Influence regularity of O₂ on dielectric and decomposition properties of C₄F₇N–CO₂–O₂ gas mixture for medium-voltage equipment

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Abstract: Fluorinated nitrile (C₄F₇N) gas mixture has been introduced as the most promising candidate to replace sulfur hexafluoride using in gas-insulated equipment. In this study, the authors explored the influence of oxygen on the dielectric and decomposition properties of C₄F₇N–CO₂–O₂ gas mixture. The authors found that the dielectric strength of the C₄F₇N–CO₂–O₂ gas mixture with 2, 4, 6, 8 and 10% O₂ was increased by 4.85%, 6.49%, 7.70%, 3.21% and 2.74% compared with C₄F₇N–CO₂. The addition of 2–6% O₂ to the C₄F₇N–CO₂ gas mixture could effectively reduce the content of most of the decomposition by-products such as CF₄, CO, CF₂F₆, CF₂F₅, CF₂F₃CN, CF₂F₂CN, (CN₂). While high content of oxygen (>6%) results in higher decomposition of C₄F₇N, which has a negative effect on the stability of C₄F₇N gas mixture. Generally, it is recommended to add 2–6% O₂ in the C₄F₇N–CO₂ gas mixture to improve its insulation properties as well as inhibit the decomposition of C₄F₇N in the discharge for medium-voltage engineering application.

1 Introduction

Sulfur hexafluoride (SF₆) is currently widely used in gas-insulated transmission and distribution network in the power industry due to its great insulation and switching characteristics [1–4]. SF₆ is a strong greenhouse gas with the global warming potential (GWP) of 23,500 and atmospheric lifetime of 3200 years [5–7]. It is reported that about 80% SF₆ produced worldwide goes to power industry [8]. In order to reduce the negative impact of SF₆ on the environment, political developments like the Paris treaty or the coming revision of the European F-gas directive in 2020 indicate that stricter regulations for the application of F-gases (including SF₆) might be expected in the future [9]. Thus, seeking for an eco-friendly gas insulating medium has become a hot topic.

Among all kinds of SF₆ alternatives investigated, the fluorinated nitrile (C₄F₇N) has been recognised as the potential solution. The dielectric strength of pure C₄F₇N is approximately twice that of SF₆ [10, 11]. However, C₄F₇N has high boiling temperature (~4.7°C) and should be used as the additive to CO₂, N₂ to avoid the liquefaction of gas at low ambient temperatures. It was reported that the gas mixture with 4, 6, 10% C₄F₇N would be suitable for −30, −25 and −10°C minimum operating temperature high-voltage (HV) gas-insulated equipment (GIE). In addition, the GWP values of these gas mixtures are 327, 462 and 690, respectively, which is only 2–3% of that of SF₆ [11]. The LC50 (rats, 4 h) of 10% C₄F₇N–90% CO₂ gas mixture is in the range of 95,500 ppm (μL/L)–100,000 ppm, which belongs to the no toxic substance according to relevant EU regulations [11].

Over the past three years, extensive studies have been made on insulation properties [12–17], decomposition characteristics [18–24], material compatibility [25–27] and arc quenching properties [28–30] of C₄F₇N gas mixture, confirming that it has the potential to be used in GIE. Also, CO₂ is mostly chosen as the buffer gas because of its superior arc quenching performance and strong cooperative effect with C₄F₇N. As for medium-voltage (MV) application, Zhang et al. studied the breakdown strength and partial discharge (PD) characteristics of C₄F₇N–CO₂ and SF₆ under AC voltages. It was found that 15% C₄F₇N–85% CO₂ gas mixture has an equivalent dielectric strength to SF₆ at 100 kPa. In non-uniform and highly non-uniform fields, SF₆ exhibits higher dielectric strength than 20% C₄F₇N–80% CO₂ mixture. The PD analysis also suggests that SF₆ has much more PDs with lower magnitude and the 20% C₄F₇N–80% CO₂ mixture has fewer PDs but with higher magnitude [14]. Relevant results confirm that C₄F₇N–CO₂ has the potential for being used in MV equipment to replace pure SF₆.

In addition, it is reported that oxygen (O₂) should be added to the mixture as a second additive gas to improve the switching performance of C₄F₇N gas mixture for HV application such as HV-GIS [31, 32]. Meyer and Kieffel explored the C₄F₇N–CO₂–O₂ using as a current interruption medium in GIS circuit breaker. The current interruption behaviour of the 6% C₄F₇N–5% O₂–89% CO₂ gas mixture was investigated via a sequence of breaking tests at 40 kA (T100) on 145 kV, 450 kA GIS circuit breaker. It was also reported that the addition of O₂ could avoid carbon deposit on insulators during the breaking operation and help to recombine the generated CO back to CO₂ for HV GIE [32, 33]. However, there are few reports on the influence mechanism of oxygen on the insulation and decomposition properties of C₄F₇N–CO₂–O₂ gas mixture for MV GIE at present. The MV GIE such as gas-insulated cabinet, ring main units has the operation pressure in the range of 0.1–0.14 MPa (absolute pressure) [34]. Thus, the C₄F₇N content in the gas mixture could be higher than that of HV GIE, making it possible to replace pure SF₆. On one hand, the addition of oxygen may affect the insulation characteristics of C₄F₇N–CO₂–O₂ gas mixture such as the breakdown voltage. On the other hand, the gas stability and decomposition properties of C₄F₇N–CO₂–O₂ gas mixture would also be affected considering the strong oxidation of oxygen itself. In addition, the optimum oxygen addition content is also missing for MV GIE engineering application.

In this paper, we explored the insulation and decomposition characteristics of C₄F₇N–CO₂–O₂ gas mixture for MV application comprehensively. The AC breakdown voltage of C₄F₇N–CO₂–O₂ gas mixture with different oxygen content was tested first. Then the gas composition of the gas mixture after the breakdown was detected and analysed based on the gas chromatography-mass spectrometry (GC-MS). The influence mechanism of oxygen on the decomposition properties of the gas mixture was discussed and
2. Test platform

2.1 Test platform

Fig. 1 gives the schematic diagram of the AC breakdown properties test platform. The voltage regulator (0–380 V) is used to control the voltage applied to the electrodes. The resistor is used to limit the current in the circuit after breakdown to protect the whole devices. The capacitive voltage divider could measure the actual HV applied to the electrodes. The cylinder gas chamber with 30 L volume made of stainless-steel could withstand the gas pressure at 150°C of the proposed pathway was searched using the Perdew–Burke–Ernzerhof (PBE) method [36]. Also, the total pressure of the gas mixture is kept at 0.14 MPa for the minimum operating temperature at −25°C. It should be noted that C₄F₇N plays a major role in the insulation performance of the gas mixture due to its high dielectric strength.

2.2 Test method

The gas chamber is first cleaned using anhydrous alcohol to remove impurities and then filled with CO₂ (99.999%) to 0.3 MPa. The gas chamber is pumped to 0 MPa using the vacuum pump and filled with CO₂ again for three times. Also, the C₄F₇N–CO₂–O₂ gas mixture is finally injected to the gas chamber to 0.14 MPa (absolute pressure) for AC breakdown tests. The selection of 0.14 MPa as the gas pressure in the experiment meets the working pressure conditions of the MV equipment. According to reference [35], the content of C₄F₇N in the gas mixture should be <18% at 0.2 MPa for the minimum operating temperature at −25°C. It should be noted that C₄F₇N plays a major role in the insulation performance of the gas mixture due to its high dielectric strength. Thus, we carried out breakdown tests for gas mixture with 15% C₄F₇N. The content of oxygen added in the C₄F₇N gas mixture is set to 2, 4, 6, 8 and 10%, as shown in Table 1.

The HV was added across the sphere electrodes using the step-voltage method and the transient breakdown voltage is recorded as the AC breakdown voltage of the gas mixture. AC breakdown tests for each group of the gas mixture are carried out for 100 times and the gas sample was analysed after every 20 breakdown.

The single ion monitoring (SIM) and SCAN methods were used to analyse the composition of the gas mixture. Table 2 gives the characteristic mass-to-charge ratios of main decomposition by-products of C₄F₇N gas mixture, where bold type m/z is chosen as the target particle. The qualitative analysis of the by-products is carried out based on the standard gas, National Institute of Standards and Technology (NIST 14.0) database. In addition, the quantitative analysis is conducted based on the external standard method for CF₃, C₂F₅, C₂F₆, C₂F₇, CO and peak area integral method for CF₃CN, C₂F₅CN, COF₂, (CN)₂ due to the reason that the standard gas for these by-products are not applicable at present.

The heat program of the column is given as follows: first, keep the column at 32°C for 7 min. Then the column is heated to 150°C with the temperature increase rate of 60°C/min. Finally, the column is kept at 150°C for 2 min. Fig. 2 shows the gas chromatogram of 15% C₄F₇N–85% CO₂ gas mixture after 20 numbers of AC breakdown discharge. It can be found that the characteristic peak of CF₃CN, C₂F₅CN, COF₂, (CN)₂ exists, confirming that the column and heat program applied is reasonable.

2.3 Theoretical method

In order to explore the decomposition mechanism of C₄F₇N under the oxygen environment, we conducted DFT calculations to obtain the energy and reaction enthalpy of the proposed pathways. Geometry optimisation and harmonic frequency calculations were performed based on the generalised gradient approximation with the Perdew–Burke–Ernzerhof (PBE) method [36]. Also, the double numerical plus polarisation is chosen as the basis set. The transition state (TS) of the proposed pathway was searched using linear synchronous transit and quadratic synchronous transit (LST-
3 Results and discussion

3.1 Influence of oxygen on the breakdown voltage of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture

Fig. 3 gives the AC average breakdown voltage of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture under different $\text{O}_2$ content conditions. We defined the average value of the first to tenth test results as the AC average breakdown voltage of the gas mixture. It can be found that the AC average breakdown voltage of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture increases with the oxygen content $\gtrsim 6\%$ first and then decreases. The dielectric strength of the $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture with 2, 4, 6, 8 and 10% oxygen was increased by 4.85, 6.49, 7.70, 3.21 and 2.74%, compared with that of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2$ gas mixture (28.06 kV).

Actually, the relative critical reduced electric field strength ($E/N$)$_{\text{rel}}$ of $\text{CO}_2$ and $\text{O}_2$ to $\text{SF}_6$ is 0.23 and 0.33 [8], indicating that $\text{O}_2$ has greater dielectric strength than that of $\text{CO}_2$. Thus, the breakdown voltage of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture increases with the increase of $\text{O}_2$ content (the decrease of $\text{CO}_2$ content). The breakdown voltage of the gas mixture shows a decreasing trend when the $\text{O}_2$ content is $\gtrsim 6\%$, which may be due to the decomposition of $\text{C}_2\text{F}_7\text{N}$ considering the oxidation reactions.

3.2 Influence of oxygen on the decomposition properties of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture

3.2.1 Variation feature of $\text{CF}_4$, $\text{CO}$, $\text{C}_2\text{F}_6$, $\text{C}_2\text{F}_7$ and $\text{C}_3\text{F}_8$. Generally, arc plasma generated by discharge will lead to complex physical and chemical reactions, which could result in the decomposition of gas molecules and the generation of several by-products. In order to understand the influence of oxygen on the discharge decomposition properties of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture, we conducted repeated AC breakdown tests and analysed the gas in the chamber based on GC-MS.

Fig. 4 shows the content of $\text{CO}$, $\text{CF}_4$, $\text{C}_2\text{F}_6$, $\text{C}_2\text{F}_7$ and $\text{C}_3\text{F}_8$ for $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture after repeated AC breakdown tests. It can be found that the yield of $\text{CF}_4$ ranks the top among all the quantitative products, followed by $\text{CO}$, $\text{C}_2\text{F}_6$, $\text{C}_2\text{F}_7$ and $\text{C}_3\text{F}_8$. The content of $\text{C}_3\text{F}_8$ is the lowest. In addition, the yield of $\text{CO}$, $\text{CF}_4$, $\text{C}_2\text{F}_6$, $\text{C}_2\text{F}_7$ and $\text{C}_3\text{F}_8$ increases with the breakdown number, confirming that the discharge could cause continuous decomposition of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture.

Fig. 5 gives the variation feature of $\text{CF}_4$ under different oxygen conditions. In this paper, we defined an effective formation rate (EFR) to reveal the influence of oxygen on the decomposition characteristic of $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture. Its definition formula is given as follows: (see (1)), where $V_p$ is the EFR, $V_{20}$, $V_{40}$, $V_{60}$ and $V_{100}$ represent the detected gas component content under 20th, 40th, 60th, 80th and 100th breakdown.

According to Fig. 5, the yield and EFR of $\text{CF}_4$ decreases gradually with the oxygen content. The content of $\text{CF}_4$ in $\text{C}_2\text{F}_7\text{N}–\text{CO}_2$ gas mixture after 100th breakdown is 4004 ppm, while the corresponding value decreases to 2548 ppm when 2% $\text{O}_2$ is added to the gas mixture. That is to say, the addition of 2% $\text{O}_2$ could effectively inhibit the production of $\text{CF}_4$. The influence mechanism of oxygen on the generation of $\text{CF}_4$ will be discussed later in the discussion section.

Moreover, the yield and formation rate of $\text{CF}_4$ keep stable when 2–4% oxygen is added in the $\text{C}_2\text{F}_7\text{N}–\text{CO}_2$ gas mixture. Then the decreasing trend occurs when the oxygen content in the $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture is $\gtrsim 6\%$, which may result from the decrease of the breakdown voltage of the $\text{C}_2\text{F}_7\text{N}–\text{CO}_2–\text{O}_2$ gas mixture.

Fig. 6 describes the yield and EFR of CO under different $\text{O}_2$ content conditions. The content of CO dropped sharply from 2277 to 1414 ppm (100th breakdown) when 2% $\text{O}_2$ is added in the
A slight increase trend of CO content exists for the gas mixture containing 2–6% O\textsubscript{2}. While the little decrease trend can be found when the O\textsubscript{2} content is >6% (6–10%). For example, the yield of CO in C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2}–O\textsubscript{2} with 6, 8, 10% oxygen after 100 times of breakdown is 1490.23 ppm, 1433.11 and 1430.82 ppm. On the whole, the change rule of CO content for gas mixture with 2–10% O\textsubscript{2} has a similar trend with the breakdown voltage. For the gas mixture with O\textsubscript{2} added, the higher the breakdown voltage, the higher the energy released by the discharge. Also, the decomposition of C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2}–O\textsubscript{2} gas mixture will be intensified.

In addition, the addition of 2% oxygen could effectively reduce the EFR of CO in the C\textsubscript{4}F\textsubscript{2}N gas mixture. With the increase of oxygen content, the yield of EFR also has a similar change trend of the breakdown voltage.

As shown in Fig. 7, the content of C\textsubscript{2}F\textsubscript{6} decreases when 2% O\textsubscript{2} is added in the C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2} gas mixture. The yield of C\textsubscript{2}F\textsubscript{6} in the C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2} gas mixture reaches 241 ppm after 100 breakdown tests, while this value is only 145 ppm for the 15% C\textsubscript{4}F\textsubscript{2}N–83% CO\textsubscript{2}–2% O\textsubscript{2} gas mixture. The yield of C\textsubscript{2}F\textsubscript{6} shows an increasing trend with the further increase in oxygen content, especially when the oxygen content is >6%. The formation of C\textsubscript{2}F\textsubscript{6} originates from the recombination of CF\textsubscript{3} particles or C\textsubscript{2}F\textsubscript{5} and F particles, indicating that the amount of these particles is higher in C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2}–O\textsubscript{2} gas mixture with oxygen >6%.

The yield and EFR of C\textsubscript{2}F\textsubscript{6} under different O\textsubscript{2} content conditions are given in Fig. 8. The yield of C\textsubscript{2}F\textsubscript{6} after 100th breakdown in C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2} gas mixture is only 8.12 ppm, which is lower than the other by-products. With the increase of O\textsubscript{2} content, the yield of C\textsubscript{2}F\textsubscript{6} shows a decreasing trend. Considering the existence of unsaturated C= C bond in the C\textsubscript{2}F\textsubscript{6} molecule, the addition of O\textsubscript{2} may bring about oxidation reaction between them.

According to the variation feature of C\textsubscript{2}F\textsubscript{6} given in Fig. 9, we can find that the addition of 2% oxygen results in the decrease of C\textsubscript{2}F\textsubscript{6} content after repeated breakdown tests. The yield of C\textsubscript{2}F\textsubscript{6} in the C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2} gas mixture after 100th breakdown is 12.38 ppm, while this value is only 5.74 ppm for the gas mixture containing 2% O\textsubscript{2}. In addition, an increasing trend of C\textsubscript{2}F\textsubscript{6} content can be found when the oxygen content is >6%. The generation of C\textsubscript{2}F\textsubscript{6} is relative to the C\textsubscript{3}F\textsubscript{7} and F particles, the increase of C\textsubscript{2}F\textsubscript{6} indicates that the decomposition of C\textsubscript{4}F\textsubscript{2}N is accelerated when the oxygen content in the gas mixture is >6%.

3.2.2 Variation feature of CF\textsubscript{3}CN, C\textsubscript{2}F\textsubscript{5}CN, (CN)\textsubscript{2} and COF\textsubscript{2}. The decomposition of C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2}–O\textsubscript{2} gas mixture also generates other by-products including CF\textsubscript{3}CN, C\textsubscript{2}F\textsubscript{5}CN, (CN)\textsubscript{2} and COF\textsubscript{2}. Considering the standard gas of these by-products is unavailable at present, we used the peak area integral method to reveal the influence of oxygen on their generation. The peak area of the characteristic peak could reveal the relative content of the detected substance.

Figs. 10 and 11 gives the yield and EFR of CF\textsubscript{3}CN and C\textsubscript{2}F\textsubscript{5}CN under different O\textsubscript{2} content conditions. We can find that the peak area of CF\textsubscript{3}CN and C\textsubscript{2}F\textsubscript{5}CN has similar variation features with the oxygen content. Their peak area decreases first when 2% O\textsubscript{2} is added into the C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2} gas mixture and then shows an increasing trend with the O\textsubscript{2} content. The gas mixture with 2% O\textsubscript{2} has the lowest EFR, indicating that the addition of 2% oxygen could effectively inhibit the decomposition of CF\textsubscript{3}CN and C\textsubscript{2}F\textsubscript{5}CN. The decomposition of CF\textsubscript{3}CN and C\textsubscript{2}F\textsubscript{5}CN need the participation of several particles including CF\textsubscript{3}, CN and F. Thus, the addition of high content O\textsubscript{2} (>8%) has a negative effect on the stability of C\textsubscript{4}F\textsubscript{2}N–CO\textsubscript{2}–O\textsubscript{2} gas mixture.

\[
V_p = \sqrt{\left(\frac{V_{100}}{20}\right)^2 + \left(\frac{V_{80} - V_{20}}{20}\right)^2 + \left(\frac{V_{60} - V_{80}}{20}\right)^2 + \left(\frac{V_{40} - V_{60}}{20}\right)^2 + \left(\frac{V_{20} - V_{40}}{20}\right)^2 + \left(\frac{V_{0} - V_{20}}{20}\right)^2}{5}
\]  

(1)
content of COF2:N is fixed to 15% in this paper, relevant changes may be attributed to the dielectric difference between O2 and CO2.

Actually, the influence of O2 on the dielectric properties of CO2–O2 gas mixture has been investigated comprehensively. Uchii et al. [38] pointed out that adding some O2 to CO2 can improve its dielectric strength and bring the better thermal interrupting capability to CO2. Zhao et al. explored the dielectric breakdown properties of CO2–O2 mixtures by considering electron detachments from negative ions [39]. The reduced ionisation coefficient (α/N), reduced attachment coefficients (η/N), (E/N)crit, breakdown reduced electric fields (E/N)breakdown was calculated. It was found that the increase of O2 in the CO2–O2 mixture enhances both reduced ionisation coefficients and reduced attachment coefficients. The increase of α/N is due to the ionisation potential of O2 (12.06 eV) is lower than that of CO2 (13.3 eV). In addition, the increase of η/N is attributed to the strong electronegativity of O2. Furthermore, the attachment cross-section of O2 is larger than CO2 for electron energy around 5–10 eV, which could lead to a reduction of the electron kinetic energy [40]. The calculated (E/N)crit of the CO2–O2 mixture at CO2 concentrations of 20, 40, 60, 80 and 100% are 116.3, 111, 104, 94.8, 77.3 Td, confirming that the addition of O2 could improve the dielectric strength of DO2.

The influence of O2 on the dielectric properties of CO2 at the elevated temperatures in discharge explored by Rong et al. [41] also indicates that CO2–O2 mixtures have a much better dielectric strength than both the pure CO2 and air. It was pointed out that the electron energy distribution function increase with O2 content due to the vibrational cross-sections of O2 is smaller than that of CO2. The α/N below 90 Td slightly increase with more O2, owing to the increase of average electron energy by the excitation reaction, ionisation reaction and attachment reactions. Although the η/N increases markedly with more O2 than that of α/N. Thus, the (E/N)crit increases with the increase of O2 content. In addition, the breakdown electric field in the temperature range from 300 to 1500 K of pure CO2 is much lower than O2. The electric breakdown field in the temperature range from 300 to 3000 K increases markedly with the increase of O2, mainly owing to the large attachment cross-sections of O2.

As mentioned above, the dielectric property of the CO2 will be markedly developed by addition of O2. For CO2:F–N–O2 gas mixture, the content of COF2:N which provides the dielectric strength to the mixture is fixed. The difference in the dielectric strength is mainly attributed to the ratio change of CO2 and O2. The larger attachment cross-sections of O2 might result in the increase of attachment coefficients and critical reduced electric field strength of the CO2:F–N–CO2–O2 mixture. Thus, the breakdown voltage of the CO2:F–N–CO2–O2 gas mixture with 2–10% O2 added is higher than that of CO2:F–N–CO2 gas mixture.

In addition, we also found that the decreasing trend of breakdown voltage occurs when the O2 ratio is >6%. This could be attributed to the strong oxidising characteristic of O2. According to the decomposition detected results, the yield of most of the by-products show an increasing trend when the O2 content is >6%. That is to say, the decomposition of COF2:N is accelerated with higher O2 ratio. According to the literature [29], COF2:N cannot recombine into itself after decomposition in high-temperature arc. Table 3 gives the relative insulation properties of CO2:N and main decomposition products. We can find that all the generated by-products have lower dielectric strength compared with COF2:N. Thus, the enhanced decomposition of COF2:N and generation of by-products with lower dielectric strength under higher O2 ratio condition cause the decrease of breakdown voltage. The influence mechanism of O2 on the decomposition properties of COF2:N will be discussed in Sections 3.3.2 and 3.3.3.

3.3 Discussion

3.3.1 Influence mechanism of O2 on insulation properties of COF2:N–CO2–O2: According to the relevant test results, we can find that the addition of oxygen in the CO2:N–CO2 gas mixture has quite an influence on its insulation properties. Considering the

Fig. 11 Yield and EFR of C2F3CN under different O2 content conditions

Fig. 12 Yield and EFR of (CN)2 under different O2 content conditions

Fig. 13 Yield and EFR of COF2 under different O2 content conditions

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CO$_2$ gas mixture also influences its stability and discharge decomposition properties. The yield of CF$_4$, CO, C$_2$F$_6$, C$_3$F$_6$, C$_3$F$_8$, CF$_3$CN, CF$_2$CN and (CN)$_2$ shows a certain degree of reduction when 2% O$_2$ is added in the C$_4$F$_7$N-CO$_2$ gas mixture, indicating that the addition of oxygen could prevent the decomposition of C$_4$F$_7$N in the C$_4$F$_7$N-CO$_2$ gas mixture to a certain extent.

Generally, the temperature of arc discharge plasma is usually in the range of 300–12,000 K [45]. As for C$_4$F$_7$N, Wu et al. [28] and Zhong et al. [29] have calculated the plasma compositions. It was pointed out that the predominant species at temperatures <3000 K include CF$_2$, CF$_4$, C$_2$F$_6$, C$_3$F$_7$N, C$_4$F$_7$N, CO and CO$_2$ [29]. The initial gas C$_4$F$_7$N is not observed at high concentration, indicating that C$_4$F$_7$N cannot recombine into itself after the decomposition in the high-temperature arc. That is the reason why all the detected by-products after discharge show an increasing trend with the breakdown number.

Actually, the arcing time constant of O$_2$ gas is known to be relatively smaller than that of CO$_2$, specifically 1.5 µs, whereas 15 µs for CO$_2$ [46]. Thus, oxygen has a preferable arc-quenching capability than CO$_2$. Uchii et al. [46] explored the quenching properties of pure CO$_2$ and 85% CO$_2$–15% O$_2$ gas mixture. They found that the post arc current of 85% CO$_2$–15% O$_2$ gas mixture is much smaller than that of pure CO$_2$, indicating that the addition of oxygen could make the decaying rate of arc conductivity faster [46].

As for C$_4$F$_7$N-CO$_2$ gas mixture, the addition of oxygen could improve the arc-quenching capability of C$_4$F$_7$N-CO$_2$ gas mixture, especially improve the decaying rate of arc conductivity [31]. According to the test results, the yield of CF$_4$, CO, C$_2$F$_6$, C$_3$F$_6$, C$_3$F$_8$, CF$_3$CN and (CN)$_2$ has decrease trend when 2–6% O$_2$ is added in the gas mixture, and the content of some by-products starts to increase when 6–10% oxygen is added. The yield of COF$_2$ and C$_2$F$_3$CN keeps relative stable when 2–4% oxygen is added, and the increasing trend can also be confirmed with the addition of oxygen >4%.

It should be noted that the formation of these decomposition by-products mainly comes from the recombination process of several kinds of particles including CF$_3$, CN, C$_3$F$_7$, F. Thus, the generated particles reduce when 2–4% O$_2$ is added. Relevant theoretical studies on the decomposition mechanism of C$_4$F$_7$N indicates that the bond-breaking processes to generate CF$_3$ and C$_3$F$_7$N requires the lowest reaction enthalpy, which is most likely to occur [18–22]. Although the breakdown voltage is increased when 2–6% O$_2$ is added in the system, the energy released by the discharge may not increase considering the great arcing characteristics of oxygen. Therefore, we can conclude that the addition of 2–6% oxygen in the C$_4$F$_7$N-CO$_2$ gas mixture results in lower by-products generation and C$_4$F$_7$N decomposition. Also, when the oxygen is added in the higher content (>6%), the negative effect of oxygen can be found. The breakdown voltage of the gas mixture starts to decrease while some of the by-products show an increasing trend with the oxygen content, indicating that the high content of oxygen results in faster decomposition of C$_4$F$_7$N.

In addition, the decomposition properties of C$_4$F$_7$N-CO$_2$–O$_2$ gas mixture for HV application have been explored by Meyer and Kieffel [31]. A circuit breaker (145 kV/40 kA) was developed and type-tested according to IEC standard using the 6% C$_4$F$_7$N–5% O$_2$–89% CO$_2$ gas mixture as the insulating medium. The minimal pressure for insulation and interruption was set to 0.75 MPa, which is 0.2 MPa higher than that of SF$_6$-filled circuit breaker. It was pointed out that CO$_2$ is used as the arc quenching medium, C$_4$F$_7$N is responsible for enhancing the dielectric withstand. Also, the addition of 5% O$_2$ could improve the electrical endurance of the circuit breaker by limiting the generation of gaseous and solid decomposition products. Especially for the tests with higher currents, a clear improvement was observed with the addition of 5% O$_2$. The decomposition by-products of the gas after short-circuit tests at 40 kA includes CO, CF$_4$, C$_2$F$_6$, C$_3$F$_6$, CF$_3$CN, C$_2$F$_2$CN, (CN)$_2$, COF, C$_2$F$_4$, C$_3$F$_6$. The concentration of these compounds is in the range of 1 to about 200 ppm, except CO, CF$_4$, C$_2$F$_6$ and C$_3$F$_6$ [31]. This type of GIS was also installed in Switzerland and Franches in 2017–2018 [33], confirming that 6% C$_4$F$_7$N–5% O$_2$–89% CO$_2$ gas mixture is suitable for HV applications. Furthermore, Ficheux et al. point out that O$_2$ plays a major role in the gas chemical decomposition. The influence of O$_2$ content in C$_4$F$_7$N–CO$_2$ is the key factor on gas decomposition and the formation of powders. For instance, the amount of carbon monoxide is lowered by 2 or 3 depending on O$_2$ ratio and the formation rate of other gaseous by-products is also significantly reduced [47]. In this paper, we also conclude that the addition of 2–6% O$_2$ to the C$_4$F$_7$N-CO$_2$ gas mixture for MV application (0.14 MPa) could effectively reduce the content of most of the decomposition by-products. Relevant conclusions are consistent well with that of HV conditions.

### Table 3 Dielectric strength of C$_4$F$_7$N and its decomposition by-products

| Gas       | Relative insulation strength to SF$_6$ | References |
|-----------|---------------------------------------|------------|
| SF$_6$    | 1                                     | [8]        |
| C$_4$F$_7$N | 2                                     | [8]        |
| CO$_2$    | 0.23                                  | [8]        |
| O$_2$     | 0.33                                  | [8]        |
| CF$_4$    | 0.4                                   | [8]        |
| C$_2$F$_6$ | 0.78                                  | [42]       |
| C$_2$F$_8$ | 0.97                                  | [42]       |
| C$_3$F$_6$ | ~1.1                                  | [43]       |
| CO        | ~0.4                                  | [43]       |
| CF$_3$CN  | 1.46                                  | [44]       |
| C$_2$F$_5$CN | 1.92                               | [44]       |

### Table 4 Proposed additional reaction pathways introduced by the addition of oxygen in the C$_4$F$_7$N gas mixture

| No. | Reaction path          | $\Delta H$, kcal/mol | $\Delta H$, kcal/mol |
|-----|------------------------|-----------------------|-----------------------|
| 1   | C$_4$F$_7$N + O -> CF$_4$ + CF$_3$COCN | -106.52              | 47.51                 |
| 2   | CF$_3$COCN -> CF$_3$COF + CN | 20.54                | —                     |
| 3   | CF$_3$COF -> CF$_3$ + COF | 85.28                | —                     |
| 4   | CF$_3$ + O -> CF$_3$O | -104.05              | —                     |
| 5   | COF$_2$ -> COF$_2$ + F | 26.56                | —                     |
| 6   | COF + F -> COF$_2$ | -120.89              | —                     |
| 7   | CO + O -> CO$_2$ | -141.99              | —                     |
| 8   | CF$_3$ + O -> CF$_3$O | -101.93              | —                     |
| 9   | CF$_3$O -> CF$_3$COF + CF | 6.53                 | —                     |
| 10  | CF$_3$COF -> CF$_3$COF | -188.84              | —                     |
| 11  | CF$_2$ + O -> COF$_2$ | -166.69              | —                     |

*$\Delta H$ and $\Delta H$ are both at 298.15 K.*
reaction enthalpy ($\Delta H$) could be obtained by subtracting reactant energy from product energy. The activation energy ($\Delta F$) is also calculated using the complete LST-QST TS search protocol.

As we can see from Table 4, the reaction between C\(_4\)F\(_7\)N and O particle through path 1 has the reaction enthalpy of $-106.52$ kcal/mol, which could generate CF\(_3\), CF\(_3\)COFCN. This reaction path needs to overcome a barrier height of 47.51 kcal/mol. It was reported that the most likely dissociation path in C\(_4\)F\(_7\)N molecule to generate products of CF\(_3\), CF\(_3\)CFCN needs to adsorb 73.14 kcal/mol [18, 22]. The activation energy of path 1 is quite $<73.14$ kcal/mol (as shown in Fig. 14), indicating that the participation of O particle makes the bond-breaking processes of C\(_4\)F\(_7\)N much easier to occur. Thus, oxygen shows a negative impact on the stability of C\(_4\)F\(_7\)N.

In addition, the dissociation of CF\(_3\)COFCN through path 2 (generating CF\(_3\)COF and CN) needs 20.54 kcal/mol. Also, the generation of CF\(_3\) and COF by path 3 has the reaction enthalpy of 85.28 kcal/mol without reaction barrier. The combination of CF\(_3\) and O has the negative reaction enthalpy of $-104.05$ kcal/mol and the generation of COF\(_3\) from COF\(_3\) needs to adsorb 26.56 kcal/mol. Meanwhile, the COF and F, CF\(_3\) and CO could also combine to generate COF\(_3\) through paths 6 and 11 with 120.89 kcal/mol and 116.69 kcal/mol release. The reaction between CF\(_3\)F and O to form CF\(_3\)O has negative reaction enthalpy of $-101.93$ kcal/mol. In addition, the dissociation of CF\(_3\)O through path 9 to generate CF\(_3\) and CF\(_3\)COF needs to adsorb 6.53 kcal/mol. The reaction between CF\(_3\)CF and O also has a negative enthalpy of $-188.84$ kcal/mol.

Overall, most of the reactions between O radical and particles generated by C\(_4\)F\(_7\)N molecule belongs to the exothermic process, which could hinder the generated particles to compound or recombine to C\(_4\)F\(_7\)N. Thus, the addition of oxygen could influence the by-products formation process.

### 3.3.4 Application suggestions for C\(_4\)F\(_7\)N–CO\(_2\)–O\(_2\) in MV equipment

As mentioned above, the addition of 2–6% O\(_2\) could improve the insulation performance and inhibit the decomposition of C\(_4\)F\(_7\)N–CO\(_2\) gas mixture. While the added content could not be too high considering its supportive flammability and strong corrosivity.

Table 5 gives the toxicity data of characteristic decomposition products of C\(_4\)F\(_7\)N–CO\(_2\)–O\(_2\) gas mixture. We can find that the fluorocarbons (C\(_2\)F\(_6\), C\(_3\)F\(_8\)) have little influence on personal safety, which belongs to asphyxiating gas. The LC50 for C\(_2\)F\(_6\), C\(_3\)F\(_8\)CN is around 3000 ppm, followed by CO (1800ppm). CF\(_3\)CN, (CN)\(_2\) and COF\(_2\) have the LC50 value quite lower than other byproducts, which is only 250 ppm, 175 and 180 ppm. Therefore, it is necessary to limit the production of highly toxic substances. According to the above test results, the addition of 2% oxygen could effectively reduce the generation of most of the by-products. Also, the yield of CO, C\(_2\)F\(_6\), CF\(_3\)CN, CF\(_3\)CN and (CN)\(_2\) keeps stable or shows little increase trend with 2–6% oxygen added. As for gas mixture with oxygen >6%, the generation of some by-products starts to accelerate, indicating that high content of oxygen has a negative effect on the stability of C\(_4\)F\(_7\)N gas mixture. Thus, the addition of 2–6% oxygen in the C\(_4\)F\(_7\)N–CO\(_2\) gas mixture is recommended, which could improve the dielectric strength and inhibit the decomposition of C\(_4\)F\(_7\)N.

### 4 Conclusion

In this paper, we explored the AC breakdown and discharge decomposition properties of C\(_4\)F\(_7\)N–CO\(_2\)–O\(_2\) gas mixture. The influence of oxygen content on the insulation and decomposition properties of the gas mixture is revealed and discussed. Relevant conclusions can be obtained as follows, which may be useful for engineering application of the new gas.

(i) The addition of oxygen could improve the insulation properties of C\(_4\)F\(_7\)N–CO\(_2\) gas mixture. The dielectric strength of the C\(_4\)F\(_7\)N–CO\(_2\)–O\(_2\) gas mixture with 2, 4, 6, 8 and 10% oxygen was increased by 4.85, 6.49, 7.70, 3.21 and 2.74% compared with C\(_4\)F\(_7\)N–CO\(_2\).

(ii) The decomposition of C\(_4\)F\(_7\)N–CO\(_2\)–O\(_2\) gas mixture mainly produced CF\(_4\), CO, C\(_2\)F\(_6\), C\(_3\)F\(_8\), C\(_3\)F\(_6\), CF\(_3\)CN, CF\(_3\)CN and (CN)\(_2\), COF\(_2\). The addition of 2–6% O\(_2\) to the C\(_4\)F\(_7\)N–CO\(_2\) gas mixture could effectively reduce the content of most of the decomposition by-products.

(iii) The yield of CO, CF\(_3\)CN, CF\(_3\)CN and (CN)\(_2\) keeps stable or shows little increase trend with 2–6% oxygen added to the C\(_4\)F\(_7\)N–CO\(_2\) gas mixture. The generation of some by-products starts to accelerate when the oxygen content is >6%, indicating that high content of oxygen has a negative effect on the stability of C\(_4\)F\(_7\)N gas mixture.

(iv) The participation of O particle makes the bond-breaking processes of C\(_4\)F\(_7\)N much easier to occur, which has the reaction enthalpy of $-106.52$ kcal/mol and the activation energy of 47.51 kcal/mol. The addition of oxygen also has a negative influence on the by-products formation process.

(v) As for MV engineering application, it is recommended to add 2–6% O\(_2\) in the C\(_4\)F\(_7\)N–CO\(_2\) gas mixture to improve its insulation performance as well as inhibit the decomposition of C\(_4\)F\(_7\)N in the discharge.

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