Breakdown Electric Field of Hot 30% CF$_3$I/CO$_2$ Mixtures at Temperature of 300–3500 K During Arc Extinction Process*

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Abstract We calculated the uniform dielectric breakdown field strength of residual 30% CF$_3$I/CO$_2$ gas mixtures during the arc extinction process over the temperature range 300–3500 K at 0.1 MPa. The limiting reduced field strengths are decided by a balance of electron generation and loss based on chemical reactions estimated by the electron energy distribution function (EEDF), which employs the Boltzmann equation method with two-term expanding approximation in the steady-state Townsend (SST) condition. During the insulation recovery phase, the hot CF$_3$I/CO$_2$ gas mixtures have maximum dielectric strength at a temperature of about 1500 K. At room temperature 300 K, the electric strength after arc extinction (90.3 Td, 1 Td=10$^{-21}$ V·m$^2$) is only 38% of the original value before arc (234.9 Td). The adverse insulation recovery ability of CF$_3$I/CO$_2$ gas mixtures in arc extinction hinders its application in electric circuit breakers and other switchgears as an arc quenching and insulating medium.

Keywords: limiting electric field strength, electron swarm parameters, Boltzmann equation, hot CF$_3$I/CO$_2$ gas mixtures

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(Some figures may appear in colour only in the online journal)

1 Introduction

Because of its good thermal and electric properties as insulation media, sulfur hexafluoride (SF$_6$) is widely utilized in gas circuit breaker (GCB) and gas insulated substation (GIS) in the electric power industry [1]. However, SF$_6$ gas has been listed among the 6 controlled global warming gases in 1997 and its use will be forbidden in 2020 according to the Kyoto protocol due to its potential influence on the global warming effect [2]. The WMO (World Meteorological Organization) has recently published the Greenhouse Gas Bulletin, which shows that the current mole fraction of SF$_6$ is about twice the level observed in the mid-1990s in the atmosphere. To deal with this problem, studies have been made on SF$_6$ gas mixtures attempting to reduce its influence on the global environment [3–5]. A more radical solution is to search for a new insulation gas to completely substitute SF$_6$ [6,7].

Generally, trifluoroiodomethane (CF$_3$I) is a nontoxic, nonflammable, odorless and colorless gas with an overall lifetime in atmosphere of less than 2 days. Thus CF$_3$I presents a GWP as low as 1 to 5 times of that of CO$_2$ without significant harm to ozone depletion [7]. Research works have revealed that the insulation strength of pure CF$_3$I is 1.23 times higher than that of pure SF$_6$ [8]. Considering its high boiling point, CF$_3$I/CO$_2$ gas mixtures with 30% CF$_3$I ratio, which has about 0.85 times insulation performance of SF$_6$ [9], have shown good comprehensive properties as insulation gas in electric power apparatus. Japanese researchers even pointed out that the interruption capability of the 30% CF$_3$I/CO$_2$ mixtures is comparable to that of the pure SF$_6$ [10]. Further investigations from other aspects as gaseous arc quenching media are urgent.

There have been relative studies on the application potential of CF$_3$I/CO$_2$ gas mixtures in electrical switchgears. Y Cressault et al. were devoted to the theoretical calculation of equilibrium compositions, thermodynamic properties and transport coefficients of CF$_3$I mixtures with air, CO$_2$ and N$_2$ [11]. H Kasuya et al. investigated the arc quenching capability and decomposed gas density of CF$_3$I/CO$_2$ mixtures, and then pointed out that CF$_3$I/CO$_2$ at CF$_3$I ratio 30% can be considered in GCB application [12]. M Taki et al. studied the quenching performance of CF$_3$I gas with a model arc-extinguishing chamber and evaluated the Short Line Fault (SLF) interruption capability [13].

Generally, arc extinction of short current in GCB must undergo 2 processes. The first phase is thermal recovery within several milliseconds affected mainly by energy equilibrium, and the other is

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insulation recovery after the arc extinguishing process affected mainly by the appearance and loss of charged particles. The thermal gas mixtures in GCB after current zero, with complex species components arisen from a series of dissociation and compound reactions, will result in an easier electrical breakdown, which is among the major concerns to assess the arc quenching performance of a gas. However, little published research can be found about the insulation strength of thermal CF$_3$I/CO$_2$. The present paper investigated the dielectric characteristics of hot CF$_3$I/CO$_2$ in the dielectric recovery phase of the arc interruption. Due to the size reduction restraint of GCB and GIS, the thermal gas at this phase is exposed to high and extreme electrostatic fields, which leads to an undesirable loss of reliability. To get a better understanding of the reluctant gas breakdown, we calculate the uniform dielectric breakdown field strength of hot 30% CF$_3$I/CO$_2$ mixtures during insulation recovery in the arc extinction process over a temperature range of 300–3500 K. Besides, the electron swarm parameters before and after arc at room temperature are also compared.

2 Particle constituents of thermal gas

A successful current thermal break for electric circuit breaker could reduce the temperature of the electric arc to 3500 K after the thermal recovery process. Thus our study at the insulation recovery phase concentrates on the temperature range from 3500 K to ambient temperature 300 K. Different from CF$_3$I/CO$_2$ mixtures at room temperature, gas mixtures at this condition have dissociated to particles of different constituents, which will substantially affect the EEDF and chemical reaction dynamic. These insulation characteristics are related to the collision cross section between electrons and particles. In the arc decaying process after current zero, equilibrium compositions of 30%CF$_3$I/70%CO$_2$ gas mixtures at 0.1 MPa are calculated in Ref. [14] in the temperature range from 300 K to 3500 K based on the Gibbs free energy minimization. The molar fraction of each particle has been transformed from the number density-temperature curves [14]. The mole proportion of each component mainly depends on the pressure and temperature of the gas condition (see Fig. 1).

3 Theoretical framework

3.1 Boltzmann equation method

The accuracy of the theoretical derivations based on the numerical solutions depends on the adopted technique [15–17]. The conventional two-term expansion method of the EEDF in spherical harmonics has been testified to give adequate accuracy in the condition of small anisotropies of EEDF and little effect from inelastic collision processes [18,19]. As for electronegative gases including CF$_3$I and CO$_2$, electrons will be attached to gas molecules in attachment collision reactions. Therefore, the Boltzmann equation is especially nonlinear, which needs iteration methods to solve. In this case, the derivation of electron swarm parameters and rate coefficients requires to be appropriately justified. Nevertheless, it has to be emphasized that the accuracy of the two-term spherical harmonic expansion can be guaranteed only in the intermediate and low ranges of reduced electric field strength $E/N$, and it could hardly illustrate the highly anisotropic electron energy distribution [20]. A brief introduction of the calculation is given below [21].

In the SST experiment, the Boltzmann equation describes the evolution of a distribution function, $f$, as

$$
(\alpha - \eta)\cos \theta f + a(\cos \theta \frac{\partial f}{\partial v} - \sin \theta \frac{\partial f}{\partial \theta}) = C[f(r,v,t)],
$$

(1)

where $\alpha$ and $\eta$ are respectively the ionization and the attachment coefficients, $\theta$ is the angle between the inverse direction of the electric field $E$ and the velocity $v$, $f$ is the electron velocity distribution function (EVDF), $a=eE/m$ is the electron acceleration under the force of electric field, $C[f(r,v,t)]$ is the general collision operator, and $r$ is the electron spatial position.

To solve the Boltzmann equation and thus obtain the value of EVDF, drastic simplifications are necessary. A classical approach is to expand the distribution function $f$ in spherical harmonics. If the EVDF can be assumed almost spherically symmetric, the series can be truncated after the second term. So $f$ takes the form as

$$
f(v, \theta) = f_0(v) + f_1(v)\cos \theta,
$$

(2)

where $f_0$ and $f_1$ are respectively the isotropic and the anisotropic parts of $f$. Replacing Eq. (3) with Eq. (2),

$$
\frac{1}{3}(\alpha - \eta)v f_1 + \frac{1}{3} \frac{eE}{mv^2} \frac{\partial}{\partial v} (v^2 f_1) = \frac{m}{M} \frac{\partial}{\partial v} \left( v^4 Q_m f_0 \right)
$$

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+ ∑_j N v^2 f_0(v_j) e^{-\Delta v Q_e(v_j) f_0(v_j)} + \frac{N v^2 f_1(v)}{1 - \Delta v} Q_i(v_1) f_0(v_1).
\]

\[ \alpha = 3N \int_0^\infty Q_a(\varepsilon) f_0(\varepsilon) d\varepsilon \left[ \int_0^\infty \varepsilon f_1(\varepsilon) d\varepsilon \right]^{-1}, \quad (6)
\]

\[ \eta = 3N \int_0^\infty Q_a(\varepsilon) f_0(\varepsilon) d\varepsilon \left[ \int_0^\infty \varepsilon f_1(\varepsilon) d\varepsilon \right]^{-1}. \quad (7)
\]

The new value of \((\alpha - \eta)\) is submitted in Eqs. (3) and (4) again, and the values of \(f_0\) and \(f_1\) are justified.

d. Repeat the proceeding a to c until we achieve an adequate convergence for the \(n\)-th effective ionization coefficient \(\alpha_n = [(\alpha - \eta)_n].\) The terminated relaxation is to meet the condition \(|(\alpha_n - \alpha_{n-1})/\alpha_n| \leq 10^{-4}\.\]

e. The electron transport coefficients such as the drift velocity \(V_e\) and the mean energy \(\varepsilon\) are derived from the determined \(f_0\) and \(f_1\).

\[ V_e = - \frac{eE}{3N} \sqrt{\frac{2}{m}} \int_0^\infty \varepsilon f_0(\varepsilon) d\varepsilon \left[ \frac{\varepsilon}{Q_m} \right], \quad (8)
\]

\[ \varepsilon = \int_0^\infty \varepsilon^2 f_0(\varepsilon) d\varepsilon, \quad (9)
\]

where \(Q_m = Q_m + \sum_j Q_e + Q_i + Q_a\) represents the total effective electron collision cross section for momentum transfer. As for gas mixtures, \(Q_m = \sum_k k_{n,m} Q_m\) and \(k_{n}\) is the mixing fraction of each gas.

### 3.2 Electron collision cross sections

In this work, we assume the gas density \(N\) as \(3.29 \times 10^{22} \text{ m}^{-3}\) in the condition of gas pressure 133.3 Pa and temperature 20°C. Due to the low pressure and the low ionization degree, the three-body collisions, as well as the Coulomb interaction between charged particles, are neglected.

Generally, relative data on \(76.3/79.7\) breakdown electric field at ambient temperature have been reported in the literatures \([22,23]\). However, the hot residual gases are very sparse in the published literature. The dielectric properties for thermal residual \(76.3/79.7\) mixtures particularly need complete data of the electron collisions cross sections for various by-products. In fact, there are 12 species of particles involved in the hot residual gas. The collision cross sections of all species could not be found in the published literatures. Complete cross sections are limited to reactions of \(e/CO_2, e/CF_4, e/CO, e/I_2, e/I, e/F, e/O_2\) and \(e/O\) \([24-29]\). Collision cross sections of reactions between electron and \(COF_2, IF, IO\) and \(OF\) have not been found completely in the literatures. Considering their physical and chemical properties, they are supposed to have similar cross sections respectively with \(CF_4, F_2, I_2\) and \(O_2\) \([25]\). The data sources of reaction collision cross sections are listed in Table 1.

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<tr>
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### 4 Results and discussion

After arc extinction of zero current, the limiting electric field strength of thermal residual plasma or thermal gas is different from that in room temperature. On one hand, particles have made a series of dissociated reactions, and thus the gaseous constituents have changed in the condition of high temperature. On the other hand, the rising temperature changes the energy property and dielectric strength of gas mixtures. This section shows the statistical relation between dielectric recovery strength and temperature of thermal \(76.3/79.7\) gas mixtures over insulation recovery phase during the arc extinction process.

#### 4.1 The dielectric breakdown field strength at different temperatures

The limiting breakdown field strength corresponds to the condition where the electron generation exactly
balances the electron loss. All the chemical dynamics relating to electron generation and loss are considered in the theoretical derivation, including elastic, vibration and excitation, ionization and attachment reactions. The interaction rates are derived from EEDF, which requires electron-molecule cross sections as import data.

Fig. 2 shows the elevated heavy-particle temperatures on EEDF in residual CF$_3$I/CO$_2$ gas mixtures at $E/N$=150 Td and 0.1 MPa. After a series of dissociation and combination reactions during the electric arc, the various constituents of gas mixtures result in different EEDF curves.

Seen from Fig. 2, despite various constituents at different temperatures, the general decreasing trends of EEDF with increasing electron energy are similar. At low electron energy below 20 eV, EEDFs at different temperatures show a relatively small difference, the maximum values of which focus on 0.15–0.30 eV$^{-3/2}$. However, the EEDF does not change consistently with temperature. In the temperature range of 3500–1500 K, the value of EEDF decreases with decreasing temperature. This phenomenon is ascribed to the significantly various amount of electron-attachment particles at different temperatures, including I, O$_2$, IF, O and F atom. In the condition of a lower temperature below 1500 K, it improves with decreasing temperature, which is attributed to the increasing ratio of electronegative gases CF$_4$ and I$_2$. The EEDFs at 1500 K to 2000 K reach the minimum because of the highest fraction of electronegative particles, which effectively hinders the drifting motion of electrons. Thus the residual 30% CF$_3$I/CO$_2$ gas mixtures are estimated to have the best electrical property and insulation strength at the temperature between 1500 K and 2000 K.

Townsend ionization coefficient $\alpha$ represents the number of electron-ion pairs generated in an inelastic collision between electron and neutral particle in a unit distance of the electrode gap. In electronegative gas, if the ionization collision balances the electron attachment, which is to say the ionization coefficient $\alpha$ and the attachment coefficient $\eta$ are equal, discharge occurs in a uniform electric field. According to the EEDF of residual gas mixtures, we have calculated normalized coefficient $\alpha/N$ and $\eta/N$ related to field strength $E/N$ at different temperatures in 0.1 MPa, as shown in Fig. 3.

![Fig. 3](image_url) Density-normalized ionization $\alpha/N$ and attachment coefficients $\eta/N$ as a function of $E/N$ at different temperatures

According to the results of ionization and attachment coefficients, Fig. 4 shows the limiting reduced field $(E/N)_{lim}$ at $(\alpha-\eta)/N=0$ as a function of temperature $T$ from 300 K to 3500 K. It is noted that the breakdown electric field strength does not vary consistently with temperature. The peak of the value is reached at the temperature of about 1500 K. This corresponds to the EEDF in Fig. 2 which decreases down to the minimum value at 1500 K. At higher temperature, elements with strong electronegativity including F, I and O tend to exist as single-atom particles. In fact, a single-atom molecule generally has a much worse electrical property than a polyatomic particle. For example, molecular iodine I$_2$ has an obvious electron-attachment ability, while the electronegativity of atom iodine I can be neglected. So despite an abundant amount, the contribution of atomic fluorine to the gas dielectric strength at these temperatures is limited. The slightly elevated dielectric strength from 3000 K to 3500 K is mainly ascribed to the electron attachment effect of O$_2$ over a large range of electron energy [24,25]. On the
other hand, when gas temperature reduces below 1000 K, fluorine element gradually combines to CF$_4$ which has an attachment collision cross sections value at least 2 orders of magnitude lower than IF$^-[24,25]$. Additionally, CO$_2$ makes the proportion of over 80% of the total gas mixtures. The limiting field strengths of pure CO$_2$ and CF$_4$ are respectively as low as 90 Td and 140 Td$-[31,32]$, which explains the weak uniform breakdown field strength at low temperature. When $E/N$ is lower than 500 K after arc extinction, CO$_2$ gas plays such an important role that the breakdown electric field strength of the residual gas mixtures approximately equals to that of pure CO$_2$.

4.2 Comparison of breakdown field strength before and after electric arc

To some degree, the wide application SF$_6$ in switching apparatus is attributed to its recombination reaction during the thermal and insulation recovery phases$-[33-36]$, other than the inertness in extremely high temperature during the arc process. The electrical and physical characteristics recover to the best state after each arc, so that SF$_6$ gas can withstand many times of arc process as arc quenching media. As for CF$_3$I/CO$_2$ gas mixtures, however, the dissociated gas during the electric arc does not totally recombine to its original composition in room temperature. The breakdown field strength before and after arc distinguishes from each other substantially. The effective ionization coefficient after arc experiences a lower value than that before arc over the whole range of $E/N$. The calculation of the limiting field strength before arc agrees reasonably with the previous result 229.1 Td made by Zhao Hu et al.$-[37]$ and 232.3 Td by Li Xingwen et al.$-[38]$. After arc extinction at 300 K, CO$_2$, CF$_4$ and CO compose more than 95% molar fraction of the whole residual gas, among which CO$_2$ and CF$_4$ have a weak electronegative effect, while CO does not have an electron-attachment capability at all. So the insulation performance of the total gas mixtures reduces significantly to the field strength magnitude of pure CO$_2$. So the key reason for the reduction of breakdown field strength is that the dissociated gases can hardly recombine to the original CF$_3$I gas which has excellent dielectric characteristics.

From the view of electron swarm parameters, the high effective ionization coefficient over the whole $E/N$ range is ascribed to the high electron drift velocity $v_e$ and mean electron energy $\varepsilon$ when comparing to that before arc (see Figs. 6 and 7). Only at low $E/N$ value below 60 Td, is the mean electron energy after arc extinction lower than that before the arc. High velocity and energy of electrons will improve the effective ionization collision, and at the same time reduce the attachment rate. Because electron-attachment reactions with molecules are observed generally for electrons with low energy below 10 eV, while the threshold energy for ionization reaction is usually over 10 eV$-[24]$. Thus high electron drift velocity and mean energy facilitate effective ionization collision and hinder the electron affinity process, which leads to a lower breakdown voltage.
5 Conclusion

The present paper is devoted to the theoretical derivation of the breakdown field strength of hot 30% CF$_3$I/CO$_2$ gas mixtures during the arc extinction process for large temperatures (300–3500 K) at 0.1 MPa. The electron swarm parameters are calculated utilizing a two-term Boltzmann equation solution. The limiting electric field ($E/N)_{lim}$ reaches a peak at a temperature of about 1500 K. At lower temperature, ($E/N)_{lim}$ is decreased by the dissociated single atom at higher temperature and by a combination of CO$_2$ and CF$_3$ with relatively bad electrical property. At room temperature 300 K, the breakdown field strength after arc extinction (90.3 Td) is only 38% of the original electric strength before arc (234.9 Td). Therefore, CF$_3$I/CO$_2$ gas mixtures can hardly recover the electrical characteristics during the arc extinction process, which hinders its application in GCB as an arc quenching and insulating medium. Further researches are urgent to make adjustment such as gas components or mixture ratio in order to avoid this aspect of defect applied in switching apparatus.

In this paper, we attempt to provide an accurate idea on the usefulness of CF$_3$I/CO$_2$ gas mixtures in the high-voltage GCB and GIS, and calls for attention to the insulation performance of residual gas mixtures after arc besides the arc process when searching for new potential arc quenching gaseous media. The process of theoretical derivation also shows the interesting relation between a basic researching study on the electron interaction and a particular application to the gas current interruption behavior during the dielectric recovery phase.

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