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# SF<sub>6</sub> degradation in a γ-Al<sub>2</sub>O<sub>3</sub> packed DBD system: Effects of hydration, reactive gases and plasma-induced surface charges

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ABSTRACT: Packed-bed DBD plasmas hold promise for effective degradation of greenhouse gases like SF<sub>6</sub>. In this work, we conducted a combined experimental and theoretical study to investigate the effect of the packing surface structure and the plasma surface discharge on the SF<sub>6</sub> degradation in a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing DBD system. Experimental results show that both the hydration effect of the surface (upon moisture) and the presence of excessive reactive gases in the plasma can significantly reduce the SF<sub>6</sub> degradation, but they hardly change the discharge behavior. DFT results show that the pre-adsorption of species such as H, OH, H<sub>2</sub>O and O<sub>2</sub> can occupy the active sites (Alm site) which negatively impacts

the SF<sub>6</sub> adsorption. H<sub>2</sub>O molecules pre-adsorbed at neighboring sites can promote the activation of SF<sub>6</sub> molecules and lower the reaction barrier for the S-F bond-breaking process. Surface-induced charges and local external electric fields caused by the plasma can both improve the SF<sub>6</sub> adsorption and enhance the elongation of the S-F bonds. Our results indicate that both the surface structure of the packing material and the plasma surface discharge are crucial for SF<sub>6</sub> degradation performance, and the packing beads should be kept dry during the degradation. Furthermore, the plasma surface effect is one main reason for the SF<sub>6</sub> effective degradation in the packed-bed system. This work helps to understand the underlying mechanisms of SF<sub>6</sub> degradation in a PB-DBD system.

KEYWORDS: SF<sub>6</sub>; DBD treatment; Hydration effect; Reactive gases; Plasma-induced surface charges

#### **1** Introduction

Sulfur hexafluoride (SF<sub>6</sub>) is a colorless, odorless, and non-toxic gas with great stability [1, 2]. It shows an excellent dielectric property and has been widely used in the power industry since the 1940s [3-4]. However, SF<sub>6</sub> is a greenhouse gas with a very high global warming potential (GWP); about 23,500 times that of CO<sub>2</sub> [5]. In 2010, the global emission of SF<sub>6</sub> raised to 5.31 Gg (gigagram), with an average annual growth rate of about 10% [6]. In 2015-2040, the global electricity demand is expected to grow by 30%, which could further increase the detrimental effects of SF<sub>6</sub> on the environment [7-8].

Since the end of the last century, great efforts have been devoted to the abatement of  $SF_6$  waste gases. However, the  $SF_6$  molecule has stable S-F bonds and is hard to decompose, and the incompletely decomposed intermediates ( $SF_x$ , x<6) can easily recombine again with F atoms into  $SF_6$ , as shown in eq.1 [9].

$$SF_x + (6-x)F \rightarrow SF_6$$
 (1)

Due to these properties, the effective degradation of SF<sub>6</sub> needs some additional conditions. Therefore, methods like thermal degradation, thermal catalysis, photocatalysis, electrocatalysis, and non-thermal plasma (NTP) have been applied for this purpose [1, 10-15]. Among them, NTP shows promising performance for SF<sub>6</sub> abatement, both in terms of degradation efficiency and energy yields, by means of various plasma types, such as dielectric barrier discharge (DBD), microwave discharge, and radio-frequency discharge [16-20]. Often, reactive gases, like H<sub>2</sub>, O<sub>2</sub>, or H<sub>2</sub>O, are added in the NTP treatment to improve the degradation efficiency [9, 21]. However, the results show a lack of product selectivity without employing a suitable catalyst [15]. Therefore, we used a packed-bed DBD (PB-DBD) for SF<sub>6</sub> treatment and found that a packing of glass beads, as well as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads, promoted the discharge and the degradation process [22]. Moreover, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing shows an ability for the activation of SF<sub>6</sub> and the regulation of its degradation products due to its surface properties [23], which prove that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is a proper packing material for SF<sub>6</sub> treatment in a DBD system.

It should be noted that the surface properties of the catalyst are of great importance for its performance [24].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has an active surface and an adsorption ability, making it a good catalyst support. During a long-term use,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads often face the problem of moisture, and the dry surface will be hydrated after the adsorption of H<sub>2</sub>O, which may affect the discharge and degradation process [25, 26]. Furthermore, the addition of reactive gases, such as H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>, etc., which is often done in practice to improve the degradation efficiency in the plasma phase (see above), may lead to changes in the surface state of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing and reduce its ability to adsorb and activate the SF<sub>6</sub> molecules [27]. In addition, during the discharge, the plasma may cause excess electrons or an external electric field on the packing material surface, which in a way affect the surface reactions [24]. However, these factors have

not been investigated yet, but are vital for understanding the SF<sub>6</sub> degradation mechanism over the packing material surface.

In recent years, plasma catalysis has been successfully applied in various fields [24], like CO<sub>2</sub> conversion [28], CH<sub>4</sub> reforming [29] and VOC treatments [30]. Density functional theory (DFT) has been widely applied to study plasma-catalytic systems in order to provide an atomistic point of view on the underlying mechanisms between the plasma and catalyst [31, 32]. For example, Bal et al. studied the adsorption and activation process of CO<sub>2</sub> molecules on supported M/γ-Al<sub>2</sub>O<sub>3</sub> (M is a single metal atom) surface and demonstrated a catalytic effect of this surface upon plasma charging [33]. Shirazi et al. conducted a DFT study to investigate the dry reforming of CH<sub>4</sub> on a Ni surface, to reveal the formation mechanism of the key products and the effects of the pre-adsorbed species [34]. Therefore, DFT simulations are an effective way to study the surface reactions of SF<sub>6</sub> in a PB-DBD plasma-catalytic system.

In this study, we conducted experiments and DFT calculations to investigate the effects of the surface structure of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing and the plasma surface discharge on SF<sub>6</sub> degradation. The hydration, excessive addition of reactive gases (H<sub>2</sub>O and O<sub>2</sub>), plasmainduced surface charges and external electric fields are proved to be effective factors in determining the degradation performance. This work provides experimental results, backed up by theoretical explanations, for a better understanding of SF<sub>6</sub> decomposition on different kinds of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface structures and under the action of plasma surface discharge.

### 2 Methods

#### 2.1 Experimental methods

Detailed information of the PB-DBD system was provided before, in Ref [22, 23]. The discharge voltage and current are recorded by an oscilloscope (Tektronix MSO44). The

discharge power is calculated by the Lissajous method [22]. SF<sub>6</sub> is detected by a gas chromatograph (GC) (Kejie GC8900). Ar, SF<sub>6</sub> and O<sub>2</sub> are mixed by a gas compounder and H<sub>2</sub>O is obtained by the evaporation of pure water through a humidity generator. Since the hydration process is closely related to the effective contact area of the packing, we compared two sizes of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads (with diameters of 2 mm and 4 mm). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads have been characterized by BET and SEM, which can be referred in our previous study [23]. For the hydration treatment, the beads are first placed in a humid environment to adsorb water, and the water content is adjusted according to the weight and the adsorption property of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads. They are exposed to the atmospheric environment for one day to reach the state of saturated water absorption. After that, they are packed into the reactor for the DBD plasma experiments. Before each degradation test, a 30-minute pre-discharge (Ar charge) is done to ensure that the discharge of the packing system tends to be stable. And the 1-hour temporal evolution of the voltage and current signals are shown in Fig. S1 and Fig. S2.

The degradation removal efficiency (DRE) and energy yield (EY) are the two most important key performance indicators. They are used to evaluate the degradation efficacy and they are calculated by measuring the SF<sub>6</sub> concentration before and after plasma abatement.

The DRE is calculated by eq.2:

$$DRE = \frac{C_{\rm i} - C_{\rm f}}{C_{\rm i}} \times 100\%$$
<sup>(2)</sup>

where  $C_i$  and  $C_f$  are the initial and final concentrations of SF<sub>6</sub>, respectively.

The EY is calculated by eq.3:

$$EY(g/kWh) = \frac{M_{SF_6}(g) \times 10^3 \times 3.6 \times 10^3}{P(W) \times t(s)}$$
(3)

where  $M_{SF_6}$  is the mass of degraded SF<sub>6</sub> gas, *P* is the input power, *t* is the degradation time, and 10<sup>3</sup> and 3.6x10<sup>3</sup> are conversion factors from W to kW, and from s to h.

#### 2.2 Computational details

We performed the DFT calculations by the CP2K 7.0 package [35]. The Quickstep module is chosen for the calculation, employing the Gaussian and plane wave method (GPW) [36, 37]. The Goedecker–Teter–Hutter (GTH) pseudopotentials as well as the polarized double- $\zeta$ (m-DZVP) basis sets are selected to describe the core-valence interactions and the expansion of the Kohn-Sham valence orbitals [38]. The cutoff value of the plane wave basis set is chosen at 600 Ry. The exchange correlation functional is described by using the GGA-PBE (Perdew-Burke-Ernzerhof) method [39], with a dispersion correction by Grimme's D3 method [40]. Besides, the K-point sampling is limited to  $\Gamma$  point only, by considering a sufficient supercell size of more than 10 Å in XY directions. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is applied for the geometry optimization and the climbing image nudged elastic band (CI-NEB) method is used for the transition state (TS) search calculations [41, 42]. During the calculation, the analysis of the charge transfer process is carried out employing the Bader charge partitioning scheme [43].

The (110) surface is a typical active and stable surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the lewis acidic sites present on this surface are considered to be the main site for catalytic and activation reactions, which have been widely adopted for use in various thermal and plasma catalysis studies such as CO<sub>2</sub> conversion [33, 44]. The remaining crystalline surfaces may also have catalytic effects, but for computational convenience and representativeness, we chose the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(110) surface structure as the typical model for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing. This model is built by a 2×2 supercell containing 160 atoms and is consist of four layers with the XYZ dimensions of 16.14 × 16.79 × 40.00 Å<sup>3</sup>. The bottom two layers are fixed during the calculation. The hydrated surface structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is based on the study of Wischert et al[45].

The setting of the induced charges on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(110) surface refers to the method

proposed by Bal et al. [33]. This method is based on positioning a point charge of +1.0|e| with no basis set assigned, above the slab surface to maintain the surface charging. The electrostatics are described by the Martyna-Tuckerman Poisson solver [46] and the periodicity is limited to XY direction to avoid the non-physical interaction of the slab with itself.

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Fig. 1 Dipole sheet method for setting an external electric field

The setting of the external electric field refers to the "dipole sheet" method proposed by Jafarzadeh et al [47], which is shown schematically in Fig. 1. By setting up two parallel plates of charged atoms at the top and the bottom of the surface structure. The atoms in the upper and lower layers of the dipole sheet are positively and negatively charged to form an electrostatic field, and its strength can be adjusted by changing the charge on the plates. Since the actual reaction process is very short, and occurs at picosecond level, the voltage of one filamentary discharge in DBD is relatively stable during one reaction, and a fixed electric field can be applied when simulate the surface adsorption process [47].

Applying the dipole sheet approach, the strength of the electric field can be expressed in eq(4):

$$E = \frac{\sigma}{\varepsilon_0} \tag{4}$$

Where *E* is the electric field with a unit of V/Å,  $\sigma$  is the surface charge density of the dipole sheet, and  $\varepsilon_0$  is the vacuum permittivity. In this method, the distance between the two charged plates and the thickness of the plate do not affect the electric field strength. To avoid the interaction with the dummy ions in the plates, the distance between the upper and lower plates is set to 40 Å and the height of the supercell in the Z direction is set to twice the plate spacing, which is 80 Å.

The adsorption energy  $E_{ad}$  for the gas molecules on the material surface can be calculated by eq(5):

$$E_{\rm ad} = E_{\rm gas+slab} - E_{\rm gas} - E_{\rm slab} \tag{5}$$

Where  $E_{\text{gas}}$  and  $E_{\text{slab}}$  are the energy of gas phase molecules and of the slab, respectively, and  $E_{\text{gas+slab}}$  is the total energy of the system after the adsorption. When  $E_{\text{ad}}$  is negative, it indicates that the energy of the system is reduced due to adsorption. A more negative value of  $E_{\text{ad}}$  is indicative of a more stable adsorption mode, corresponding to a stronger interaction between the adsorbed species and the surface.

#### **3** Results and discussion

#### 3.1 Hydration effect on SF<sub>6</sub> degradation

#### 3.1.1 Discharge parameters

We first study the effect of moisture exposure. As shown in Fig. 2, the hydration process shows reduction effects on the discharge voltage for both the 2 mm and 4 mm packing systems. In the 2 mm system, the voltage of hydrated beads packing is always lower than that in the dry system. By contrast, in the 4 mm system, the voltage of the hydrated system becomes close to the dry system when the input power arrives 80 W. This result indicates

that the effect of moisture on the discharge process of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing varies with the bead size. Besides, the filamentary character is reduced in the hydrated systems, especially in the 2 mm packing system, as shown in Fig. S3, which could be attributed to the change of surface properties of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing by the hydration treatment.



Fig. 2 Effects of hydration on the discharge voltage vs input power, for the 2 mm and 4 mm  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing systems (3% SF<sub>6</sub> - 97% Ar, 100 mL/min)

The Q-V plots for the 2 mm and 4 mm packing systems before and after the hydration are shown in Fig. S4. The slope of line AB and CD decreases in both systems, corresponding to a decrease of the equivalent dielectric capacitance ( $\zeta_{diel}$ ) in the discharge-on phase [48, 49]. This indicates that the discharge in the hydrated system is less stable. It should be noted that the relative permittivity of H<sub>2</sub>O (78.5) is obviously greater than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (10.0), and the equivalent dielectric capacitance of the packing should be increased after the hydration. However, the decrease of  $\zeta_{diel}$  indicates that the discharge is inhibited by moisture adsorption [49, 50]. This may be caused by two main reasons. Firstly, the adsorbed H<sub>2</sub>O on the packing surface could reduce the filamentary discharge character, thus inhibiting the maintenance of the plasma. On the other hand, H<sub>2</sub>O could ionize or evaporate during the discharge, thus consuming energy.

#### 3.1.2 DRE and EY

We present the DRE and EY results in Fig. 3. In Fig. 3(a), the DRE is significantly reduced by the hydration treatment and the 2 mm packing system is more seriously affected than the 4 mm packing. In the 2 mm packing system, the DRE is ca. 40% at 50 W and gradually increases to ca. 50% at 100 W, much lower than in the dry system (where it varies between 65% and 100%). In the 4 mm packing system, the DRE increases from ca. 58% at 50 W to ca. 68% at 100 W. In contrast, the DRE in the 2 mm and 4 mm dry packing systems exceeds 99% and 90%, respectively, when the input power exceeds 80W. The above results indicate that the hydration process significantly inhibits the SF<sub>6</sub> degradation, and makes the DRE rather insensitive to the input power. In Fig. 3(b), the hydrated packing also significantly reduces the EY. In the 2 mm hydrated packing system, the EY drops from 9.46 g/kWh at 50 W to 5.82 g/kWh at 100 W. In the 4 mm hydrated packing system, the EY drops from 13.51 g/kWh at 50 W to 7.99 g/kWh at 100 W. In our previous study, the EY could reach about 5 g/kWh in a non-packed system at 150 mL/min and 2% SF<sub>6</sub> initial concentration [22]. Therefore, the inhibition caused by the hydration almost compensates for the promotion effect of the packing system on the SF<sub>6</sub> abatement.



Fig. 3 DRE and EY as a function of input power in two γ-Al<sub>2</sub>O<sub>3</sub> packing systems, before

#### and after hydration (3% SF<sub>6</sub> - 97% Ar, 100 mL/min)

Compared with the change in the discharge signals and the discharge power, the DRE is more seriously reduced by the hydration. This suggests that, rather than a change in discharge parameters, a change in surface state of the packing beads will be responsible for the dramatic inhibition of the SF<sub>6</sub> degradation. Moreover, since the 2 mm packing has a larger effective contact area than the 4 mm packing, it is more severely reduced by the hydration process, which also suggests that the surface structure of the beads is a key factor for the effect on the DRE. As discussed in the Introduction, the hydration process leads to the adsorption of H<sub>2</sub>O molecules on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, which can hinder the adsorption and activation of SF<sub>6</sub> on the packing surface. We will discuss this in more detail when analyzing the DFT results in section 3.3.2 below.

Fig. S5 shows the FTIR results of the degradation products in the hydrated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packed bed DBD system. Except for the remaining SF<sub>6</sub>, the other gases involve SF<sub>4</sub>, S<sub>2</sub>F<sub>10</sub>, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub> and SOF<sub>4</sub>, which shows a typical product distribution of the DBD treatment [15]. However, there is no signal of SO<sub>2</sub>, which indicates that the degradation is not sufficient to fully dissociate SF<sub>6</sub> into S and F atoms. We hypothesize that pre-adsorption of H<sub>2</sub>O on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface reduces the decomposition of SF<sub>6</sub> molecules, thus prohibiting the further decomposition of the intermediates. The reaction mechanism will be further analyzed by our DFT calculations in section 3.3.2 below. Moreover, SOF<sub>4</sub> and SO<sub>2</sub>F<sub>2</sub> in the tail gas are two gases relatively difficult to be treated [51]. This means that the hydration of the packing not only negatively impacts the degradation performance, but also has a negative effect on the product distribution.

In summary, the surface state should be carefully evaluated when choosing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the

packing material in industrial applications. First of all, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing should be kept dry for the first packing. Second, in the case of long-term operation, the packing in the reactor should be heated and dehydrated before a degradation treatment. If the reactor is not resistant to high temperature, dry air or other gases (Ar, N<sub>2</sub> etc.) should be introduced to pre-treat the packing, so that the possible adsorbed H<sub>2</sub>O can be removed, to prevent it from affecting the SF<sub>6</sub> degradation.

#### 3.2 H<sub>2</sub>O and O<sub>2</sub> addition on SF<sub>6</sub> degradation

In this section, we focus on the effect of the presence of H<sub>2</sub>O and O<sub>2</sub> on the degradation process. Previous studies have demonstrated that a proper amount of reactive gas contributes to the SF<sub>6</sub> degradation, while an excessive addition has negative effects [52]. Both the discharge parameters and the degradation efficiency are considered here. Subsequently, the optimal gas concentrations of H<sub>2</sub>O and O<sub>2</sub> for this packed bed system and the trend of the DRE variation are determined.

#### 3.2.1 Discharge parameters

Fig. S6 shows the discharge voltage and current of the systems with H<sub>2</sub>O and O<sub>2</sub> added, for the DRE-optimal (a,b) and maximum (c,d) added concentrations. Compared to the dry 4 mm packing without reactive gases in Fig. S3(d), the amplitudes of voltage and current in Fig. S6 are a bit smaller, because the input power is lower than in Fig. S3. However, the filamentary character in the current signals of both systems after adding H<sub>2</sub>O or O<sub>2</sub> is slightly more apparent, indicating that the micro-discharges are slightly enhanced, which promotes the generation of reactive species, thus facilitating the SF<sub>6</sub> degradation. By comparison within Fig. S6, we can see that the concentration of the reactive gases shows limited effects on neither the amplitudes nor the filaments. Furthermore, the Q-V plots for the discharge systems with and without additional gases, shown in Fig. S7, are quite similar for all three conditions. These results show that the reactive gases hardly affect the discharge parameters, which is probably due to their low concentrations.

#### 3.2.2 DRE and EY

In Fig.5, we plot the DRE and EY as a function of added H<sub>2</sub>O and O<sub>2</sub> concentration, for an input power of 80 W. Since we observed before [52] that H<sub>2</sub>O and O<sub>2</sub> can promote the SF<sub>6</sub> degradation in plasma without packing, we increased the flow rate to 200 mL/min to test their promotion potentials. From Fig. 4 we can see that with increase of the additional gases, the DRE and EY first increase and eventually decrease. In Fig. 4(a), 0.5% is the optimal concentration for H<sub>2</sub>O addition, reaching a DRE of 93% and an EY of 24.94 g/kWh. When the H<sub>2</sub>O concentration exceeds 0.5%, the DRE and EY gradually decrease and finally reach 65% and 17.70 g/kWh at 2.5% H<sub>2</sub>O. Similarly, the DRE and EY first increase to a maximum of 81% and 21.63 g/kWh, respectively, at 0.1% O<sub>2</sub>, but with increasing O<sub>2</sub> concentration, they eventually drop to 43% and 11.63 g/kWh at 4% O<sub>2</sub>.



Fig. 4 DRE and EY upon H<sub>2</sub>O or O<sub>2</sub> addition (80 W, 200 mL/min, 3% SF<sub>6</sub>, 4 mm γ-Al<sub>2</sub>O<sub>3</sub> packing)

Generally, these two gases both show a promotion effect at low concentrations, and  $H_2O$  is a bit better than  $O_2$ . In Ref[52], the optimal ratio of  $O_2$ :SF<sub>6</sub> is 1:1 in the non-packed system

which is much higher than that in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packed system (1:30, Fig.4(b)). Meanwhile, our previous study found that the variation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bead size slightly affects the discharge behavior, but significantly changes the degradation performance. Lowing the bead size increases the contact area, resulting in a higher DRE and SO<sub>2</sub> yields, which corresponds to a more efficient SF<sub>6</sub> degradation and S-F detachment. This indicates that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface could be the main reaction area. In this experiment, the DRE starts to decrease significantly when the (reactive gas:SF<sub>6</sub>) ratio was much less than 1:1 for either H<sub>2</sub>O or O<sub>2</sub>, while their discharge parameters did not change significantly compared to the dry bead system (Fig. S6). On the other hand, the most extreme condition of excessive H<sub>2</sub>O addition should be similar to the hydration system, i.e., the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface has excessive or saturated moisture accumulation. The results from Fig. 2 and Fig. 3 show that the decrease in DRE due to hydration is more significant than the suppression of discharge. Therefore, we may speculate that the excess reactive gas inhibited the degradation effect mainly by affecting the gas-solid interface reactions. This will be further investigated by our DFT calculations in the following sections.

# 3.3 SF<sub>6</sub> adsorption and decomposition on different types of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (110) surfaces: Effects of hydration and addition of reactive gases, revealed by DFT calculations

#### 3.3.1 Adsorption

According to our previous study, the Alm is selected as the active site for adsorption [23]. We consider three surface conditions (hydrated, H<sub>2</sub>O and O<sub>2</sub>), as they correspond to the experimental conditions when the surface of the packing material is hydrated, or when additional gases (H<sub>2</sub>O and O<sub>2</sub>) are added [52-54]. Here we present the calculated configurations of SF<sub>6</sub> molecules adsorbed on these three types of surfaces (Fig. S8 and Fig. S9), as well as the  $E_{ad}$  values (Table 1).

As shown in Table 1, on the hydrated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface,  $E_{ad}$  is -0.39 eV. Its absolute value is slightly smaller than that on the perfect surface (-0.41 eV). Meanwhile, Fig. S8(a) shows that there is no obvious bonding process after the adsorption, which indicates that the SF6 adsorption is weakened on the hydrated surface, as the Al<sub>III</sub> sites are occupied by OH and H. Besides, on the H<sub>2</sub>O pre-adsorbed surface, the system has a larger adsorption energy when H<sub>2</sub>O is pre-adsorbed at the Al<sub>III</sub> site, with a total  $E_{ad}$  reaching -1.72 eV. If SF6 is adsorbed at the Al<sub>IV</sub> site, the total  $E_{ad}$  is only -1.59 eV. However, on the O<sub>2</sub> pre-adsorbed surface, the system with SF6 adsorbed at the Al<sub>III</sub> site has a larger  $E_{ad}$  of -1.03 eV. The above results indicate that H<sub>2</sub>O molecules are more likely to occupy the Al<sub>III</sub> site rather than O<sub>2</sub> and it could form a stable adsorption structure when the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing surface is subjected to moisture. In contrast, the effect of O<sub>2</sub> addition is relatively weak and the overall  $E_{ad}$  on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface is much lower.

Surface type	Site for pre-adsorbed molecules	Site for SF <sub>6</sub>	$E_{\rm ad}({\rm eV})$
Perfect γ-Al <sub>2</sub> O <sub>3</sub>		$Al_{III}$ site	-0.41[23]
Hydrated γ-Al <sub>2</sub> O <sub>3</sub>		Unbonded	-0.39
H <sub>2</sub> O	Al <sub>III</sub>	Unbonded	-1.72 <sup>a</sup>
pre-adsorbed	$Al_{IV}$	Al <sub>III</sub> site	-1.59 <sup>a</sup>
O <sub>2</sub>	Al <sub>III</sub>	Unbonded	-0.88 <sup>b</sup>
pre-adsorbed	$Al_{IV}$	Al <sub>III</sub> site	-1.03 <sup>b</sup>

Table 1  $E_{ad}$  of SF<sub>6</sub> molecules on different  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces

<sup>a</sup>  $E_{ad}$  is the total adsorption energy of H<sub>2</sub>O and SF<sub>6</sub>

<sup>b</sup>  $E_{ad}$  is the total adsorption energy of O<sub>2</sub> and SF<sub>6</sub>

In summary, the pre-adsorbed species, i.e., H, OH, H<sub>2</sub>O and O<sub>2</sub>, occupy the active sites and weaken the SF<sub>6</sub> adsorption process, which could be the main reason for the reduction of SF<sub>6</sub> degradation when the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is hydrated or excessive reactive gases are added. Meanwhile, in Fig. S9, the adsorption of SF<sub>6</sub> molecules at the Al<sub>III</sub> site does not have a bonding process, even if H<sub>2</sub>O or O<sub>2</sub> does not occupy this site. This indicates that the adsorbed species near the active site may also have some slight reduction effects on SF<sub>6</sub> adsorption. It should be noted that the high-energy H and OH species that may participate in the reaction could be generated from the ionization of H<sub>2</sub>O in the plasma [55]. Besides, the H<sub>2</sub>O molecule approaches the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface could occur a decomposition to form adsorbed H\* and OH\* species (\* means the adsorption state) [45]. Overall, the occupation of the active sites could play an important role in the reduction of the degradation performance caused by either the excess reactive gases or by the hydration of the packing beads.

#### 3.3.2 Initial bond-breaking process

We calculated the initial bond-breaking processes of SF<sub>6</sub> on the three  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces. The activation barrier  $E_a$  and the reaction heat  $\Delta E$  are presented in Table 2. The reaction occurs in eq(6):

$$SF_6 \rightarrow SF_5 + F$$
 (6)

	0	2		
Table 2 Activation b	parrier and react	ion heat in d	lifferent co	onditions

Condition	$E_{\rm a}({\rm eV})$	$\Delta E (eV)$
Gas phase	4.20 [23]	
Perfect $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.80 <sup>[23]</sup>	-1.29
Hydrated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.92	0.69
H <sub>2</sub> O pre-adsorbed <sup>a</sup>	1.50	-1.35
O <sub>2</sub> pre-adsorbed <sup>a</sup>	1.97	-0.69

 $^{a}H_{2}O$  or  $O_{2}$  adsorbed at sites near the Al<sub>III</sub> site.

The direct S-F bond breaking in the gas phase needs an  $E_a$  of 4.20 eV, which is much higher than on each  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. If the surface is hydrated or has O<sub>2</sub> pre-adsorbed (at an Al<sub>IV</sub> site), the  $E_a$  increases to 1.92 and 1.97 eV, respectively. Besides, if a H<sub>2</sub>O molecule is pre-adsorbed at an Al<sub>IV</sub> site (near the Al<sub>III</sub> site), the  $E_a$  decreases to 1.50 eV. The reaction heats are different at the four different surfaces. The reaction is endothermic only on the hydrated surface and exothermic on the other three surfaces.

To further investigate the possible facilitating role of H2O pre-adsorption, the TS process

of this reaction on H<sub>2</sub>O pre-adsorbed surface is shown in Fig. 5, and the TS processes of SF<sub>6</sub> initial bond breaking on the O<sub>2</sub> pre-adsorbed and hydrated surfaces are shown in Fig. S10.



Fig. 5 TS process of SF<sub>6</sub> initial bond breaking on the H<sub>2</sub>O pre-adsorbed surface

In Fig. 5, the lateral S-F bond breaks and the F-5 atom (see label in left panel) creates a bond with two surface Al atoms, while the SF<sub>5</sub> remains attached to the Al<sub>III</sub> atom. In this process, the H<sub>2</sub>O remains stable without obvious structure deformation. However, on the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, the bottom S-F bond breaks first and the SF<sub>5</sub> radical displaces and creates a bond with the surface O atom, while the bottom F remains attached to the Al<sub>III</sub> atom [23]. Therefore, the TS process over a H<sub>2</sub>O pre-adsorbed surface is different from that on the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, which indicates a change of the bond-breaking process of the adsorbed SF<sub>6</sub> caused by the pre-adsorbed H<sub>2</sub>O.

Table 3 Bader charge distribution of SF6 before and after the initial S-F bond breaking inthe gas phase, on perfect and H2O pre-adsorbed surfaces

	_	Gas ph	ase	Р	erfect γ-A	$l_2O_3$	H <sub>2</sub> O pro	e-adsorb	ed γ-Al <sub>2</sub> O <sub>3</sub>
Atom	Refore	After	Charge	Before	After	Charge	Before	After	Charge
	Defote	11101	difference	Deloie	711101	difference	Deloie	711101	difference
S	0	0.79	0.79	0.00	0.00	0.00	0.00	2.47	2.47
F-1	8.01	7.98	-0.03	8.01	7.97	-0.03	8.01	7.93	-0.08
F-2	7.99	8.04	0.05	8.02	7.97	-0.05	8.02	8.02	-0.00
F-3	7.99	7.98	-0.01	8.01	8.01	0.00	8.00	7.59	-0.41
F-4	8.01	7.97	-0.04	8.01	8.01	0.00	8.01	8.08	0.07
F-5	8.00	7.26	-0.74	7.99	8.02	0.03	8.00	8.02	0.02
F-6	8.00	7.98	-0.02	8.00	8.00	-0.00	8.00	7.90	-0.10

									,	-
Sum	0	0	0	0.04 <sup>a</sup>	-0.02 <sup>a</sup>	-0.05	$0.04^{a}$	2.01 <sup>a</sup>	1.97	

<sup>a</sup> The total charge here is the value after deducting the number of electrons in the valence layer of each atom of S and F (6 for S and 7 for F), which shows the overall charge change of the  $SF_6$  molecule itself after the chemical reaction. Positive values indicate the gain of electrons. F atoms are labeled in Fig. 5.

The Bader charge of SF<sub>6</sub> before and after the initial S-F bond breaking in both the perfect and H<sub>2</sub>O pre-adsorbed conditions are shown in Table 3. On the H<sub>2</sub>O pre-adsorbed surface, the S atom gains 2.47|e| electrons, and its valence state changes after the bond breaking. By contrast, the electron distribution of the S atom remains unchanged on the perfect surface and the change in the partial charge of the F atoms on the perfect surface is smaller than on the H<sub>2</sub>O pre-adsorbed surface. In the gas phase, the leaving F-5 atom loses 0.74|e| and the S atom gains 0.79|e|. This suggests that on the H<sub>2</sub>O pre-adsorbed surface, a charge transfer process from the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slab to SF<sub>6</sub> occurs during the S-F bond-breaking, resulting in a lower valence state of the S atom.

Fig. S11 shows the differential charge distribution of SF<sub>6</sub> on the H<sub>2</sub>O pre-adsorbed surface before the bond breaking, where the yellow and cyan regions indicate an increase and decrease in charge density, respectively. In Fig. S11, the H<sub>2</sub>O pre-adsorption affects the surface charge transfer process. At the surface Alm site, yellow regions near the Al and S atoms indicate their gain of electrons, while the cyan region near the bottom F indicates the loss of electrons. The electron transfer process could be the main reason for stretching of the S-F bond and the activation of SF<sub>6</sub>, promoting its degradation. Meanwhile, the overall color of H<sub>2</sub>O is cyan, which indicates the loss of electrons. This phenomenon indicates that some electrons may be transferred from H<sub>2</sub>O to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface after the pre-adsorption, changing the electron distribution on the surface, and eventually resulting in the promotion of the SF<sub>6</sub> bond breaking. This could be a reason for the better promotion effect of H<sub>2</sub>O than O<sub>2</sub> in Fig. 5.

#### 3.4 Plasma-induced surface effects, as revealed by DFT calculations

#### 3.4.1 Effect of excess electrons

By adding one +1.00 |e| charged proton above the slab surface, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface is negatively charged with 1.00 |e|. The adsorption energy  $E_{ad}$  and the length variation of the bottom S-F bond over three surfaces are listed in Table 4 and the configurations are shown in Fig. 6. In Fig. 6(a), on the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, the  $E_{ad}$  increased from -0.41eV without excess electrons to -3.55eV, corresponding to a chemical adsorption, along with the bottom S-F bond length stretching from 1.61 Å to 2.11 Å [23]. On the H<sub>2</sub>O and O<sub>2</sub> pre-adsorbed surfaces, the  $E_{ad}$  increased from -1.59eV and -1.03eV to -5.36eV and -3.93eV, with the S-F bond stretching from 1.61 Å to 2.29 Å and 2.10 Å, respectively. Compared with the three systems, SF<sub>6</sub> has the strongest adsorption process on the H<sub>2</sub>O pre-adsorbed surface and the stretching of the bottom S-F bond is close to a bond breaking process. In other words, the plasma-induced surface charge may enhance the SF<sub>6</sub> adsorption and elongate the S-F bonds, which promotes the activation of SF<sub>6</sub> molecules on the packing surface.

Table 4 Adsorption energy  $E_{ad}$  and bottom S-F bond length variation at the Al<sub>III</sub> site on three

Surface ture	$E_{-}(\mathbf{a}V)$	Bottom S-F
Surface type	$L_{ad}(ev)$	bond length (Å)
Perfect y-Al <sub>2</sub> O <sub>3</sub>	-3.55	2.11
H <sub>2</sub> O pre-adsorbed γ-Al <sub>2</sub> O <sub>3</sub>	-5.36 <sup>a</sup>	2.29
O2 pre-adsorbed y-Al2O3	-3.93 <sup>a</sup>	2.10

surfaces

 ${}^{a}E_{ad}$  is the total adsorption energy of SF<sub>6</sub> and the pre-adsorbed species



(a) Perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b) H<sub>2</sub>O pre-adsorbed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (c) O<sub>2</sub> pre-adsorbed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fig 6 SF<sub>6</sub> adsorption configurations on three 1.00|e| negatively charged

To further study the effect of plasma-induced surface charges on the SF<sub>6</sub> adsorption process, we carried out the Bader charge analysis, as shown in Table 5. Compared to the electrically neutral system in Table 3, the surface induced electrons significantly change the charge distribution of SF<sub>6</sub>, especially the S atom. The S atoms obtained 1.89 |e|, 2.15 |e| and 1.66 |e| on the perfect surface, the H<sub>2</sub>O pre-adsorbed surface and the O<sub>2</sub> pre-adsorbed surface, respectively. Besides, SF<sub>6</sub> gains more charges than in the electrically neutral system. Within the SF<sub>6</sub> molecule, the S atom gained electrons while the F atoms mainly lost electrons, which is supported by the differential charge distribution results in Fig. S12. Comparing Fig. S12 (a) and (b), both systems show significant charge transfers between the bottom F atom and the Al<sub>III</sub> site, the H<sub>2</sub>O pre-adsorbed system is stronger. This charge transfer process leads to a change in the valence state of S and F atoms, which could enhance the chemical adsorption and activation of SF<sub>6</sub> molecules over the packing surface.

Table 5 Bader charge analysis of the SF<sub>6</sub> molecule on three 1.00|e| negatively charged

	Perfec	t γ-Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O pre-ad	sorbed $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	O <sub>2</sub> pre-ads	orbed γ-Al <sub>2</sub> O <sub>3</sub>
Atom	Bader	Charge	Bader	Charge	Bader	Charge
	charge	variation	charge	variation	charge	variation
S	1.89	1.890	2.15	2.15	1.66	1.66
F-1	7.83	-0.17	7.90	-0.10	7.80	-0.200
F-2	7.59	-0.41	7.57	-0.43	7.59	-0.41
F-3	7.77	-0.23	8.00	0.00	7.55	-0.45
F-4	8.11	0.11	8.07	0.07	8.12	0.12
F-5	8.04	0.04	7.88	-0.12	8.02	0.02
F-6	7.64	-0.36	7.51	-0.49	8.09	0.09
Sum		$0.87^{a}$		1.08 <sup>a</sup>		0.83 <sup>a</sup>

surfaces

<sup>a</sup> The total charge here is the value after deducting the number of electrons in the valence layer of each atom of S and F (6 for S and 7 for F). F atoms are labeled in Fig. 7.

#### 3.4.2 Effect of external electric field

We take the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slab as the example to study the effects of the external field. Two directions of the electric field are considered. The " $\downarrow$ " and " $\uparrow$ " symbols are used to describe the direction of the electric field which is opposite or along the z-axis direction. The adsorption energy and bottom S-F bond length of SF<sub>6</sub> on the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface under different electric field strengths are summarized in Table 6 and Fig. 7. The aggregated surface partial charges of the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slab under different electric field strengths are shown in Fig. S13.

Table 6 Adsorption energy  $E_{ad}$  and bottom S-F bond length variation for SF<sub>6</sub> adsorption on perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface under different electric fields

	↓ <sup>a</sup> (	electric field	↑ <sup>a</sup> (	↑ <sup>a</sup> electric field		
E-field strength V/ Å	$E_{\rm c}({\rm aV})$	Bottom S-F bond	$E_{\rm c}({\rm aV})$	Bottom S-F bond		
	$L_{ad}(ev)$	length (Å)	$L_{ad}(ev)$	length (Å)		
0.00	-0.41	1.70	-0.41	1.70		
0.25	-0.38	1.67	-0.62	1.73		
0.50	-0.34	1.65	-0.84	1.78		
0.60	-0.35	1.70	-0.89	1.80		
0.75	-0.69	2.08	-1.08	1.84		
0.80	-0.92	2.14				
0.85	-1.00	2.15				
0.90	-1.18	2.18				
1.00			-1.41	1.94		
1.25			-1.84	2.00		

<sup>a</sup>The " $\downarrow$ " and " $\uparrow$ " symbols mean that the direction of the external electric field is opposite or along the z-axis direction.



strength

When the  $\downarrow$  electric field is applied, the  $E_{ad}$  of SF<sub>6</sub> slightly decreases and then increases rapidly with increasing the electric field. When the electric field strength is less than 0.75 V/Å, the  $E_{ad}$  as well as the bottom S-F bond length are smaller than on the natural surface, corresponding to a physical adsorption of SF<sub>6</sub> on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, as shown in Fig. 8(a). When the  $\downarrow$  electric field strength exceeds 0.75 V/Å, the adsorption process changed significantly, and the  $E_{ad}$  increases to -0.69 eV with the S-F bond length stretching to 2.08 Å. The state of SF<sub>6</sub> is likely to change from physical adsorption to chemical adsorption. At 0.80 V/Å, the  $E_{ad}$  increased to -0.92 eV and the S-F bond length increased to 2.14 Å. In Fig. 8(b), SF<sub>6</sub> undergoes a significant chemical adsorption.



(c) 0.50V/ Å of  $\uparrow$  electric field

(d) 1.00V/ Å of  $\uparrow$  electric field

Fig 8 SF<sub>6</sub> adsorption configurations under two electric field strengths (↓ and ↑ means the direction of the electric field opposite or along the z-axis direction, respectively)

Bader analysis of the SF<sub>6</sub> adsorption configurations under different electric fields are shown in Table 7. At the range of 0.50V/ Å  $\downarrow$  electric field, SF<sub>6</sub> gains almost no additional charge and the valence state of the S atom remains unchanged. However, when the electric

field increases to 0.80V/ Å  $\downarrow$ , the S atom gains +1.686 |e| electrons and the SF<sub>6</sub> molecule gains +0.59 |e|, which is also verified in the differential charge distribution results in Fig. S14. This indicates that increasing the electric field promotes the charge transfer from the slab surface to SF<sub>6</sub>, causing significant stretching of the bottom S-F bond. By comparison, applying the  $\uparrow$ electric field has slightly impacts the Bader charge of the SF<sub>6</sub> molecules, and the number of electrons obtained by S decreases with the  $\uparrow$  electric field. As shown in Fig. S13, the amount of positive charge on the top slab surface increases with the field strength and it may inhibit the charge transfer from slab to SF<sub>6</sub>, especially to the S atom.

 Table 7 Bader charge analysis of SF6 adsorption configurations under different electric field

 strengths

		↓ electi	ric field		↑ electric field			
Atom	0.5	0V/ Å	0.8	0V/ Å	0.5	0V/ Å	1.0	0V/ Å
7 ttom	Bader charge	Charge variation	Bader charge	Charge variation	Bader charge	Charge variation	Bader charge	Charge variation
S	0.00	0.00	1.69	1.69	0.24	0.24	0.15	0.15
F-1	8.03	0.03	7.81	-0.19	7.72	-0.28	7.71	-0.29
F-2	8.02	0.02	7.76	-0.24	8.02	0.02	7.98	-0.02
F-3	8.01	0.01	8.15	0.15	8.02	0.02	8.09	0.09
F-4	8.02	0.02	8.04	0.04	8.03	0.03	8.04	0.04
F-5	7.97	-0.03	7.67	-0.33	7.99	-0.02	8.00	0.00
F-6	7.99	-0.01	7.48	-0.52	8.05	0.05	8.08	0.08
Sum		0.04		0.59		0.06		0.05

<sup>a</sup> The total charge here is the value after deducting the number of electrons in the valence layer of each atom of S and F (6 for S and 7 for F). F atoms are labeled in Fig. 8.

The PDOS (Projected density of state) of the above systems are shown in Fig. 9. In Fig. 9 (b) and (d), the distributions of the outer valence electron orbitals of the atoms are shifted toward the Fermi level, indicating a stronger overlapping of orbitals between SF<sub>6</sub> and surface atoms, which does not happen in Fig. 9(a) and only happens in O orbitals in Fig. 9(c). This indicates that the increase of the electric field improves the interaction between SF<sub>6</sub> molecules and surface atoms, leading to a stronger charge transfer process and the electron orbital interactions, eventually affecting the surface bonding between SF<sub>6</sub> and the surface atoms. In

general, this process eventually leads to the transition of SF<sub>6</sub> adsorption type from physical to chemical, accompanied by the stretching of S-F bonds.



Fig 9 PDOS of SF<sub>6</sub> adsorption configurations under different electric field strengths It should be noted that the field strength of 0.25-0.90 V/Å is a large value that far exceeds

the average applied field strength in an ordinary DBD system. However, in realistic conditions, phenomena such as charge accumulation and the micro discharge formations could lead to a sudden increase in local electric fields inside a DBD reactor bringing it to the ranges computationally discussed here [24, 56]. Besides, the DFT simulations used here are aimed at understanding the atomic and molecular interactions via an isolated and computationally approximated approach, to give a qualitative explanation for the electric field effect, similar to the studies that have shown methodological feasibility [47, 57].

#### 3.4.3 Synergistic effect of excess electrons and external electric field

Here we use the dipole sheet method to investigate the combined effects of excess electrons and external electric field on the SF<sub>6</sub> adsorption. The surface induced charge is kept at -1.00|e| and the  $\downarrow$  electric field strength is varied from 0.10 to 0.50 V/Å. The adsorption results are shown in Table 8 and Fig. 10.

Table 8 Adsorption energy  $E_{ad}$  and bottom S-F bond length variation for SF<sub>6</sub> adsorption under the condition of 1.00|e| electrons and different  $\downarrow$  electric field strengths

E-field strength V/ Å	$E_{\rm ad}({\rm eV})$	Bottom S-F bond length (Å)
0.10	-3.35	2.09
0.20	-3.51	2.15
0.30	-3.66	2.17
0.40	-3.78	2.17
0.50	-4.00	2.17

Compared with the 'electron only' results in Table 4, applying a 0.10V/ Å electric field slightly reduces the  $E_{ad}$  of SF<sub>6</sub> and the elongation of the bottom S-F bond. The SF<sub>6</sub> configuration at 0.10V/Å + 1.00|e| condition in Fig. 10(a) is similar to "no electric field" condition shown in Fig. 6 (a). This indicates the electric field at this level has only a marginal effect on the adsorption system. However, when the field strength continued to increase, the adsorption process of SF<sub>6</sub> is enhanced. At  $0.50 \downarrow V/$ Å+1.00|e|, the  $E_{ad}$  increases to -4.00 eV while the S-F bond length stays constant at 2.17 Å, as shown in Fig. 10(b). At this stage, the SF<sub>6</sub> molecule is fully activated and is prone to a further decomposition. In Section 3.4.2, when 0.50 V/ Å electric field is applied without excess electrons, the  $E_{ad}$  is only -0.34 eV, much less than the -4.00 eV in this system. Therefore, the excess electrons and external electric field have an obvious synergistic effect and can jointly promote the adsorption and activation of SF<sub>6</sub> over the packing surface.



Fig 10 SF<sub>6</sub> adsorption configurations with excess electrons and external electric field In summary, the regulation of the plasma-induced surface effects could be an effective way to enhance the SF<sub>6</sub> degradation rate as well as the product selectivity. In practice, the reaction conditions for the gas-solid interface can often be conditioned by three aspects: catalyst, discharge and reactive gases.

(1) The change of catalyst structure is of great importance in regulating surface reactions, such as forming a porous structure and increasing the micro-discharge [58]. Another method is to load metals over the support catalyst ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), thus affecting the surface reactions by metal active sites and the metal-support interaction [59]. In addition, this study indicates that the over-adsorption on the catalyst surface needs to be prevented, which affects the interaction of the active sites with the SF<sub>6</sub> (target) molecules.

(2) For NTP discharge, increasing the reduced electrical field strength (E/N) in a certain range is a practical method, which facilitates the active particle density and enhancing the adsorption as well as the activation process of gas molecules over the catalyst surface [17].

(3) In NTP treatment, the addition of proper reactive gases such as O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, etc. should also be considered. Active particles are generating in the plasma region and affect the surface reactions via Langmuir– Hinshelwood and Eley–Rideal mechanisms [59], thus hindering the SF<sub>6</sub> self-recovery process and enhancing the S-F separation.

Therefore, multiple methods could be considered for the  $SF_6$  degradation enhancement in the future. At the same time, advanced experenental methods like in-situ diacharge diagnosis and surface characterizations, and multi-scale physi-chemical simulations should be applied to gain more detailed insights for the  $SF_6$  decomposition mechamisn in the complicated plasma treatment.

#### **4** Conclusions

In this study, we performed both experiments and DFT calculations to investigate the effects of hydration and of reactive gas addition as well as the plasma-induced surface effects on SF<sub>6</sub> degradation in a packed bed DBD plasma. Our experiments reveal that the degradation process is significantly reduced when the packing is hydrated by exposure to moisture, especially for small size packing. However, the hydration process hardly changes the discharge behavior and only slightly decreases the effective dielectric capacitance. In addition, in a 4 mm  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing system, the optimal concentrations of H<sub>2</sub>O and O<sub>2</sub> are 0.5% and 0.1%, respectively. Higher addition of H<sub>2</sub>O or O<sub>2</sub> reduces both the DRE and EY, while also barely affecting the discharge parameters.

Our DFT calculations reveal that the occupation of the active sites (Al<sub>III</sub> site) by adsorbed species such as OH, H<sub>2</sub>O, and O<sub>2</sub> can reduce the SF<sub>6</sub> adsorption ability and prevent its surface binding process. This corresponds well with the poor SF<sub>6</sub> degradation results in our experiments. Besides, the H<sub>2</sub>O pre-adsorbed near the Al<sub>III</sub> site can promote the initial decomposition of SF<sub>6</sub> and this may be due to the change of the electronic structure of the  $\gamma$ -

Al<sub>2</sub>O<sub>3</sub> surface by the H<sub>2</sub>O adsorption, leading to an enhancement of the activation process of SF<sub>6</sub> molecules. Plasma-induced surface charges and external electric field caused by the plasma on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface can improve the adsorption and activation of SF<sub>6</sub>. We found that 1.00 |e| negatively charged surface shows chemisorption of SF<sub>6</sub>. 0.75 V/Å is the turning point of '\p' direction electric field strength where the adsorption energy as well as the bottom S-F bond length dramatically increase when exceeding this electric field strength. However, this phenomenon does not happen in the  $\uparrow$  direction electric field. Moreover, we found that the synergistic effect of the plasma-induced surface charges and local electric field on SF<sub>6</sub> decomposition. 0.50V/Å ( $\downarrow$  direction) + 1.00|e| condition could lead to a stable chemisorption of SF<sub>6</sub> over the perfect  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface.

In summary, our study indicates that the surface structure of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> packing and the plasma effects are crucial for the catalytic degradation of SF<sub>6</sub>. Hence, the input gas conditions as well as the packing surface structure should be carefully evaluated when using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the packing material or the catalyst support in SF<sub>6</sub> DBD treatment. It is important to keep the packing surface dry with sufficient active sites during the SF<sub>6</sub> degradation. Moreover, our DFT results indicate that the plasma-induced surface charges significantly impact the packing surface properties as well as the surface reactions. Therefore, regulating the plasma-induced surface effects could be an effective way to enhance the SF<sub>6</sub> degradation rate as well as the product selectivity.

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