Chapter 5

Comparative Study of Materials to SF_6 Decomposition Components

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Abstract

In order to judge the inside insulation fault of SF_6 insulated equipment, the gas-sensing properties to a series of characteristic SF_6 decomposition components, SOF_2, SO_2F_2, SO_2, H_2S, CF_4, HF, and SF_6, have been studied. In this study, a comparative study of these gas-sensing materials has been made in theoretical and experimental fields to find the optimal gas-sensing material, and put forward the effective approaches to improve the gas-sensing properties of materials.

Keywords: SF_6 decomposed gases, carbon nanotubes, TiO_2 nanotubes, graphene gas sensor, gas-sensing comparison

1. Theoretical study comparison

To detect, evaluate, and diagnose the insulation status of SF_6 gas insulated equipment using the characteristics of SF_6 decomposition, a series of characteristic SF_6 decomposition components, SOF_2, SO_2F_2, SO_2, H_2S, CF_4, HF, and SF_6, are detected by gas sensors, including metal functionalized single wall carbon nanotubes (SWCNTs) [1–6], TiO_2 nanotubes [7–9], and graphene gas sensors [10, 11], as shown in **Table 1**. According to the theoretical calculation results, these three kinds of gas-sensing materials are not sensitive to the background gas SF_6 and decomposition component CF_4. And the concentration of HF in decomposition components is less than the concentration of the other typical gases. Therefore, we compare the adsorption properties four types of SF_6 decomposition components: SOF_2, SO_2F_2, SO_2, and H_2S, under the detection of metal functionalized SWCNTs, TiO_2 nanotubes, and graphene gas sensors.

Material	Dopant	Typical decomposition components						
SWCNTs	/	SOF_2	SO_2F_2	SO_2	H_2S	CF_4	HF	SF_6
	Pd	SOF_2	SO_2F_2	SO_2	H_2S	CF_4	/	/
	Ni	SOF_2	SO_2F_2	SO_2	/	/	/	/
	Al	SOF_2	SO_2F_2	SO_2	H_2S	CF_4	/	/
	Pt	/	/	SO_2	H_2S	/	/	/
	Au	/	/	SO_2	H_2S	/	/	/
TiO_2	/	SOF_2	SO_2F_2	SO_2	/	/	/	/
	Pt	SOF_2	SO_2F_2	SO_2	/	/	/	/
	Au	SOF_2	SO_2F_2	SO_2	/	/	/	/
Graphene	/	SOF_2	SO_2F_2	SO_2	H_2S	/	/	/
	Au	SOF_2	SO_2F_2	SO_2	H_2S	/	/	/

Table 1. The typical decomposition components of SF_6 detected by gas sensor.

Metal atom modification not only greatly improves the gas-sensing properties to SF_6 decomposition components, but also enhances the gas-sensing selectivity of sensors to different gas molecules. Upon SOF_2 and SO_2F_2 detection, intrinsic gas sensors show weak sensitivity to SOF_2 because of the weak interaction between gas molecules and the surface of gas-sensing materials. After metal atoms modification, which acts as the active sites, SOF_2 molecule tends to approaches the adsorption site by fluorine atom due the its strong chemical activity. Generally, the strong activity breaks the chemical bonds of SOF_2. Similarly, SO_2F_2 interacts with the metal atom-doped gas-sensing material by chemisorption, reflecting in aspect that the fluorine atom breaks from SO_2F_2 to build new bond with metal atoms. Upon SO_2 and H_2S detection, these two small gas molecules are generally adsorbed on the surface of gas sensors by physisorption, which was benefit to gas desorption process. SO_2 and H_2S get approach to the surrounding of metal dopant by oxygen and sulfur atom, respectively, because of its polyvalency property.

Comparing the gas-sensing properties of different sensor materials, the regular porous structure of TiO_2 nanotubes contributes to gas desorption and reusability. In addition, its big specific surface area helps the metal dopant modification and gas-sensing sites. But, TiO_2 nanotubes sensor usually needs high work temperature, and its high resistance hinders the transmission of detection signals. In comparison, metal atom-doped SWCNT and graphene sensor can work effectively at room temperature, and its low resistance helps to transfer detection signals, resulting in reducing gas-sensing time.

2. Experimental study comparison

Using the own design platform which is used to test the performance of TiO_2 nanotubes sensor, the gas response characteristics and temperature characteristics of the intrinsic TiO_2 nanotubes sensor to three main SF_6 gas decomposition compositions SO_2, SOF_2, and SO_2F_2 were studied. The same sensing experiments were also carried out on Pt and Au-doped TiO_2

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nanotubes sensors. The results are compared as shown in **Table 2** for TiO_2 nanotubes gas sensor and **Table 3** for graphene gas sensor.

It is concluded that the Au-doped TiO_2 nanotubes sensor has better selectivity to SO_2F_2 gas. Pt nanoparticles doping changes gas selectivity of TiO_2 nanotubes sensor to SO_2, SOF_2, and SO_2F_2. Compared with the intrinsic sensor, Au nanoparticles doped significantly changed the selectively of sensor to SO_2, SOF_2, and SO_2F_2 (**Table 3**).

Pristine graphene is considered a promising adsorbent for H_2S selective detection. Compared with the performance on pristine graphene films, Au-doped graphene emerges significant response to H_2S, SOF_2, and SO_2F_2 but weak interaction to SO_2, with the sequence of $SO_2F_2 > H_2S > SOF_2 > SO_2$. Among them, only H_2S shows the opposite response with its resistance increase, while SO_2, SOF_2, and SO_2F_2 decrease the resistance of Au-doped graphene.

Doping metal	**Doping time**	**Gas-sensing parameters to typical decomposition components**		
		SO_2	**SOF_2**	**SO_2F_2**
/	0 s	−74.6%	−7.82%	−5.52%
Pt	10 s	−53.3%	−24.2%	−5.4%
	20 s	−33.9%	−22.1%	−19.2%
	30 s	−13.8%	−19.1%	−50.6%
	40 s	−6.7%	−5.1%	−10.7%
Au	–	−23.75%	−28.37%	−42.31%

Table 2. The typical decomposition components of SF_6 detected by TiO_2 nanotubes gas sensor.

Doping metal	**Gas-sensing parameters to typical decomposition components**			
	H_2S	**SO_2**	**SOF_2**	**SO_2F_2**
/	−15.78%	−1.5%	−0.8%	−0.3%
Au	28.15%	−6.98%	−23.83%	−33.91%

Table 3. The typical decomposition components of SF_6 detected by graphene gas sensor.

3. Conclusions

In order to evaluate and diagnose the insulation status of SF_6 insulated equipment, gas sensor detection becomes an effective new method to realize the function by detecting the decomposition components of SF_6. Theoretical simulations are performed to understand the adsorption process of gas sensors and typical components of SF_6. And using carbon nanotubes (CNTs) based as novel kind of sensors show high sensitivity and quick responses to target gases. For TiO_2-based gas sensor, the adsorption of typical components of SF_6 on different surfaces of TiO_2 is reviewed in this section. It is found that the metal decoration improves the sensitivity and selectivity to SO_2 and SOF_2, and SO_2F_2 also reduces the working temperature for gas detection. Pristine graphene exhibits weak adsorption and absence of charge transfer, which indicates barely satisfactory sensing for decomposed components. SOF_2 and SO_2F_2 exhibit a strong chemisorption interaction with Au-graphene, while H_2S and SO_2 exhibit quasi-molecular binding effects. Only H_2S exhibits n-type doping to Au-graphene, whereas the rest gases exhibit p-type doping. In general, the sensors array composed of modified gas sensors can be used in the GIS to realize the highly precise detection of related gases, thus accurately deducing the related insulation faults.

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