [4]. Therefore, the emission and treatment of SF₆ is a hot issue in environment field in recent years.

Methods like thermal degradation [5]–[8], photodegradation [9]–[11], catalyst decomposition [12] and electrical degradation have been applied for abating SF₆. The first three methods have disadvantages such as low processing efficiency and harsh reaction conditions, and are not suitable for large-scale industrial use. Electrical degradation methods are based on nonthermal plasmas include microwave discharge, radio frequency discharge, dielectric barrier discharge (DBD)

and other means. The active particles in plasma collide with the SF₆ molecule and decompose S-F bonds [13]–[16]. DBD discharge, as a low-temperature plasma, has relatively simple discharge conditions and experimental setup, and is relatively safe to operate. It is widely used to treat VOCs and other industrial tail gases [17]–[19]. In recent years, some scholars have studied the degradation of SF₆ with DBD and the effects of factors such as addition gases and humidity on the degradation of SF₆ were researched [20]–[22]. Lee *et al.* used DBD and combined plasma catalysis (CPC) methods to treat SF₆ and studied the effects of different added gases such as Ar, O₂, C₂H₄ and H₂O on degradation. They mainly studied the degradation process of a very low concentration of SF₆ (300 ppm). Zhuang *et al.* used a DBD discharge to degrade 820 ppm of SF₆ at 623 ml/m, which the SF₆ degradation rate is close to 100%. Zhang *et al.* used DBD discharge to degrade SF₆, CF₄ and SF₅CF₃ gases, and analyzed the composition of degradation products by infrared spectroscopy. None of the above studies detected and analyzed active particles in DBD processes by means of optical emission spectrum.

Emission spectrum analysis can effectively obtain parameters such as active particle contents in the plasma region,

and does not interfere with the gas discharge process. It is a common research method for gas discharge phenomena. In 1989, Radovanov *et al.* [23] studied the emission spectrum of SF₆/N₂/Ar under RF discharge. In 1990, Sadeghi *et al.* studied the production of SF₂ in pure SF₆ over the discharge process by emission spectroscopy [24]. Thereafter, the formation processes of SF_x and F atoms in SF₆ decomposition were studied [25]–[30]. However, the emission spectrum of the SF₆ decomposition process with additional gases (H₂O and O₂) has not been studied.

In this paper, we obtained the emission spectra of SF₆/Ar mixed gas with the participation of O₂ and H₂O, and analyzed the composition of active particles. The decomposition products were detected by fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometer (GC-MS). Finally, the degradation effect of SF₆ under the participation of H₂O and O₂ was discussed. Relevant research results provide reference for further efficient and harmless treatment of high concentration SF₆.

II. METHOD

A. TEST PLATFORM

The schematic diagram of the DBD plasma system is shown in Figure 1. The plasma is generated by the plasma power supply (CTP-2000K, Nanjing Suman Electronics), with power frequency of 5–20 kHz, operating voltage of 0–30 kV, output power of 0–300 W. The reactor is a concentric double quartz tube. The outer diameter of the inner tube is 8 mm, the thickness of the inner tube is 2 mm. The inner diameter of the outer tube is 20 mm, the thickness of the outer tube is 2.5 mm. The gap distance is 6 mm, the length of the tube is 300 mm and the discharge length is 200 mm. The volume of the discharge area is 86 cm³. The electrode material is copper.

The reaction gas was mixed by a gas distributor (GC500, Tunkon Electric Technology Co. Ltd.) with a maximum ratio of 300:1 and a precision of ±1%FS. The standard gas (Newradargas Co., Ltd, Wuhan) were 10% SF₆, 10% O₂ and 99.999% pure Ar. Ar was used as a carrier gas during this experiment as it has been proven to have a good discharge effect in our previous studies [31]. H₂O was added to the reactor through a gas-washing bottle and the H₂O concentration was measured by a mirror dewpoint meter (GE600, Henan Relations Co., Ltd.). After testing, the temperature of the gas washing-bottle was maintained at about 298 K. Under the flow rate of 50~100 ml/min, the concentration of H₂O was basically maintained at 0.5%. The treated gas is introduced into the gas-washing bottle with saturated NaOH solution for further treatments.

The concentration of SF₆ was detected by gas chromatograph (GC) (GC-450, Shanghai Huishi Instrument). The concentration of SF₆ was determined by internal peak integration method using a TCD detector. SF₆ peak time is 2.4–2.6 min and the carrier gas is 99.999% high purity Helium. Several decomposition products (SO₂F₂, SOF₂, SO₂ and SOF₄) were quantitatively detected by GC-MS (Shimadzu Ultra 2010plus

with CP-Sil 5 CB column, SHIMADZU Co., Ltd.), using the internal peak integration method, 99.999% Helium as the carrier gas. The remaining product was detected by an FTIR (IRTracer-100, SHIMADZU Co., Ltd.) with a detection band of 400–4000 cm⁻¹, with a resolution of 1 nm, and 10 scanning times.

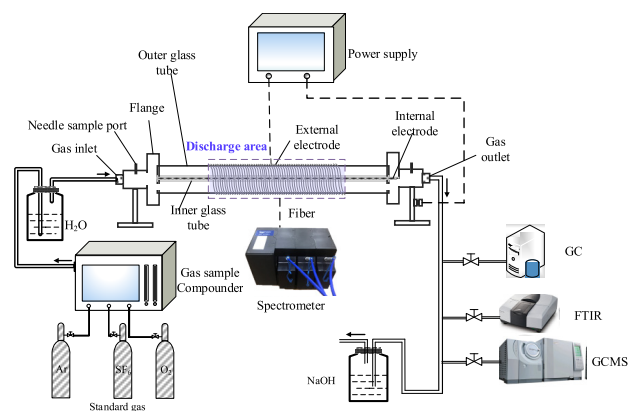


FIGURE 1. Schematic diagram of the DBD plasma system (Input voltage: 8–12 kV; Discharge current: 0–0.15 mA; Output power: 0–100 W; Actual discharge length: 20 cm; SF₆ initial concentration: 2%).

The emission spectrum is detected by a three-channel spectrometer (MX2500+, Ocean optics Co., Ltd.), which uses a grating as a beam splitting element and a CCD array as a detector. The wavelength measurement range is 300–800 nm, the optical resolution is 0.1 nm, the integration time is 1 ms–65 s, and the trigger delay and trigger jitter are ± 450 ns and ± 10 ns, respectively.

The experimental conditions are summarized as follows: SF₆ concentration is fixed at 2%. The additives are H₂O (0.5%), O₂ (0.5%–8%). The ratio of O₂ to SF₆ was O₂/SF₆ = 1/2–4/1 (Volume fraction). The reactor pressure was 101.3 kPa and the mixed gas temperature was 298 K. Power discharge frequency was 8.7 kHz, the input voltage was around 7–13.6 kV. The gas flow rate was controlled at 50 ml/min. The flow rate is relatively low and it's limited by the size of the discharge tube. When considering the practical application, tens of discharge tubes can form a matrix, which greatly increases the flow rate and throughput, and meets the requirements of industrial applications. This is one of our current research works.

B. PARAMETER CALCULATION METHOD

The product compositions were based on molar concentrations of the effluent. The destruction and removal efficiencies of SF₆ (DRE) were calculated as follows:

$$DRE(\%) = \frac{C_{in} - C_{out}}{C_{in}} \quad (1)$$

where C_{in} and C_{out} are the SF₆ concentrations before and after the treatment.

Energy yield (EY) is calculated based on the DRE and the input power P_i . EY is defined as the mass (g) of SF₆

degradation per unit of energy (kWh). The formula is:

$$EY(g/kWh) = \frac{m_{SF_6\text{converted}}}{P_i \times t} \quad (2)$$

Where, $m_{SF_6\text{converted}}$ is the mass of SF₆, the unit is g. P_i is the input power and is directly read through the display on the voltage regulator table, the unit is kW. t is the reaction time and the unit is h.

The selectivity calculation of the main sulfur-containing by-products is as follows:

$$S_K(\%) = \frac{C_K}{C_{in} - C_{out}} \times 100\% \quad (3)$$

Where K represents the name of the product and C_K is the concentration of the product in the degraded gas.

III. RESULTS AND DISCUSSION

A. DRE AND EY

1) DRE

Figure 2 shows the SF₆ DREs changed with input power under different gas additions. When no H₂O or O₂ was added, the DRE was relatively low. When the input power was 34W, DBD discharge began to occur in the reactor, electrons and active particles reacted with SF₆ to make the S-F bonds broken by equation (4). SF₆ was likely to be recombined by equation (5) and reduced the DRE. When the input power was increased, active particles were accumulated in the discharge area, which resulted in the decomposition process of SF₆ being much faster than that of the recombination process. Meanwhile, SF_x also decomposed continuously by electron collisions, resulting in a significant increase in the DRE. When the input power was 90 W, the DRE reached 60%.

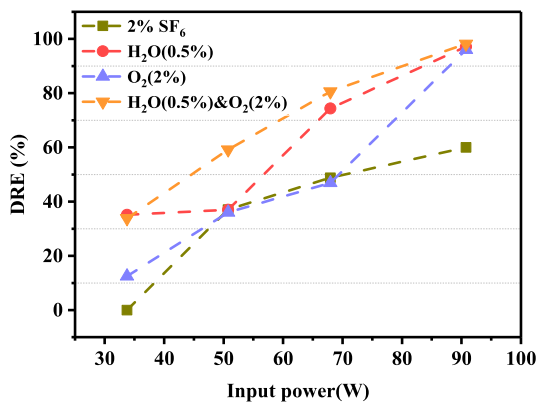
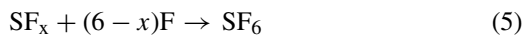
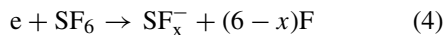


FIGURE 2. Relationship between SF₆ DREs and input power with different gases addition (2% SF₆, 50ml/min).

When O₂ and H₂O were added, the DRE showed a significant increase. The DRE reached 36% under 34W input power with 0.5% H₂O, which may be due to the ionization of H⁺ and OH⁻ in the electric field. The two kind of ions

can react with SF_x and restrict the recombination process. Similarly, O₂ can oxidize the SF_x and restricts the recombination process. Therefore, when O₂ or H₂O were added, DRE exceeded 90% under 90W. In Figure 2, when the input power was low, the effect of adding H₂O was better than that of O₂. When the input power was 68W, the DRE under 0.5% H₂O reached 74.37%, while the DRE under 2% O₂ was only 46.91%. The degradation effect with O₂ addition is similar to the degradation effect without it. This may be due to that H₂O is easier to ionize and generates active particles [32]. The low-fluorine sulfides and F⁻ ions are more likely to react with OH⁻ and H⁺. Besides, when the input power is low, O₂ acts as an electronegative gas, and O₂ ionization in the electric field needs to absorb energy, resulting in a decrease in energy for SF₆ breaking bond decomposition, which affects the DRE. However, when H₂O and O₂ were added together, the DRE was highest, indicating that H₂O and O₂ can simultaneously provide effective active particles and restrict the recombination process.

Besides, we obtained the SF₆ DREs under different O₂ concentrations with input power of 90W. The results are shown in Figure 3.

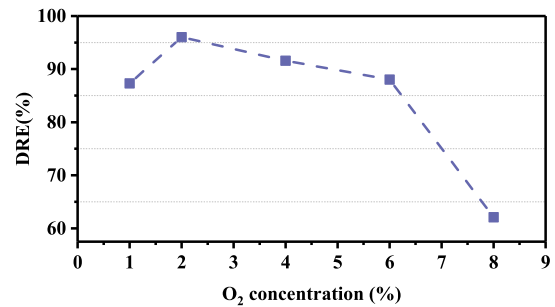


FIGURE 3. Influence of DREs and O₂ concentrations (2% SF₆, 90W input power, 50ml/min).

In Figure 3, the DRE of SF₆ increased firstly and then decreased with the O₂ concentration changing from 1% to 8%. The DRE reached the maximum under 2% O₂ while $c(SF_6)/c(O_2) = 1/1$. The change of O₂ concentration may affect the density of active particles in the discharge area. Too high or too low O₂ concentrations may cause the decrease of active particles, affecting the DRE of SF₆.

Similarly, we maintain the input power of 90W unchanged, adding 0.5% H₂O and changing the concentration of O₂. The DRE change results are shown in Figure 4. In Figure 4, when the O₂ concentration does not exceed 2%, SF₆ has a high DRE, more than 95%. When the O₂ concentration exceeds 4%, the DRE dropped rapidly, only 83.81%, indicating that too high concentration of O₂ also had inhibition effect when H₂O was added. Therefore, under this experimental conditions, it is best to keep the ratio of O₂ to SF₆ at 1/1.

The 2% SF₆ DREs under different applied gases were summarized, as shown in Table 1. The flow rate was 50 ml/min and the input power was 90 W. More details about C_{in} and C_{out} are summarized in supplementary data.

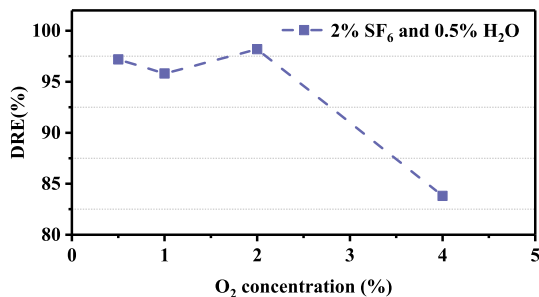


FIGURE 4. Influence of DREs and O₂ concentrations with H₂O addition (2% SF₆, 0.5% H₂O, 90W input power, 50ml/min).

TABLE 1. SF₆ DREs under different additive gas conditions.

Mixtures	DREs	Mixtures	DREs
Without additive	60.0	-	-
H ₂ O (0.5%)	97.14	O ₂ (1%)	87.31
H ₂ O(0.5%)/O ₂ (0.5%)	97.19	O ₂ (2%)	96.01
H ₂ O(0.5%)/O ₂ (1%)	95.81	O ₂ (4%)	91.57
H ₂ O(0.5%)/O ₂ (2%)	98.19	O ₂ (6%)	88.02
H ₂ O(0.5%)/O ₂ (4%)	83.81	O ₂ (8%)	62.09

2) EY

According to Equation 2, the EYs of SF₆ degradation were calculated and compared with the related studies [20], [21]. The results are shown in Figure 5.

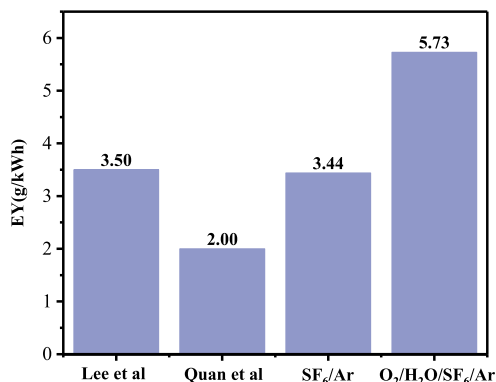


FIGURE 5. EYs for different gases mixture from this study and Lee et al. [20] and Quan et al. [21].

Compared with [20], [21], this experiment obtained a high DRE of 98.2% and the EY reached 5.73 g/kWh. This may indicate that the coordination between the power supply and the DBD reactor can generate a strong discharge space in the reactor. Meanwhile, with the participation of H₂O and O₂, the active particles were effectively increased and restricted the SF₆ recombination.

B. EMISSION SPECTRA AND BY-PRODUCT ANALYSIS

1) H₂O

Figure 6 is the emission spectrum of the SF₆/H₂O/Ar system. There are many characteristic lines in this figure.

The intensity of the line between 700~800 nm is much larger than other parts. Compared with the NIST database [33], the SF₆/H₂O/Ar plasma emission was initially diagnosed. Several strong main lines in the spectrum are : Ar (696.64 nm), F (739.87 nm), Ar (750.38 nm), Ar (763.51 nm), Ar (794.82 nm), and Ar (800.62 nm). The Ar lines are all I-type, which were generated when the excited state Ar atom transited to a lower energy level. The proportion of Ar in the reaction gas was as high as 97.5%, so the intensity of the lines was relatively large. The production process of these excited state particles Ar* is as follows:

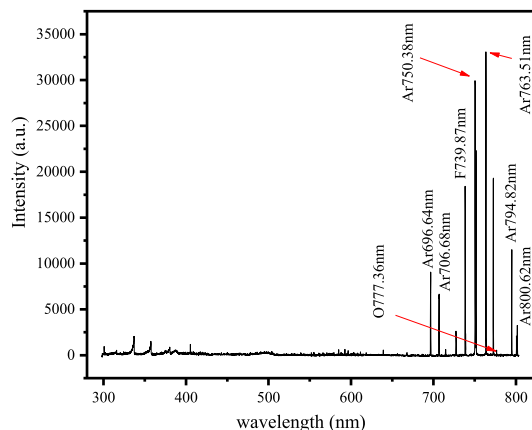
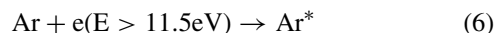
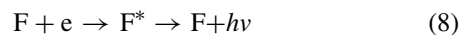
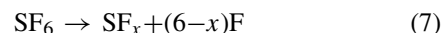
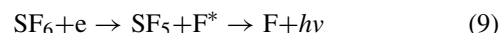


FIGURE 6. The optical emission spectrum of SF₆/ H₂O/Ar plasma (2% SF₆, 0.5% O₂, 97.5% Ar, 10kV, 50ml/min).

The electron energy distribution in the SF₆/H₂O/Ar plasma system were calculated by Zhang et al. [31]. The number of electrons in this system with energy greater than 11.5 eV were relatively large, so a large amount of Ar* could be produced. In addition to the Ar lines, F I-type line at 739.87 nm was relatively large, which was generated by the dissociation of SF₆ molecules, and the production processes may be following the equations (7)-(9):



Or



At the same time, a weak O line was also found at 777.36 nm. In order to analyze the emission spectra of other particles during the discharge, the spectra in the range of 300-450 nm and 450-680 nm were filtered and amplified, as shown in Figures 7(a) and (b), and detailed active particles were analysed.

In the range of 300~450 nm, the main active particles were OH (308 nm), N₂ (308 nm, 357.61 nm and 380.46 nm), O (362.77 nm), F (385.14 nm), Ar (402.47 nm) and H (434.11 nm). In the range of 450-680 nm, the main active

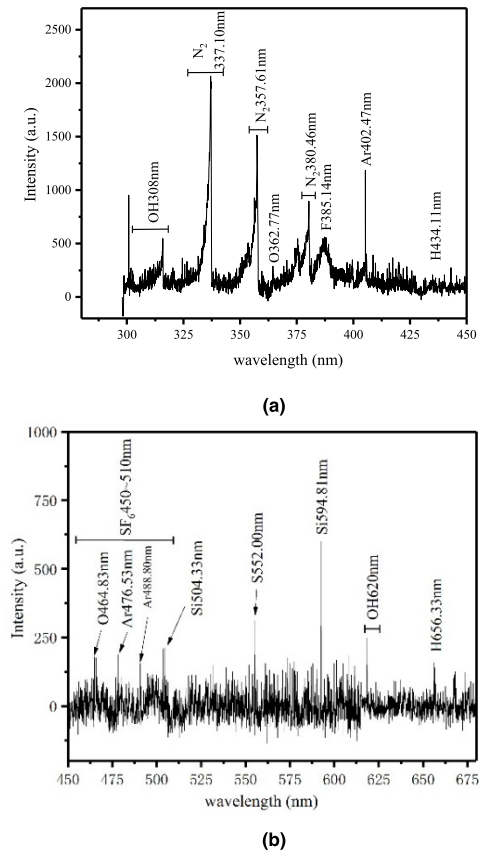


FIGURE 7. The partial emission spectra of SF₆/H₂O/Ar plasma. (a) 300~450 nm. (b) 450~680 nm

particles were O (464.83 nm), Ar (476.53 nm and 488.80 nm), S (550.91 nm), OH (620 nm), Si (504.33 nm and 594.81 nm) and H (656.33 nm). Moreover, the characteristic peaks of SF₆ molecules were detected at 450~510 nm, which is consistent with the results of [29]. The source of OH and H radicals is water vapor in the reaction gas, wherein OH is a strong oxidizing group and played an important role in promoting chemical reactions. Since the Si line was detected, it indicates that the active F radicals generated by the dissociation of SF₆ reacted with SiO₂ in the quartz wall. However, the etching process is very slow, and can be neglected when the amount of SF₆ is not large. One reason for using quartz glass as the tube material is to better observe the discharge phenomenon. On the other hand, we have begun to use ceramic tubes as the discharge medium. The ceramic tubes have a similar dielectric barrier effect and are resistant to high temperatures and hardly react with the decomposition products of SF₆, which is suitable for industrial applications. In the semiconductor manufacturing industry, the above reaction is also called the etching reaction. Therefore, O radicals may have two sources, etching of SiO₂ and further decomposition of OH groups. N₂ was absent from the reaction gas, but the band of N₂ was detected in the emission spectrum, and this may be because of traces of N₂ leaking into the reactor. Due to the limitations of the emission spectroscopy technique, only the above active

particles were detected, but this does not mean that only these active particles are present in the SF₆/H₂O/Ar plasma.

In this experiment, the by-products were qualitatively analyzed using FTIR, and Figure 8 is the FTIR spectrum of the degradation products under 0.5% H₂O. According to Kurte *et al.* [34], [35], the degradation products corresponding to each characteristic peak were determined. In Figure 8, the main products include SOF₂, SOF₄, SO₂F₂, SO₂, SiH₄, SiF₄, SF₄ and S₂F₁₀, similar to the results of Lee *et al.* [20]. Among them, SF₄ and S₂F₁₀ are the primary products of degradation, which were directly decomposed by SF₆, and didn't react with H₂O and its free radicals. The presence of SiH₄ and SiF₄ demonstrates that SiO₂ in quartz glass participated in the reaction.

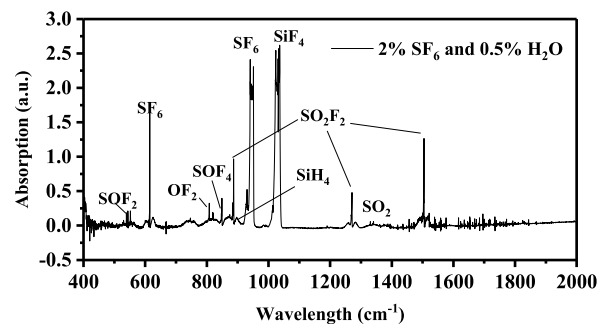


FIGURE 8. FTIR spectrum of by-products under 0.5% H₂O (90W input power, 50 ml/min).

In order to analyse the formation characteristics of by-products, the four products of SOF₄, SO₂F₂, SOF₂, and SO₂ were quantitatively detected by GC-MS, and their selectivity was calculated by equation (3), as shown in Figure 9. SOF₄ is the main product, with the highest selectivity, above 50%. Followed by SO₂, the selectivity is also higher, above 25%, while the production of SO₂F₂ and SOF₂ is smaller. The specific concentration values for the four gases are summarized in the supplementary data.

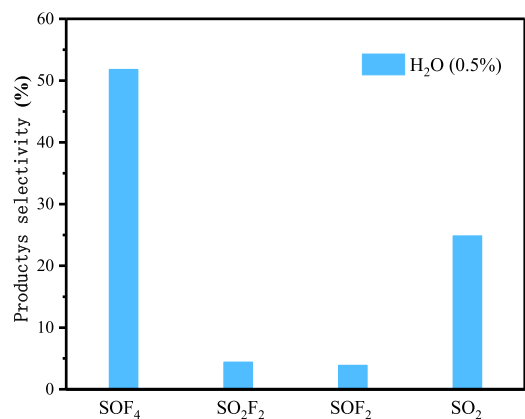


FIGURE 9. Comparison of the selectivity of the main sulphur containing products with H₂O.

2) O₂

In the experiment, the emission spectrum of the SF₆/O₂/Ar system was measured in the range of 300-800 nm. Figure 10 shows the measured emission spectrum, which is very similar to the spectrum of SF₆/H₂O/Ar plasma. The intensity of the line in the range of 690~800 nm is relative large, mainly are Ar, F and O lines.

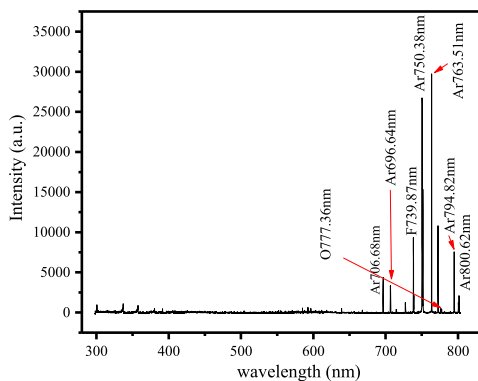
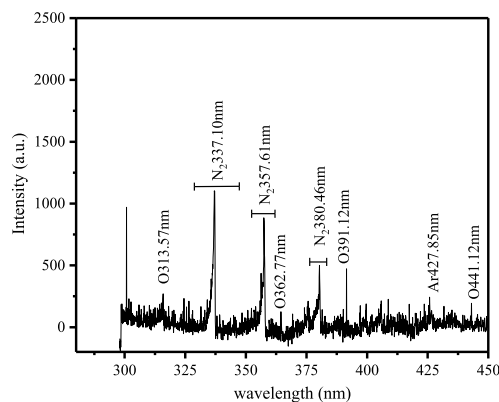


FIGURE 10. The optical emission spectrum of SF₆/ O₂/Ar plasma (2% SF₆, 2% O₂, 96% Ar, 10kV, 50ml/min).

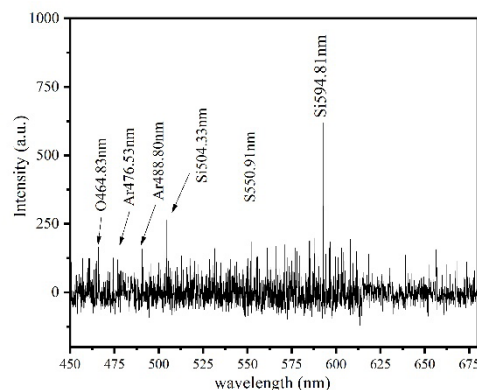
Similarly, the emission spectrum of Figure 10 was filtered and amplified in the range of 300-450 nm and 450-680 nm to obtain detailed information, as shown in Figure 11 (a) and (b). In the 300~450 nm spectrum, the main active particles detected were O (313.57 nm, 362.77 nm, 391.12 nm and 441.12 nm), N₂ (308 nm, 357.61 nm and 380.46 nm), F (385.14 nm) and Ar (427.85 nm). In the range of 450~680 nm, the main active particles detected were O (464.83 nm), Ar (476.53 nm and 488.80 nm), S (550.91 nm) and Si (504.33nm and 594.81 nm). Compared with the SF₆/H₂O/Ar plasma spectrum, since there was no water vapor in the reaction gas, no OH line was detected, but the O lines increased. It can be seen that O radicals are the main strong chemically active groups in the SF₆/O₂/Ar discharge system. Since the Si line was detected, there were also two sources of O radicals. Some water vapor may leak into the reactor and caused the etching reaction of SiO₂. However, there is no SF₆ characteristic peaks at 450~510 nm, which may because SF₆ was degraded thoroughly before the measurement.

Figure 12 is the FTIR spectrum of by-products in SF₆/O₂/Ar system. It can be seen that the main degradation products are SOF₂, SOF₄, SO₂F₂, SO₂, SiF₄, SF₄ and S₂F₁₀. These products were also present under SF₆/H₂O/Ar conditions, but since there were no H-containing particles in the plasma system, no SiH₄ was detected. This also indicates that changes in the applied gas will affect the type of degradation products. The specific concentration values for the four gases are summarized in the supplementary data.

The four products of SOF₄, SO₂F₂, SOF₂, and SO₂ were also quantitatively and their selectivity was calculated, as shown in Figure 13. SOF₄ is still the most important product, with the highest selectivity, above 40%, lower than that in SF₆/H₂O/Ar system. Compared to H₂O conditions,



(a)



(b)

FIGURE 11. The partial emission spectrum of SF₆/O₂/Ar plasma. (a) 300~450 nm. (b) 450~680 nm.

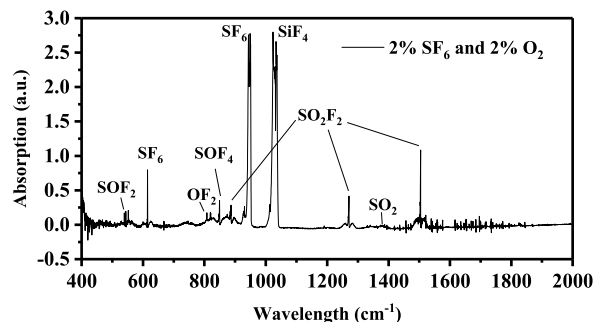


FIGURE 12. FTIR spectrum of by-products under 2% O₂ (90W input power, 50ml/min).

the selectivity of SO₂F₂ was increased by more than 25%, while the selectivity of SO₂ was reduced. Although the selectivity of SOF₂ has increased, it is still low. Therefore, the addition gas not only affects the type of products, but also determines the selectivity of each degradation product.

According to the emission spectra, when H₂O and O₂ participate in the reaction, O, H and OH radicals were generated to react with SF₆ and SF_x to produce products such as SOF₄, SO₂F₂, SOF₂ and SO₂, which hinder the SF₆ recombination process. In Figure 6, the line intensity of H₂O/SF₆/Ar

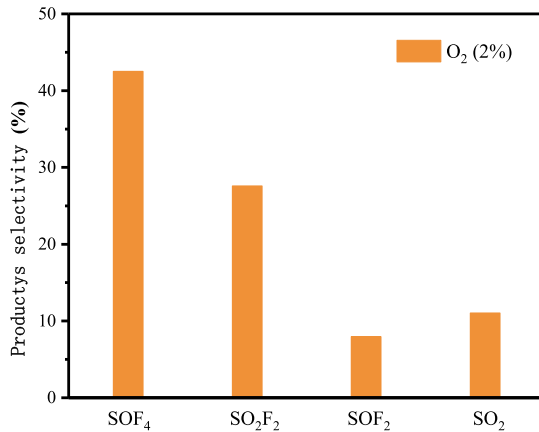


FIGURE 13. Comparison of the selectivity of the main sulphur containing products with O₂.

is stronger than that of SF₆/O₂/Ar in Figure 10. This may be because the electronegativity of O₂ is stronger than that of H₂O, and more electrons were adsorbed by O₂ which decreased the spectral intensity.

In our previous work, we've analyzed the possible decomposition paths of SF₆ under the participation of H₂O and O₂ [32]. The reactions involved in the decomposition of SF₆ molecules with additional gases were summarized in Table 2 [32], [35]. Without additional gases, SF₆ caused reactions (10)-(16) in the discharge region and break bonds. Since these reactions are endothermic, the decomposition of SF₆ is relatively slow and recombination reactions may occur to produce SF₆. Adding O₂ will generate a large amount of O radicals in the discharge area, promoted the reactions (17)-(24) and inhibited the recombination process of SF₆, making SF₆ more inclined to produce SO₂F₂ and SOF₂. With H₂O addition. The emission spectra in this experiment can prove that the addition of H₂O will introduce a large amount of H and OH radicals in the discharge region, promoted the reactions (25)-(30), which make SF₆ molecules more inclined to produce SO₂. Meanwhile, reaction (33) will also cause an etching process on the inner wall of the reactor. Beside, the reaction (30) occurred and reduced the SOF₄ production, which is consistent with the Figure 13. Since SO₂F₂ is slightly soluble in water, and SO₂ is easily reacted with an alkali solution [36], SO₂ is more easily treated, so the product with H₂O addition is relatively better than the gas products with O₂ addition.

In this study, 2% SF₆ at a flow rate of 50 ml/min was degraded thoroughly with the participation of H₂O and O₂. The DRE could reach 98.2%. However, the flow rate is relatively low and there are some primary by-products such as SF₄ and S₂F₁₀, indicating that the degradation of SF₆ is not complete. Therefore, designing DBD reactor matrix or using packed bed materials may improve the SF₆ processing efficiency and this is the focus of our current study.

TABLE 2. Formation reactions of the by-products and their reaction heat.

No.	Reaction	Reaction heat (kcal/mol)
(10)	$SF_6 + e^* \rightarrow SF_5 \cdot + F \cdot + e$	86.09
(11)	$SF_5 + e^* \rightarrow SF_4 \cdot + F \cdot + e$	41.46
(12)	$SF_4 + e^* \rightarrow SF_3 \cdot + F \cdot + e$	97.15
(13)	$SF_3 + e^* \rightarrow SF_2 \cdot + F \cdot + e$	53.32
(14)	$SF_2 + e^* \rightarrow SF \cdot + F \cdot + e$	86.18
(15)	$SF + e^* \rightarrow S \cdot + F \cdot + e$	113.79
(16)	$2SF_6 + e^* \rightarrow S_2F_{10} + F_2$	118.28
(17)	$SF_5 + O \rightarrow SOF_4 + F$	-42.53
(18)	$SF_4 + O \rightarrow SOF_4$	-126.63
(19)	$SF_2 + O \rightarrow SOF_2$	-130.89
(20)	$SF + O + F \rightarrow SOF_2$	-217.07
(21)	$SOF_2 + O \rightarrow SO_2F_2$	-39.03
(22)	$SO_2F_2 \rightarrow SO_2 + 2F \cdot$	81.26
(23)	$SOF_4 + O \rightarrow SO_2F_2 + 2F$	88.46
(24)	$S + 2O \rightarrow SO_2$	-274.71
(25)	$SF_5 + OH \rightarrow SOF_4 + HF$	4.51
(26)	$SF_4 + OH + F \rightarrow SOF_4 + HF$	-156.64
(27)	$SF_3 + OH \rightarrow SOF_3 + HF$	-107.59
(28)	$SF_2 + OH + F \rightarrow SOF_2 + HF$	-160.91
(27)	$SF + OH + 2F \rightarrow SOF_2 + HF$	-247.09
(29)	$SOF_2 + H_2O \rightarrow SO_2 + 2HF$	-18.33
(30)	$SOF_4 + H_2O \rightarrow SO_2F_2 + 2HF$	-26.35
(31)	$F + F \rightarrow F_2$	-55.95
(32)	$H + F \rightarrow HF$	-145.95
(33)	$HF + SiO_2 \rightarrow SiF_4 + H \cdot + O \cdot$	313.57

IV. CONCLUSION

In this paper, a DBD-based SF₆ decomposition platform is provided, which can effectively degrade high concentration SF₆. The degradation of SF₆ at 2% concentration with H₂O and O₂ involved was studied experimentally. The effects of the two gases on the DRE and EY were studied. The active species and by-products were also analyzed.

The results show that the participation of H₂O and O₂ can effectively promote the DRE of SF₆. The DRE of SF₆ first increased and then decreased with the increase of O₂ concentration. The best degradation effect can be obtained at SF₆/O₂ = 1/1. Under the conditions of 0.5% H₂O and 2% O₂, the DRE of 2% SF₆ was 98.2% at 50 ml/min flow rate and the EY reached 5.73 g/kWh.

By the emission spectrum detection, we found a large number of Ar I-type lines were generated in the plasma region. At the same time, the lines of O, OH, F and S were detected in the reaction zone, which indicated that the addition of H₂O and O₂ could effectively produce more active particles like OH, H and O, and promote the bond breaking process of SF₆. In addition, it was found that there was a Si line in SF₆/H₂O/Ar system, indicating that HF was generated during the reaction with H₂O addition, to etch the inner wall of the reactor. The product analysis shows that the addition of H₂O promotes the production of SO₂, while the addition of O₂ promotes the production of SO₂F₂, but SOF₄ is the major decomposition product in both discharge systems.

This paper provided the experimental support for better understanding the decomposition mechanism of SF₆ and the engineering application of SF₆ exhaust gas treatment by using low-temperature plasma.

REFERENCES

- [1] R. Ullah, A. Rashid, A. Rashid, F. Khan, and A. Ali, "Dielectric characteristic of dichlorodifluoromethane (R12) gas and mixture with N₂/air as an alternative to SF₆ gas," *High Voltage*, vol. 2, no. 3, pp. 205–210, Sep. 2017.
- [2] J. Reilly *et al.*, "Multi-gas assessment of the Kyoto protocol," *Nature*, vol. 401, no. 6753, pp. 549–555, 1999.
- [3] M. Rabie and C. M. Franck, "Assessment of eco-friendly gases for electrical insulation to replace the most potent industrial greenhouse gas SF₆," *Environ. Sci. Technol.*, vol. 52, no. 2, pp. 369–380, 2018.
- [4] S. Xiao, Y. Li, X. Zhang, J. Tang, S. Tian, and Z. Deng, "Formation mechanism of CF₃I discharge components and effect of oxygen on decomposition," *J. Phys. D, Appl. Phys.*, vol. 50, no. 15, p. 155601, 2017.
- [5] D. Kashiwagi *et al.*, "Metal phosphate catalysts effective for degradation of sulfur hexafluoride," *Ind. Eng. Chem. Res.*, vol. 48, no. 2, pp. 632–640, 2009.
- [6] D. Kashiwagi *et al.*, "Catalytic activity of rare earth phosphates for SF₆ decomposition and promotion effects of rare earths added into AlPO₄," *J. Colloid Interface Sci.*, vol. 332, no. 1, pp. 136–144, 2009.
- [7] J. Zhang, J. Z. Zhou, Q. Liu, G. Qian, and Z. P. Xu, "Efficient removal of sulfur hexafluoride (SF₆) through reacting with recycled electroplating sludge," *Environ. Sci. Technol.*, vol. 47, no. 12, pp. 6493–6499, 2013.
- [8] J. Zhang *et al.*, "Decomposition of potent greenhouse gas sulfur hexafluoride (SF₆) by Kirschsteinite-dominant stainless steel slag," *Environ. Sci. Technol.*, vol. 48, no. 1, pp. 599–606, 2014.
- [9] L. Huang *et al.*, "Photoreductive degradation of sulfur hexafluoride in the presence of styrene," *J. Environ. Sci-China.*, vol. 20, no. 2, pp. 183–188, 2008.
- [10] X. Song, X. Liu, Z. Ye, J. He, R. Zhang, and H. Hou, "Photodegradation of SF₆ on polyisoprene surface: Implication on elimination of toxic byproducts," *J. Hazardous Mater.*, vol. 168, no. 1, pp. 493–500, 2009.
- [11] Y. Yamada, H. Tamura, and D. Takeda, "Photochemical reaction of sulfur hexafluoride with water in low-temperature xenon matrices," *J. Chem. Phys.*, vol. 134, no. 10, p. 104302, 2011.
- [12] L. Zámstná and T. Braun, "Catalytic degradation of sulfur hexafluoride by rhodium complexes," *Angew. Chem. Ed.*, vol. 54, no. 36, pp. 10652–10656, 2015.
- [13] M. Shih, W.-J. Lee, and C.-Y. Chen, "Decomposition of SF₆ and H₂S mixture in radio frequency plasma environment," *Ind. Eng. Chem. Res.*, vol. 42, no. 13, pp. 2906–2912, 2003.
- [14] Y. Kabouzi *et al.*, "Abatement of perfluorinated compounds using microwave plasmas at atmospheric pressure," *J. Appl. Phys.*, vol. 93, no. 12, pp. 9483–9496, 2003.
- [15] C.-H. Tsai and J.-M. Shao, "Formation of fluorine for abating sulfur hexafluoride in an atmospheric-pressure plasma environment," *J. Hazardous Mater.*, vol. 157, no. 1, pp. 201–206, 2008.
- [16] J. H. Kim, C. H. Cho, D. H. Shin, Y. C. Hong, and Y. W. Shin, "Abatement of fluorinated compounds using a 2.45 GHz microwave plasma torch with a reverse vortex plasma reactor," *J. Hazardous Mater.*, vol. 294, pp. 41–46, Aug. 2015.
- [17] N. Jiang, N. Lu, K. Shang, J. Li, and Y. Wu, "Effects of electrode geometry on the performance of dielectric barrier/packed-bed discharge plasmas in benzene degradation," *J. Hazardous Mater.*, vol. 262, no. 22, pp. 387–393, 2013.
- [18] N. Jiang, N. Lu, K. Shang, J. Li, and Y. Wu, "Innovative approach for benzene degradation using hybrid surface/packed-bed discharge plasmas," *Environ. Sci. Technol.*, vol. 47, no. 17, pp. 9898–9903, 2013.
- [19] H. Zhang, K. Li, C. Shu, Z. Lou, T. Sun, and J. Jia, "Enhancement of styrene removal using a novel double-tube dielectric barrier discharge (DDBD) reactor," *Chem. Eng. J.*, vol. 256, no. 8, pp. 107–118, 2014.
- [20] H. M. Lee, M. B. Chang, and K. Y. Wu, "Abatement of sulfur hexafluoride emissions from the semiconductor manufacturing process by atmospheric-pressure plasmas," *J. Air Waste Manage.*, vol. 54, no. 8, pp. 960–970, 2004.
- [21] Q. Zhuang, B. Clements, A. McFarlan, and Y. Fasoyinu, "Decomposition of the most potent greenhouse gas (GHG) sulphur hexafluoride (SF₆) using a dielectric barrier discharge (DBD) plasma," *Can. J. Chem. Eng.*, vol. 92, no. 1, pp. 32–35, 2014.
- [22] R. Zhang, W. Jingting, C. Xu, and H. Huiqi, "Decomposition of potent greenhouse gases SF₆, CF₄ and SF₅CF₃ by dielectric barrier discharge," *Plasma. Sci. Technol.*, vol. 18, no. 4, pp. 388–393, 2016.
- [23] S. B. Radovanov, B. Tomčik, Z. L. Petrovič, and B. M. Jelenković, "Optical emission spectroscopy of RF discharge in SF₆," *J. Appl. Phys.*, vol. 67, no. 1, pp. 97–107, 1990.
- [24] N. Sadeghi, H. Debontride, G. Turban, and M. C. Peignon, "Kinetics of formation of sulfur dimers in pure SF₆ and SF₆-O₂ discharges," *Plasma Chem. Plasma Process.*, vol. 10, no. 4, pp. 553–569, 1990.
- [25] M. B. Roque, R. B. Siegel, K. E. Martus, V. Tarnovsky, and K. Becker, "Production of fluorine ^{2,4}P→²P⁰ resonance radiation by electron impact on SF₆, CF₄, NF₃, and CCl₂F₂," *J. Chem. Phys.*, vol. 94, no. 1, pp. 341–350, 1991.
- [26] A. M. Casanovas *et al.*, "Optical detection of corona discharges in SF₆, CF₄, and SO₂ under DC and 50-Hz AC voltages," *J. Appl. Phys.*, vol. 70, no. 3, pp. 1220–1226, 1991.
- [27] Z. L. Petrovič, F. Tochikubo, S. Kakuta, and T. Makabe, "Spatiotemporal optical emission spectroscopy of RF discharges in SF₆," *J. Appl. Phys.*, vol. 73, no. 5, pp. 2163–2172, 1993.
- [28] R. Foest, J. K. Olthoff, R. J. Van Brunt, E. C. Benck, and J. R. Roberts, "Optical and mass spectrometric investigations of ions and neutral species in SF₆ radio-frequency discharges," *Phys. Rev. E, Stat. Phys. Plasmas Fluids Relat. Interdiscip. Top.*, vol. 54, no. 2, p. 1876, 1996.
- [29] A. Lemzadmi, N. Bonifaci, A. Denat, and M. Nemačcha, "Light emission from corona discharge in SF₆ and SF₆/N₂ gas mixtures at high pressure," *Eur. Phys. J. Appl. Phys.*, vol. 33, no. 3, pp. 213–219, 2007.
- [30] S. P. Koiraal, I. Awaah, S. L. Burkett, and M. H. Gordon, "Correlation of plasma characteristics to etch rate and via sidewall angle in a deep reactive ion etch system using Langmuir probe and optical emission spectroscopy," *J. Vac. Sci. Technol. A.*, vol. 29, no. 1, pp. 011008-1–011008-6, 2011.
- [31] X. Zhang, H. Xiao, X. Hu, and Y. Gui, "Effects of background gas on sulfur hexafluoride removal by atmospheric dielectric barrier discharge plasma," *AIP Adv.*, vol. 6, no. 11, p. 115005, 2016.
- [32] H. Xiao, X. Zhang, X. Hu, and Q. Zhu, "Experimental and simulation analysis on by-products of treatment of SF₆ using dielectric barrier discharge," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 24, no. 3, pp. 1617–1624, Jun. 2017.
- [33] K. R. Ryan and I. C. Plumb, "Gas-phase combination reactions of SF₄ and SF₅ with F in plasmas of SF₆," *Plasma Chem. Plasma Process.*, vol. 8, no. 3, pp. 281–291, 1988.
- [34] *NIST Chemistry WebBook*. [Online]. Available: <https://webbook.nist.gov/chemistry/30/09/2018>
- [35] R. Kurte, C. Beyer, H. Heise, and D. Klockow, "Application of infrared spectroscopy to monitoring gas insulated high-voltage equipment: Electrode material-dependent SF₆ decomposition," *Anal. Bioanal. Chem.*, vol. 373, no. 7, pp. 639–646, 2002.
- [36] X. Zhang, H. Xiao, J. Tang, Z. Cui, and Y. Zhang, "Recent advances in decomposition of the most potent greenhouse gas SF₆," *Crit. Rev. Environ. Sci. Technol.*, vol. 47, no. 18, pp. 1763–1782, 2017.



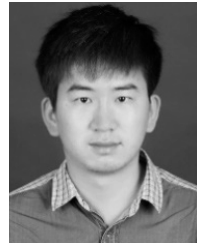
XIAOXING ZHANG was born in Qianjiang, Hubei, China, in 1972. He received the bachelor's and master's degrees from the Hubei Institute of Technology, and the Ph.D. degree from Chongqing University. He is currently a Professor with the School of Electric Engineering, Wuhan University. He is involved in the online monitoring and fault diagnosis of high voltage electrical insulation equipment, alternative gases of SF₆, the decomposition mechanism of insulating gas SF₆, and the new nano-sensor.



HANYAN XIAO was born in Tianmen, Hubei, China, in 1992. She received the Ph.D. degree in electrical engineering from Chongqing University. She is currently a Senior Engineer with the Electric Power Research Institute, China State Grid Jiangsu Electric Power Co., Ltd. She is involved in the study of the treatment of SF₆ exhaust gas using dielectric barrier discharge.



ZHAOLUN CUI was born in Binzhou, Shandong, China, in 1993. He received the bachelor's degree in electrical engineering from Wuhan University, Wuhan, China, where he is currently pursuing the Ph.D. degree with the School of Electric Engineering. His research interests include the decomposition mechanism of insulating gas SF₆, and gases spectrum detection technology.



YI LI was born in Shangluo, Shanxi, China, in 1994. He received the bachelor's degree in electrical engineering from Wuhan University, Wuhan, China, where he is currently pursuing the Ph.D. degree with the School of Electric Engineering. His research interests include alternative gas of SF₆ and fault diagnosis of high voltage electrical insulation equipment.



YALONG LI was born in Zhumadian, Henan, China, in 1989. He received the bachelor's degree in electrical engineering from Wuhan University, Wuhan, China, where he is currently pursuing the M.A. degree with the School of Electric Engineering. His research interests include SF₆ abatement technology.



JU TANG was born in Pengxi, Sichuan, China, in 1960. He received the bachelor's degree from Xi'an Jiaotong University, and the master's and Ph.D. degrees from Chongqing University. He is currently a Professor with the School of Electric Engineering, Wuhan University, and a Chief Scientist of the National Basic Research Program of China (973 Program) (2009CB724500). He is involved in high-voltage electric equipment insulation online monitoring and fault diagnosis.

...