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The SF₆ Decomposition Mechanism: Background and Significance

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Abstract

Gas Insulated Switchgear (GIS) has been widely used in substations. The insulating medium used in GIS is sulfur hexafluoride (SF₆) gas. However, the internal insulation defect existed in GIS would inevitably lead to partial discharge (PD), and cause the composition of SF₆ to SOF₂, SO₂F₂ and SO₂ and other characteristic component gases. The decomposition phenomenon would greatly reduce the insulation performance of SF₆ insulated equipment, and even paralyze the whole power supply system. In this chapter, we first discuss the objective existence, decomposition mechanism and harmness of insulation defects. Then the methods for insulation defects detection used to avoid the insulation accidents are introduced. Comparing all of the detection methods, diagnosing the insulation defect through analyzing the decomposed gases of SF₆ by chemical gas sensors is the optimal method due to its advantages, such as high detection accuracy and stability, signifying the importance of developing chemical gas sensor used in SF₆ insulated equipment. In conclusion, there kinds of gas sensor material, carbon nanotubes, graphene, are chosen as the gas sensing materials to build specific gas sensors for detecting each kind of SF₆ decomposed gases, and then enhance the gas sensitivity and selectivity by material modification.

Keywords: SF₆-insulated equipment, insulation defect, SF₆ decomposition components, detection methods

1. The purpose of study on SF₆ decomposition components

Gas-insulated equipment using SF₆ as insulation and arc extinguishing media such as gas-insulated station (GIS), gas-insulated transformer (GIT), and gas-insulated line (GIL) has been widely used in the field of high voltage and extra-high and ultra-high voltage power systems.

It gradually became the most ideal equipment and one of the important symbols of modern substation because of its high reliability, easy maintenance, less occupied area, and flexible allocation since it was first commissioned in Germany in 1967 [1–3].

However, SF₆ gas-insulated equipment will inevitably have insulation defects. The insulation defects mainly come from the following aspects: (1) residual metal burrs or protrusions on the buses or electrodes during the manufacturing process, (2) loose contacts during the installation or transportation, (3) internal free metal particles, (4) insulation aging, and (5) corrosion and other problems [4, 5]. The positions where the insulation defects existed can occur at the interface or inside of insulators. For the insulation at the surface of insulators, the defect is usually caused by secondary effects of other types of defects, such as the uncleaned remnants, metal powder, partial discharge decomposition components, condensed fluid water on the surface of insulators, and insulator surface air gap [6]. Internal insulation defects are usually small and hard to detect. They are usually formed in the manufacturing processes, such as internal gas gap or delamination caused by the different thermal expansion. Besides, the solid insulators used in GIS are usually made of organic polymer material. The insulation performance of these materials is greatly affected by the strong electric field and thermal field. If small failures occur in the internal equipment, the insulation performance of the solid insulator at fault point would deteriorate significantly due to the continuous strong electric field and thermal field and ultimately would lead to electric breakdown or thermal breakdown. However, the insulation performance of the insulator cannot be self-restored [7–9].

When SF₆ gas-insulated equipment malfunctions, its fully enclosed structure makes it very difficult to carry out the fault location and repairing work. The average power-off overhaul time of the SF₆ gas-insulated equipment after its failure is longer than that of other electrical equipment and it affects a wider range [10]. As the key part of transportation and distribution of electrical energy, the safety and stability of SF₆ gas-insulated equipment play an important role in successful operation of the power system. Once the improper protection appears or timely removal of faults cannot be done, it causes a cascading failure, which will result in an enormous economic loss and even a sudden public safety issue. Therefore, online monitoring of SF₆ gas-insulated equipment becomes a task that must be accomplished by the power grid staff. Analyzing the running status of the equipment by a long-time and reliable data accumulation and studying the characteristic parameters that indicate the state of SF₆ gas-insulated equipment are the major issues for electric power research institutes. The purpose is to find latent or early insulation failure timely by inspecting and identifying key parameters to prevent the development of accidents.

When defects of solid insulation in SF₆ gas-insulated equipment mentioned above occur, these cause the distortion of the electric field in the equipment, which may result in PD or partial overheating (PO) before it completely breaks down [11]. When serious PD or PO appears, it will accelerate the damage of internal insulation, which will ultimately lead to insulation faults and power failure. This is a potential hazard to the running SF₆ gas-insulated equipment, also known as “insulation tumor.” On the other hand, PD or PO is one of the key parameters that can represent the internal solid insulation condition of the SF₆ gas-insulated equipment. The insulation defects and their types in SF₆ gas-insulated equipment can

be detected to some extent by detecting PD or PO combined with pattern recognition [12]. Therefore, detecting PD or PO has important significance for ensuring reliable operation of SF₆ gas-insulated equipment and can greatly improve the ability and level of monitoring of the SF₆ gas-insulated equipment.

Based on the existing research results, the continuation of PD and PO will cause SF₆ decomposition. The decomposition products of SF₆ contain some highly active substances, such as F, HF, and SO₂. They will further corrode solid insulation material and metal fasteners and generate substances such as CF₄, COF₂, C₃F₈, C₄F₈, C₄F₁₀, C₅F₁₀, C₆F₁₂, CF₃S, CF₃S₂, CO, CO₂, etc., which will form a vicious cycle and cause further solid insulation deterioration and finally induce sudden failures [13–15]. To sum up, the contents of decomposition components of SF₆ and solid insulating materials and their change rule under continuous PD or PO have a close relationship with the type and severity of internal faults in the equipment. Hence, monitoring the sorts and contents of the decomposition products has become an effective means to determine the cause and the degree of development of thermal and electrical failures. By a theoretical and experimental study of SF₆ decomposition under PD or PO caused by internal faults, the characteristic parameters of decomposition products which can reflect and distinguish different types and severity of faults can be extracted. They can be used to establish fault diagnosis method and comprehensive evaluation system of SF₆ gas-insulated equipment. Thus, the internal insulation failure of SF₆ gas-insulated equipment could be found timely through detection of the decomposition products of SF₆ and the state of insulation could be estimated scientifically, which can reduce the probability of sudden failures of SF₆ gas-insulated equipment and build the first defense system against the sources of large accidents.

2. The current developments of the SF₆ decomposition mechanism and influence factors

So far, researches on SF₆ decomposition under the effect of discharge have mainly been carried out on the decomposition mechanism under arc discharge, spark discharge, and partial discharge, and initial progress has been made. However, a study on the evaluation and fault diagnosis of SF₆ gas-insulated equipment using the characteristics of SF₆ decomposition under different conditions has not yet been reported. As a whole, research about fault diagnosis for equipment evaluation research using the decomposed components analysis (DCA) method is still in the early stage. Most of the results are limited to discussing the influence of partial discharge and the impurity of gas on SF₆ decomposition components, but the content of decomposition gases and gas production characteristics under different insulation flaws has not been studied, and the corresponding mechanism has not been reported so far [16]. As for SF₆ decomposition characteristics and mechanism under overheat conditions, no report exists. Based on the specificity of SF₆ decomposition components under different insulation defects, such as gases types and concentration, it is feasible to develop specific gas sensors to detect corresponding characteristic SF₆ decomposition components, realizing the online evaluation and fault diagnosis of SF₆ gas-insulated equipment.

Pure SF₆ is odorless, colorless, non-toxic, non-combustible, and inert gas, and its chemistry property is very stable under 150°C. Extensive domestic and overseas studies show that when PD occurs in SF₆ gas-insulated equipment, SF₆ will decompose under the effect of electric field energy and generate low fluorine sulfide products such as SF₅, SF₄, SF₃, SF₂, SF, etc. [17]. If PD appears in pure SF₆, these low fluorine sulfur products will recombine into SF₆ after they diffuse out of the local high voltage area. The transient decomposition process of SF₆ has little influence on the insulation performances of SF₆-insulated equipment [18, 19, 20]. However, various impurities, such as trace amounts of air and water, exist in SF₆ gas-insulated equipment inevitably (at present, the content of impurity of SF₆ produced in our country can meet the requirement of International Electrotechnical Commission (IEC) standards and technical conditions in our country). These impurities can react with low fluorine sulfur products mentioned above and generate other oxygen-containing gas components. Some stable decomposition components are shown in **Figure 1**. The decomposition mechanism of SF₆ under corona discharge is shown in **Figure 2**. Therefore, insulation monitoring and fault diagnosis of SF₆ gas-insulated equipment can be achieved by detecting the SF₆ decomposition components and their contents.

The scholars have done a lot of research on the SF₆ decomposition components under arc, spark, and PD conditions, and the decomposition mechanism and decomposition components of SF₆, including SO₂, CF₄, SOF₄, SO₂F₂, HF, SOF₂, and S₂F₁₀O under the PD condition, have also been preliminarily understood. According to an experimental study, S₂F₁₀ and S₂F₁₀O are the unique decomposition components under spark discharge, and they cannot be detected under PD. Therefore, S₂F₁₀ and S₂F₁₀O can be used as the characteristic gases of spark discharge. However, the decomposition components of SF₆ under PD mainly contain SOF₄, CF₄, SO₂F₂, SOF₂, H₂S, SO₂, and HF. It should be noted that HF is an acid gas, which can easily react with insulation materials, metal connectors, and other equipment components and generate corresponding fluorides, and the content of HF will decrease with the development of PD. For this reason, HF cannot be regarded as the characteristic component of PD [21]. SOF₄ is extremely unstable and can easily react with water to generate SO₂F₂. When the equipment has a certain moisture content inside or a small amount of water infiltrates into the gas during

Figure 1. Formation of SF₆ decomposition components.

Figure 2. SF₆ decomposition mechanism under corona discharge.

the gas sampling and detecting process, the results will be seriously affected. Therefore, SOF₄ also cannot be used as the characteristic component of PD [22]. Although SOF₂ can be hydrolyzed, it is relatively stable. Based on the above research results, H₂S, SO₂, SOF₂, and SO₂F₂ were chosen as the characteristic components of SF₆ decomposition under PD to conduct the analysis of online monitoring [21, 23].

Up to now, no research scholars have built a unified system for the SF₆ decomposed component analysis method, and gas-insulated equipment insulation online monitoring & fault diagnosis technology. These research areas are not adequate for the electrical equipment online monitoring and fault diagnosis field but have broad prospects. Considering the characteristics of SF₆ decomposition caused by PD or PO with different typical insulation defects in gas-insulated equipment, insulation monitoring and fault diagnosis of gas-insulated equipment can be realized by SF₆ decomposition components and their tendency to change content. The method has become a leading domestic and international detection technology. The progress has attracted wide peer attention worldwide, and some achievements have been used in electric power enterprises. Now, the results of the project have been cited to formulate international standards by the International Council on Large Electric Systems (CIGRE).

3. The detection methods of SF₆ decomposition components

So far, the main methods to detect the decomposition components of SF₆ in GIS are gas chromatography, infrared absorption spectroscopy, photoacoustic spectroscopy, and chemical gas sensor.

3.1. Gas chromatography

The principle of gas chromatography is that the adsorption or dissolving capacity of the stationary phase to various SF₆ decomposition components is different. In other words, the distribution coefficients of different components in the two phases are different. When there is relative motion

between two phases, decomposition components are distributed repeatedly when they move forward in two phases. Different components can be separated because of the different velocities of different components along the column [24–27]. The separated SF₆ decomposition components pass through the detector according to the separation order, and the detector turns the concentrations of components in mobile phase into corresponding electrical signals [28]. This method can measure the concentration of SOF₂, SO₂F₂, SO₂, and CF₄ with high detection sensitivity that can reach 10⁻⁹. However, it cannot detect HF and SOF₄. Besides, the testing time is too long for continuous detection. It also demands a high standard of the environment since the separation effect is influenced by the temperature and chromatographic columns need to be washed after using for a period of time. Therefore, this method cannot be used in *in situ* monitoring of GIS [29].

3.2. Photoacoustic spectroscopy

Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.

The absorbed energy from the light causes local heating and a pressure wave (or sound) is generated through thermal expansion. A photoacoustic spectrum of a sample can be recorded by measuring the sound at different wavelengths of the light. This spectrum can be used to identify the absorbing components of the sample and their concentrations with very high sensitivity. However, this method relies deeply on the experimental environment and is susceptible to external interference [29].

3.3. Infrared absorption spectroscopy

The principle of infrared absorption spectroscopy is that the degree of absorption of infrared light when it passes through the detected gas is linear to the volume fraction of the detected gas. The intensity ratio of the transmitted and incident light and the wavelength form a function, which is the infrared absorption spectrum of the detected gas. During the detection, the gas absorption peak will appear at different detected gases' best absorption wavelength of their infrared spectrum [30]. Based on the above principle, Fourier infrared spectrometer can detect SO₂, SOF₂, SOF₄, SO₂F₂, and CF₄ at the μL/L level. However, the background gas SF₆ will lead to the displacement of the absorption peak of the characteristic gases, and there is also interference among each detected gas. So, the detection results must be corrected when using infrared absorption spectroscopy. In addition, the detection requires large gas volume because the gas pool of infrared absorption spectroscopy is large. The detection sensitivity is also low when detecting trace gases because the difference of the intensity of incident and transmission light is very small. Besides, its accuracy for quantitative detection is easily affected by the reflected and scattered light. In view of the above shortcomings, infrared absorption spectroscopy is not a good option for the online monitoring of GIS. It can only exert its advantage of high detection sensitivity in laboratory studies.

3.4. Gas sensor method

The principle of gas sensor method is that the chemical properties of gas-sensitive materials will change after gas molecules are absorbed on its surface, and this can lead to the change

of electrical properties of the gas-sensitive materials. The gas sensor has the features of high detection speed, high efficiency, and small volume; it can be used with computers to realize automatic online monitoring and diagnosis. However, it can only detect a single gas, so the detection of each gas needs a specific gas sensor [31]. Therefore, a gas sensor array must be developed to detect different SF₆ gas decomposition components. So far, some research results exist on detection of H₂S and SO₂ by gas sensors, but the research about detection of SO₂F₂, SOF₂, CF₄, SF₄, SOF₄, and H₂S using gas sensors is rare.

4. The significance of gas-sensing material on online monitoring SF₆ decomposition components

For the online monitoring of SF₆ gas-insulated equipment, there were no report about suitable online monitoring devices of SF₆ decomposition characteristic components in gas-insulated equipment. Although photoacoustic spectrum method, gas chromatography, infrared absorption spectroscopy, and gas sensors have been used for detecting SF₆ decomposition components at present, there is still lack of fast and low-cost online monitoring means to detect characteristic gases of SF₆ decomposition components in gas-insulated equipment. With the rapid development of nano-sensing technology, the gas sensor method to detect SF₆ decomposition components has become the trend of research hotspot [31–33]. Study of the gas sensor method to detect SF₆ decomposition components not only enriches and develops the new method of online monitoring, but also has important engineering significance and broad application prospects of realizing online monitoring of SF₆ decomposition components in gas-insulated equipment and its condition-based maintenance.

Based on the study of response mechanism and testing experiments of nanometer sensors for detecting SF₆ decomposition components, the first condition for realizing online monitoring SF₆ decomposition components using gas sensor method is to develop nano-sensor technology. Developing composite nanometer sensor technology by various modification methods with a single response for different components of SF₆ decomposition and establishing relationship between a single component of SF₆ decomposition and the intensity of gas-sensitive characteristic signal in order to obtain the sensor array gas-sensitive element are the key technical problems that need to be resolved in order to realize online monitoring of SF₆ decomposition components with the gas sensor method. In this chapter, the following two aspects are investigated about the nanosensors for detecting SF₆ decomposition components. First, for the theoretical simulation, analyzing the characteristics of the mechanism of SF₆ decomposition components absorbing on the surface of nano sensors based on the first principle of density function theory is the theoretical basis of realizing the online monitoring of SF₆ decomposition components. Next, from the aspect of experiments, we need to develop gas sensors of high performance according to the theoretical results and prepare gas sensors with high sensitivity and selectivity to SF₆ decomposition components.

Carbon nanotubes, titanium dioxide nanotubes, and graphene are used for detecting SF₆ decomposition components in this chapter. These three materials are hotspots of new types of functional materials in the field of gas-sensitive sensor. They not only have strong response

sensitivity, selectivity, small size, low working temperature, easy processing, and many other traditional advantages but also have unique atomic structure and excellent electrochemical properties. Hence, gas sensors have great research potential and broad prospects in the field of electrochemistry and gas-sensing technology. Carbon nanotubes have abundant pore structure, large specific surface area, strong surface adsorption ability, good electrical conductivity, and electronic transmission characteristics. These unique physical and chemical properties and excellent gas-sensitive properties make them the hotspots in the field of nanometer gas-sensitive materials [34]. The carbon nanotube gas sensor is featured with high sensitivity, fast response speed, small size, and low power consumption, and it can work at room temperature [35]. It has broad application prospects in the aspect of gas sensor. TiO₂ nanotube array (TNTA) has three-dimensional nanopore structure, which results in many virtues: fast gas-sensitive response speed, high sensitivity, possible surface modification, and excellent gas-sensitive selectivity. In order to further improve the gas-sensing properties of TiO₂ nanotubes, domestic and overseas researchers came up with metal doping, nonmetal doping, semiconductor doping, and functional group modification to realize the modification of intrinsic TiO₂ nanotubes [36–39]. Graphene has a unique two-dimensional structure, large specific surface area, excellent conductivity, extremely low Johnson noise and thermal switch noise, and few crystal defects. Theoretical analysis shows that graphene has the ability to detect ultra-low concentration of gas, so it becomes a kind of new functional materials in the field of sensors. In addition, graphene is a material with the best electrical conductivity in room temperature to date. It not only has strong adsorption ability to chemical gas composition, but also has excellent desorption ability. It can reduce the operation temperature of the gas sensors, thereby reducing the energy loss, compared with semiconductor metal oxide sensors of high operating temperature.

Carbon nanotubes, titanium dioxide nanotubes, and graphene materials are applied in the study of detection of SF₆ decomposition characteristic components to explore the practical application in engineering of new gas-sensing nano materials in the field of electrical equipment online monitoring. It can further enrich and develop the online monitoring method of characteristic gases of electrical equipment failure. The achievement of the gas-sensing mechanism based on density functional theory also provides scientific theoretical guidance for developing high-performance sensors.

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