Chapter 1

The SF_6 Decomposition Mechanism: Background and Significance

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Additional information is available at the end of the chapter

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Abstract

Gas Insulated Switchgear (GIS) has been widely used in substations. The insulating medium used in GIS is sulfur hexafluoride (SF_6) gas. However, the internal insulation defect existed in GIS would inevitably lead to partial discharge (PD), and cause the composition of SF_6 to SOF_2, $SO2F_2$ and SO_2 and other characteristic component gases. The decomposition phenomenon would greatly reduce the insulation performance of SF_6 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 SF_6 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 SF_6 decomposed gases, and then enhance the gas sensitivity and selectivity by material modification.

Keywords: SF_6-insulated equipment, insulation defect, SF_6 decomposition components, detection methods

1. The purpose of study on SF_6 decomposition components

Gas-insulated equipment using SF_6 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, SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 gas-insulated equipment. The insulation defects and their types in SF_6 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 SF_6 gas-insulated equipment and can greatly improve the ability and level of monitoring of the SF_6 gas-insulated equipment.

Based on the existing research results, the continuation of PD and PO will cause SF_6 decomposition. The decomposition products of SF_6 contain some highly active substances, such as F, HF, and SO_2. They will further corrode solid insulation material and metal fasteners and generate substances such as CF_4, COF_2, C_3F_8, C_4F_8, C_4F_{10}, C_5F_{10}, C_6F_{12}, CF_8S, CF_6S_2, CO, CO_2, 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 SF_6 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 SF_6 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 SF_6 gas-insulated equipment. Thus, the internal insulation failure of SF_6 gas-insulated equipment could be found timely through detection of the decomposition products of SF_6 and the state of insulation could be estimated scientifically, which can reduce the probability of sudden failures of SF_6 gas-insulated equipment and build the first defense system against the sources of large accidents.

2. The current developments of the SF_6 decomposition mechanism and influence factors

So far, researches on SF_6 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 SF_6 gas-insulated equipment using the characteristics of SF_6 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 SF_6 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 SF_6 decomposition characteristics and mechanism under overheat conditions, no report exists. Based on the specificity of SF_6 decomposition components under different insulation defects, such as gases types and concentration, it is feasible to develop specific gas sensors to detect corresponding characteristic SF_6 decomposition components, realizing the online evaluation and fault diagnosis of SF_6 gas-insulated equipment.

Pure SF_6 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 SF_6 gas-insulated equipment, SF_6 will decompose under the effect of electric field energy and generate low fluorine sulfide products such as SF_5, SF_4, SF_3, SF_2, SF, etc. [17]. If PD appears in pure SF_6, these low fluorine sulfur products will recombine into SF_6 after they diffuse out of the local high voltage area. The transient decomposition process of SF_6 has little influence on the insulation performances of SF_6-insulated equipment [18, 19, 20]. However, various impurities, such as trace amounts of air and water, exist in SF_6 gas-insulated equipment inevitably (at present, the content of impurity of SF_6 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 SF_6 under corona discharge is shown in **Figure 2**. Therefore, insulation monitoring and fault diagnosis of SF_6 gas-insulated equipment can be achieved by detecting the SF_6 decomposition components and their contents.

The scholars have done a lot of research on the SF_6 decomposition components under arc, spark, and PD conditions, and the decomposition mechanism and decomposition components of SF_6, including SO_2, CF_4, SOF_4, SO_2F_2, HF, SOF_2, and $S_2F_{10}O$ under the PD condition, have also been preliminarily understood. According to an experimental study, S_2F_{10} and $S_2F_{10}O$ are the unique decomposition components under spark discharge, and they cannot be detected under PD. Therefore, S_2F_{10} and $S_2F_{10}O$ can be used as the characteristic gases of spark discharge. However, the decomposition components of SF_6 under PD mainly contain SOF_4, CF_4, SO_2F_2, SOF_2, H_2S, SO_2, 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]. SOF_4 is extremely unstable and can easily react with water to generate SO_2F_2. When the equipment has a certain moisture content inside or a small amount of water infiltrates into the gas during

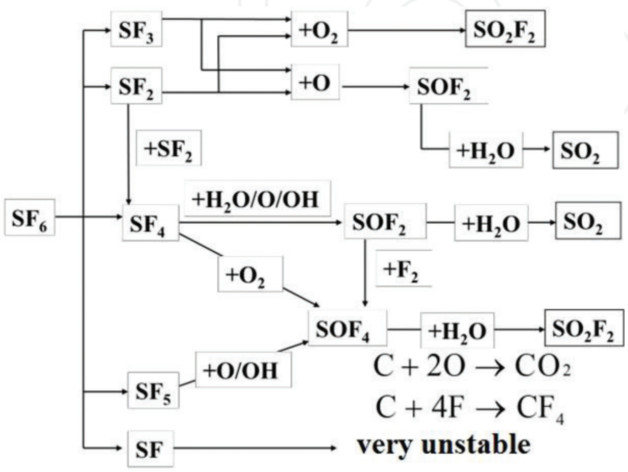

Figure 1. Formation of SF_6 decomposition components.

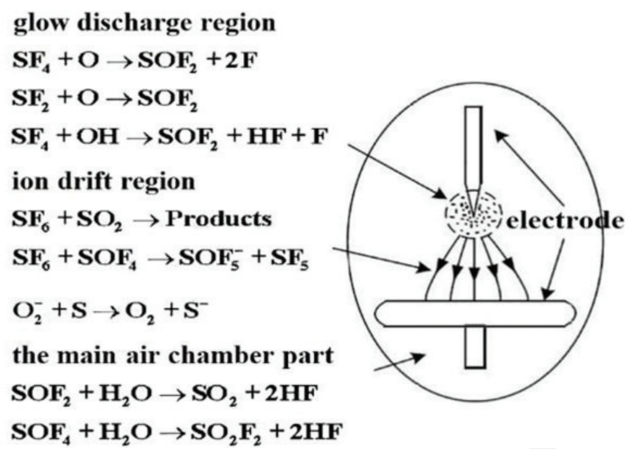

Figure 2. SF_6 decomposition mechanism under corona discharge.

the gas sampling and detecting process, the results will be seriously affected. Therefore, SOF_4 also cannot be used as the characteristic component of PD [22]. Although SOF_2 can be hydrolyzed, it is relatively stable. Based on the above research results, H_2S, SO_2, SOF_2, and SO_2F_2 were chosen as the characteristic components of SF_6 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 SF_6 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 SF_6 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 SF_6 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 SF_6 decomposition components

So far, the main methods to detect the decomposition components of SF_6 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 SF_6 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 SF_6 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 SOF_2, SO_2F_2, SO_2, and CF_4 with high detection sensitivity that can reach 10^{-9}. However, it cannot detect HF and SOF_4. 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 SO_2, SOF_2, SOF_4, SO_2F_2, and CF_4 at the μL/L level. However, the background gas SF_6 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 SF_6 gas decomposition components. So far, some research results exist on detection of H_2S and SO_2 by gas sensors, but the research about detection of SO_2F_2, SOF_2, CF_4, SF_4, SOF_4, and H_2S using gas sensors is rare.

4. The significance of gas-sensing material on online monitoring SF_6 decomposition components

For the online monitoring of SF_6 gas-insulated equipment, there were no report about suitable online monitoring devices of SF_6 decomposition characteristic components in gas-insulated equipment. Although photoacoustic spectrum method, gas chromatography, infrared absorption spectroscopy, and gas sensors have been used for detecting SF_6 decomposition components at present, there is still lack of fast and low-cost online monitoring means to detect characteristic gases of SF_6 decomposition components in gas-insulated equipment. With the rapid development of nano-sensing technology, the gas sensor method to detect SF_6 decomposition components has become the trend of research hotspot [31–33]. Study of the gas sensor method to detect SF_6 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 SF_6 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 SF_6 decomposition components, the first condition for realizing online monitoring SF_6 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 SF_6 decomposition and establishing relationship between a single component of SF_6 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 SF_6 decomposition components with the gas sensor method. In this chapter, the following two aspects are investigated about the nanosensors for detecting SF_6 decomposition components. First, for the theoretical simulation, analyzing the characteristics of the mechanism of SF_6 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 SF_6 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 SF_6 decomposition components.

Carbon nanotubes, titanium dioxide nanotubes, and graphene are used for detecting SF_6 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 TiO_2 nanotubes, domestic and overseas researchers came up with metal doping, nonmetal doping, semiconductor doping, and functional group modification to realize the modification of intrinsic TiO_2 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 SF_6 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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