INVESTIGATION OF DIELECTRIC BREAKDOWN PROPERTIES OF SF$_6$–N$_2$ AND SF$_6$–CF$_4$ MIXTURES AT 0.4 MPA AND GAS TEMPERATURES UP TO 3000 K

HU ZHAO[1], XINGWEN LI[1]*, ANTHONY B MURPHY[2], SHENLI JIA[1]

[1]State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University
No.28, Xianning West Road, Xi'an, Shaanxi, 710049, China
[2] CSIRO Materials Science and Engineering, PO Box 218, Lindfield NSW 2070, Australia
xwli@mail.xjtu.edu.cn

ABSTRACT

The critical reduced electric field strength $(E/N)_{cr}$ is an important parameter for the prediction of dielectric breakdown performance of SF$_6$ and its mixtures. This paper aims to analytically investigate and compare the dielectric breakdown properties of SF$_6$–N$_2$ and SF$_6$–CF$_4$ mixtures for different concentrations of SF$_6$ at 0.4 MPa and gas temperatures up to 3000 K. First, the equilibrium compositions of those gas mixtures are calculated by minimizing the Gibbs free energy under the assumptions of local thermodynamic and chemical equilibrium. Then the $(E/N)_{cr}$ of those hot gases, defined as the value for which the balance is reached between the total ionization rate coefficient and the total attachment rate coefficient, are determined by Boltzmann equation analysis. It is found that for T > 2000 K, both these mixtures have superior dielectric breakdown properties to pure SF$_6$, and $(E/N)_{cr}$ increases with decreasing concentration of SF$_6$. Unlike the cases of pure SF$_6$ and SF$_6$–N$_2$ mixtures, $(E/N)_{cr}$ in SF$_6$–CF$_4$ mixtures increases with temperature for T > 2500 K, as a result of the products of dissociation of CF$_4$, in particular CF$_2$. In addition, for the full gas temperature range considered, $(E/N)_{cr}$ in 50% SF$_6$-50% N$_2$ is clearly higher than that in 50% SF$_6$-50% CF$_4$.

1. INTRODUCTION

Due to its excellent dielectric and arc-quenching properties, SF$_6$ gas is widely used in gas-insulated switchgear and high-voltage gas circuit breakers. However, SF$_6$ gas is an extremely strong greenhouse gas (its global warming potential (GWP) is 24 000 times greater than CO$_2$ [1]), and its liquefaction temperature is relatively high at high pressure, so it is unsuitable for use at very low temperatures. Therefore, finding a substitute for SF$_6$ as an insulation and arc quenching medium is an urgent and important task. In an effort to deal with this problem, many studies have been performed on SF$_6$–CF$_4$ or SF$_6$–N$_2$ mixtures, which have much lower GWP.

A mixture of 50% SF$_6$–50% CF$_4$ has been proposed as an insulating gas for electrical apparatus [2]. In fact, this mixture has already been successfully utilized for circuit breakers installed in Manitoba [3]. CF$_4$ has many advantages, including a large electron attachment coefficient, low toxicity and relatively low cost. Its GWP is significantly lower than that of SF$_6$. Besides, CF$_4$ is widely used for materials etching in semiconductor industry and for deposition of fluorinated polymer films [4]. In addition, N$_2$ gas remains an attractive potential substitute for SF$_6$ gas, due to its inherent advantages, such as non-flammability, non-toxicity and relatively good dielectric properties [5]. Therefore, a thorough understanding of the dielectric breakdown properties of SF$_6$–N$_2$ and SF$_6$–CF$_4$ mixtures is very important.

The recent trend towards miniaturized designs exposes the hot dissociated gas in the arcing chamber to the higher electric field derived from the recovery voltage after current zero in high-voltage gas circuit breakers. This may increase the probability of gas breakdown, and consequently reduce the reliability of such circuit breakers. As a consequence, the dielectric breakdown properties of hot gases are beginning to attract strong attention.

Most previous studies of gas dielectric breakdown properties concentrated on room temperature values [6]; however, a few numerical studies were reported on dielectric

breakdown in hot gases, especially for SF_6 mixtures or substitutes. The authors have investigated the dielectric breakdown properties of SF_6–N_2 and SF_6–CF_4 mixtures at different gas pressures and gas temperatures up to 3000 K [7, 8].

This paper is devoted to the investigation and comparison of the dielectric breakdown properties in SF_6–N_2 and SF_6–CF_4 mixtures for different concentrations of SF_6, at 0.4 MPa and gas temperatures up to 3000 K. The equilibrium compositions of those gas mixtures were calculated first, by minimizing the Gibbs free energy under the assumptions of local thermodynamic and chemical equilibrium. Then, the critical reduced electric field strength $(E/N)_{cr}$, defined as the value for which the total ionization rate coefficient is equal to the total attachment rate coefficient, was obtained by two-term Boltzmann equation analysis. The results indicate that at gas temperature above 2000 K, mixtures of both SF_6–N_2 and SF_6–CF_4 have a higher value of $(E/N)_{cr}$ than that of pure SF_6, and for the full gas temperature range considered, $(E/N)_{cr}$ in 50% SF_6–50% N_2 is clearly higher than that in 50% SF_6–50% CF_4.

2. CALCULATION METHOD AND PARAMETERS

Because of the influence of increased gas temperature on the total number density, the gas composition and the energy exchange rate, the dielectric breakdown in a hot gas is different from that in a cold gas. The method for the determination of the dielectric breakdown strength in a hot gas has been introduced in the authors' previous work [7]. The value of $(E/N)_{cr}$, where E and N represent the electric field and the particle number density respectively, can be determined as that at which the total ionization rate coefficient equals the total attachment rate coefficient. This means that the number of electrons generated from collisional ionization reactions is balanced by the number of electrons disappearing through collisional attachment reactions. Because of its convenience for the case of electronegative gases, the two–term Boltzmann equation is employed to calculate the electron energy distribution function (EEDF), which is the basis for calculation of reaction rate coefficients.

2.1 Equilibrium compositions

The equilibrium compositions of SF_6–N_2 and SF_6–CF_4 mixtures at different concentrations of SF_6 and 0.4 MPa are calculated by minimizing the Gibbs free energy under the assumptions of local thermodynamic and chemical equilibrium. In present calculation, we considered 14 and 16 main species for SF_6–N_2 and SF_6–CF_4 respectively, including SF_6, SF_5, SF_4, SF_3, SF_2, SF, SSFF, FSSF, S_2, S, F_2, F, N_2 and N in SF_6–N_2, and SF_6, SF_5, SF_4, SF_3, SF_2, SF, SSFF, FSSF, S_2, S, F_2, F, CF, CF_2, CF_3, and CF_4 in SF_6–CF_4.
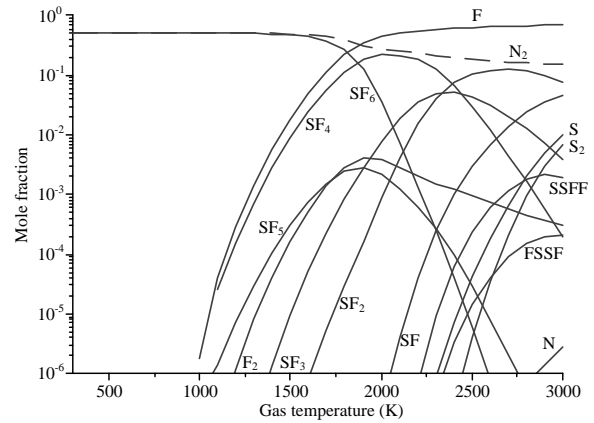

Fig. 1 Equilibrium composition of 50% SF_6–50% N_2 mixtures as a function of gas temperature at 0.4 MPa
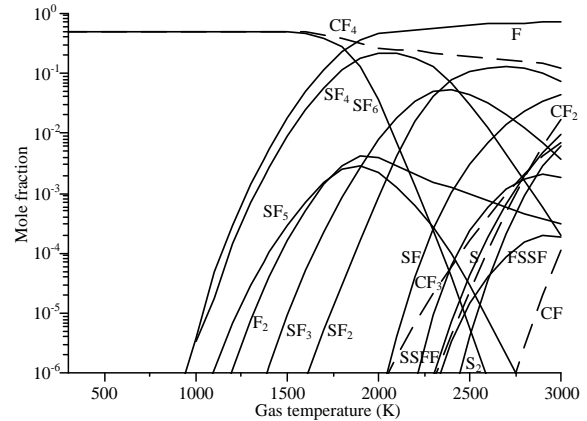

Fig. 2 Equilibrium composition of 50% SF_6–50% CF_4 mixtures as a function of gas temperature at 0.4 MPa

Figs. 1 and 2 show the composition of 50% SF_6–50% N_2 and 50% SF_6–50% CF_4 mixtures at 0.4 MPa and gas temperatures up to 3000 K. (All percentages used are mole percentages.) It can be seen that, in both cases, SF_6 molecules start to dissociate into smaller molecules or atoms from about 1000 K, and SF_4 reaches its largest mole fraction at around 1800–2200 K. Further, CF_4 starts to dissociate at about 2000 K, but almost no dissociation occurs for N_2 molecules. The dissociation reactions in the gas mixtures greatly affect their dielectric breakdown properties.

2.2 Two-term Boltzmann equation

In order to calculate the EEDF, the zero-dimensional two-term spherical harmonic approximation is adopted to simplify the Boltzmann equation. In the present calculations, all particles are assumed to be in their ground states for simplicity, and effects of collisions with vibrationally-excited molecules are neglected. We also assume that both the secondary electron and the ionizing electron have equal energies during an ionization collision. The calculations were performed using the two-term Boltzmann equation solver in the Plasma module of the commercial software COMSOL.

Collision cross sections for all species in those gas mixtures are required to solve the Boltzmann equation. However, due to the lack of collision cross section data for some species, some approximate treatments are necessary. Details for the approximations used for the unknown cross sections for the products of dissociation of SF_6 and the sources of cross section data for other species were presented in previous papers [7].

3. CRITICAL REDUCED ELECTRIC FIELD STRENGTH

Based on the parameters mentioned above, the critical reduced electric field strength $(E/N)_{cr}$ is calculated by two-term Boltzmann analysis. The cases of a 50% SF_6–50% N_2 mixture at 1000 K and 2000 K are presented as examples, Fig. 3 shows the variation of the ionization coefficient α/N and attachment coefficient η/N. For a given temperature, $(E/N)_{cr}$ corresponds to the E/N value for which ionization coefficient is equal to attachment coefficient, that is the crossover point between the α/N and η/N curves.
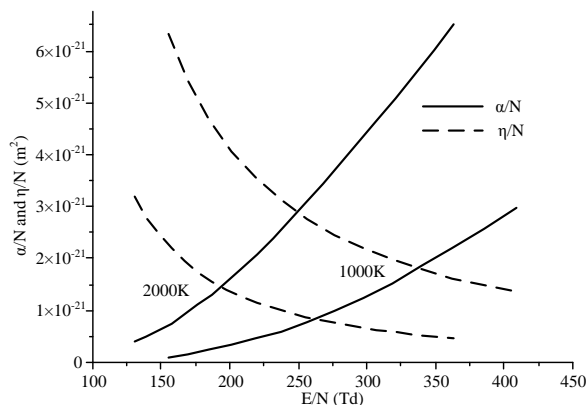
Fig. 3 Ionization and attachment coefficients as a function of E/N for 50% SF$_6$–50% N$_2$ mixture at 0.4 MPa and two temperatures

Fig. 4 and Fig. 5 respectively show $(E/N)_{cr}$ in SF_6–N_2 and SF_6–CF_4 mixtures with different concentrations of SF_6, for 0.4 MPa and gas temperatures up to 3000 K.
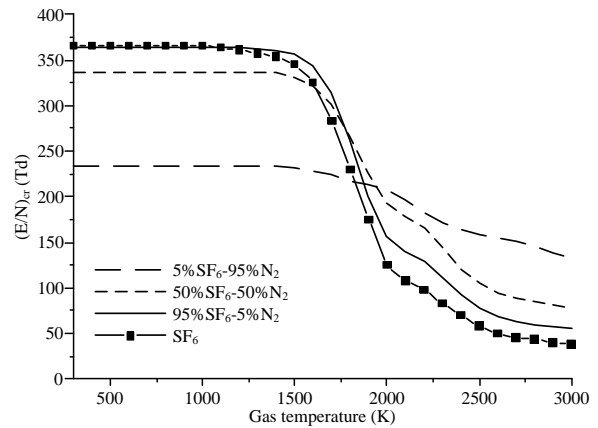
Fig. 4 (E/N)$_{cr}$ in different SF$_6$–N$_2$ mixtures as a function of gas temperature at 0.4 MPa

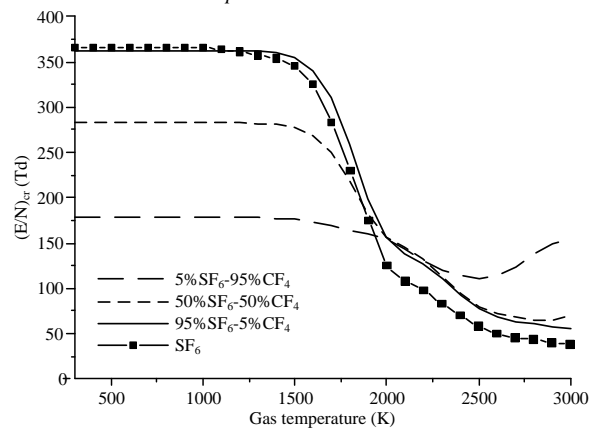*Fig. 5 (E/N)$_{cr}$ in different SF$_6$–CF$_4$ mixtures as a function of gas temperature at 0.4 MPa*

For both cases in SF_6–N_2 and SF_6–CF_4 mixtures, no temperature dependence of $(E/N)_{cr}$ for T < 1000 K is found, mainly because no dissociation occurs. At these relatively low gas temperatures, $(E/N)_{cr}$ is enhanced by increasing the concentration of SF_6. As the gas temperature increases above 1500 K, the $(E/N)_{cr}$ in all SF_6–N_2 and SF_6–CF_4 mixtures drops sharply. However, the rate of these decreases is much greater for higher concentrations of SF_6. This is mainly caused by the fast dissociation of SF_6 molecules into smaller molecules and atoms, whose dielectric breakdown performance is much lower than that of SF_6.

For comparison, the $(E/N)_{cr}$ in pure SF_6 is also calculated and plotted in Figs. 4 and 5. It can be seen that in the gas temperature range from around 2000 K to 3000 K, $(E/N)_{cr}$ in SF_6–N_2 and SF_6–CF_4 mixtures is enhanced greatly by decreasing the concentration of SF_6, and the $(E/N)_{cr}$ values are all higher than for pure SF_6. The main reason for this is the greater

dissociation of SF_6 compared to N_2 and CF_4 molecules. As mentioned above, N_2 hardly dissociates for gas temperatures below 3000 K and CF_4 molecules start to dissociate from about 2000 K. At T > 2000 K, the concentration of F atoms is much larger than that of other species, and its dielectric breakdown property is relatively poor. N_2 has large vibrational excitation cross sections, which effectively reduce the number of high-energy electrons by frequent vibrational excitation reactions. CF_4 is an electronegative gas, and electrons can attach to CF_4 molecules by attachment collision reactions. Another notable point is that at temperatures above 2500 K, unlike the cases of pure SF_6 and SF_6–N_2 mixtures, $(E/N)_{cr}$ in SF_6–CF_4 mixtures increases with temperature, as a consequence of the products of dissociation of CF_4, in particular CF_2, whose attachment cross section is larger than that of CF_4.
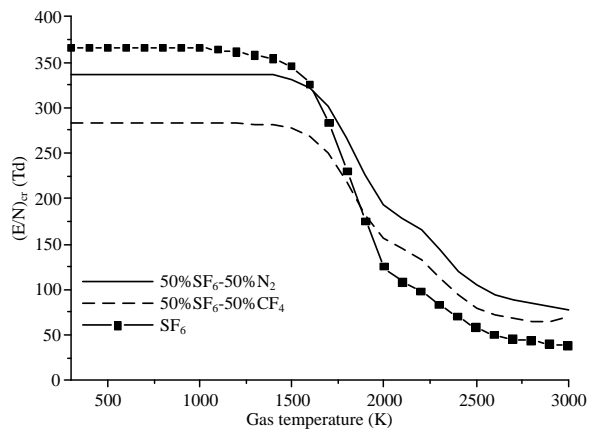

Fig. 6 Comparison of the $(E/N)_{cr}$ in 50% SF_6-50% N_2 and 50% SF_6-50% CF_4 mixtures at 0.4 MPa

Fig. 6 directly compares the $(E/N)_{cr}$ values of 50% SF_6–50% N_2 and 50% SF_6–50% CF_4 mixtures at 0.4 MPa. $(E/N)_{cr}$ has similar trends in both gas mixtures, however, $(E/N)_{cr}$ of 50% SF_6–50% N_2 is clearly higher than that of 50% SF_6–50% CF_4 for the full temperature range.

4. CONCLUSIONS

The dielectric breakdown properties of SF_6–N_2 and SF_6–CF_4 mixtures for different concentrations of SF_6 at 0.4 MPa and gas temperatures up to 3000 K were investigated numerically by Boltzmann equation analysis. First, the equilibrium compositions of SF_6–N_2 and SF_6–CF_4 mixtures were calculated by minimizing the Gibbs free energy under the assumptions of local thermodynamic and chemical equilibrium. Then based on those data,

values of $(E/N)_{cr}$, at which the balance is reached between the total ionization rate coefficient and the total attachment rate coefficient, of the gas mixtures were determined. Through the studies presented in the paper, the following conclusions could be drawn:

1) At gas temperatures above 2000 K, both the SF_6–N_2 and the SF_6–CF_4 mixtures have higher values of $(E/N)_{cr}$ than that in pure SF_6, and $(E/N)_{cr}$ increases with decreasing concentration of SF_6.

2) At gas temperatures above 2500 K, unlike the cases of pure SF_6 and SF_6–N_2 mixtures, the $(E/N)_{cr}$ of SF_6–CF_4 mixtures increases with temperature, as a consequence of the properties of the products of dissociation of CF_4, in particular CF_2.

3) At all the gas temperature range considered, $(E/N)_{cr}$ of 50% SF_6–50% N_2 is clearly higher than that of 50% SF_6–50% CF_4.

REFERENCES

[1] L. Christophorou, J. Olthoff and R. Brunt, "Sulfur hexafluoride and the electric power industry," IEEE Electr. Insul. Mag., 13, 20-24, 1997.

[2] C. Pradayrol, A. Casanovas, A. Hernoune and J. Casanovas, "Spark decomposition of SF_6 and SF_6+50%CF_4 mixtures," J. Phys. D: Appl. Phys., 29, 1941-1951, 1996.

[3] X. Liu and D. Xiao, "Monte Carlo simulation of electron swarm parameters in the SF_6/CF_4 gas mixtures," Jpn. J. Appl. Phys., 46, 1663-1667, 2007.

[4] T. W. Pi, M. Huang, W. Lee, L. Chu, T. Lin, T. Chiang, et al, "High-resolution core-level photoemission study of CF_4-treated Gd_2O_3 (Ga_2O_3) gate dielectric on Ge probed by synchrotron radiation, " Appl. Phys. Lett., 98, 062903, 2011.

[5] M. S. Dincer, O. C. Ozerdem and S. Bektas, "Effective ionization coefficients and transport parameters in ultradilute SF_6+N_2 mixtures," IEEE Trans. Plasma Sci., 35, 1210-1214, 2007.

[6] H. S. Uhm, E. H. Choi, G. Cho and H.-Y. Ryu, "Breakdown temperature of electrons in SF_6 gas," Appl. Phys. Lett., 97, 161501, 2010.

[7] H. Zhao, X. Li, S. Jia and A. B. Murphy, "Dielectric breakdown properties of SF_6–N_2 mixtures at 0.01–1.6 MPa and 300–3000 K," J. Appl. Phys., 113, 143301, 2013.

[8] X. Li, H. Zhao, S. Jia and A B Murhphy, "Study of the dielectric breakdown properties of hot SF_6–CF_4 mixtures at 0.01–1.6MPa, " J. Appl. Phys., 114, 053302, 2013.