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Comparative Study of Materials to SF₆ Decomposition Components

Song Xiao, Xiaoxing Zhang, Ju Tang, Fuping Zeng, Cheng Pan and Yingang Gui

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Abstract

In order to judge the inside insulation fault of SF₆ insulated equipment, the gas-sensing properties to a series of characteristic SF₆ decomposition components, SOF₂, SO₂F₂, SO₂, H₂S, CF₄, HF, and SF₆, 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: SF₆ decomposed gases, carbon nanotubes, TiO₂ nanotubes, graphene gas sensor, gas-sensing comparison

1. Theoretical study comparison

To detect, evaluate, and diagnose the insulation status of SF₆ gas insulated equipment using the characteristics of SF₆ decomposition, a series of characteristic SF₆ decomposition components, SOF₂, SO₂F₂, SO₂, H₂S, CF₄, HF, and SF₆, are detected by gas sensors, including metal functionalized single wall carbon nanotubes (SWCNTs) [1–6], TiO₂ 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 SF₆ and decomposition component CF₄. 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 SF₆ decomposition components: SOF₂, SO₂F₂, SO₂, and H₂S, under the detection of metal functionalized SWCNTs, TiO₂ nanotubes, and graphene gas sensors.

Material	Dopant	Typical decomposition components						
SWCNTs	/	SOF ₂	SO ₂ F ₂	SO ₂	H ₂ S	CF ₄	HF	SF ₆
	Pd	SOF ₂	SO ₂ F ₂	SO ₂	H ₂ S	CF ₄	/	/
	Ni	SOF ₂	SO ₂ F ₂	SO ₂	/	/	/	/
	Al	SOF ₂	SO ₂ F ₂	SO ₂	H ₂ S	CF ₄	/	/
	Pt	/	/	SO ₂	H ₂ S	/	/	/
	Au	/	/	SO ₂	H ₂ S	/	/	/
TiO ₂	/	SOF ₂	SO ₂ F ₂	SO ₂	/	/	/	/
	Pt	SOF ₂	SO ₂ F ₂	SO ₂	/	/	/	/
	Au	SOF ₂	SO ₂ F ₂	SO ₂	/	/	/	/
Graphene	/	SOF ₂	SO ₂ F ₂	SO ₂	H ₂ S	/	/	/
	Au	SOF ₂	SO ₂ F ₂	SO ₂	H ₂ S	/	/	/

Table 1. The typical decomposition components of SF₆ detected by gas sensor.

Metal atom modification not only greatly improves the gas-sensing properties to SF₆ decomposition components, but also enhances the gas-sensing selectivity of sensors to different gas molecules. Upon SOF₂ and SO₂F₂ detection, intrinsic gas sensors show weak sensitivity to SOF₂ 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, SOF₂ 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 SOF₂. Similarly, SO₂F₂ interacts with the metal atom-doped gas-sensing material by chemisorption, reflecting in aspect that the fluorine atom breaks from SO₂F₂ to build new bond with metal atoms. Upon SO₂ and H₂S detection, these two small gas molecules are generally adsorbed on the surface of gas sensors by physisorption, which was benefit to gas desorption process. SO₂ and H₂S 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 TiO₂ nanotubes contributes to gas desorption and reusability. In addition, its big specific surface area helps the metal dopant modification and gas-sensing sites. But, TiO₂ 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 TiO₂ nanotubes sensor, the gas response characteristics and temperature characteristics of the intrinsic TiO₂ nanotubes sensor to three main SF₆ gas decomposition compositions SO₂, SOF₂, and SO₂F₂ were studied. The same sensing experiments were also carried out on Pt and Au-doped TiO₂

nanotubes sensors. The results are compared as shown in **Table 2** for TiO₂ nanotubes gas sensor and **Table 3** for graphene gas sensor.

It is concluded that the Au-doped TiO₂ nanotubes sensor has better selectivity to SO₂F₂ gas. Pt nanoparticles doping changes gas selectivity of TiO₂ nanotubes sensor to SO₂, SOF₂, and SO₂F₂. Compared with the intrinsic sensor, Au nanoparticles doped significantly changed the selectivity of sensor to SO₂, SOF₂, and SO₂F₂ (**Table 3**).

Pristine graphene is considered a promising adsorbent for H₂S selective detection. Compared with the performance on pristine graphene films, Au-doped graphene emerges significant response to H₂S, SOF₂, and SO₂F₂ but weak interaction to SO₂, with the sequence of SO₂F₂ > H₂S > SOF₂ > SO₂. Among them, only H₂S shows the opposite response with its resistance increase, while SO₂, SOF₂, and SO₂F₂ decrease the resistance of Au-doped graphene.

Doping metal	Doping time	Gas-sensing parameters to typical decomposition components		
		SO ₂	SOF ₂	SO ₂ F 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 SF₆ detected by TiO₂ nanotubes gas sensor.

Doping metal	Gas-sensing parameters to typical decomposition components			
	H ₂ S	SO ₂	SOF ₂	SO ₂ F 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 SF₆ detected by graphene gas sensor.

3. Conclusions

In order to evaluate and diagnose the insulation status of SF₆ insulated equipment, gas sensor detection becomes an effective new method to realize the function by detecting the decomposition components of SF₆. Theoretical simulations are performed to understand the adsorption process of gas sensors and typical components of SF₆. And using carbon nanotubes (CNTs) based as novel kind of sensors show high sensitivity and quick responses to target gases. For TiO₂-based gas sensor, the adsorption of typical components of SF₆ on different surfaces of TiO₂ is reviewed in this section. It is found that the metal decoration improves the sensitivity

and selectivity to SO₂ and SOF₂, and SO₂F₂ 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. SOF₂ and SO₂F₂ exhibit a strong chemisorption interaction with Au-graphene, while H₂S and SO₂ exhibit quasi-molecular binding effects. Only H₂S 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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