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Characteristics of emissive spectrum and the removal of nitric oxide in $N_2/O_2/NO$ plasma with argon additive

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Abstract

Although the approach using non-thermal plasma (NTP) for deNO*x* has been studied for over 15 years, how to achieve higher removal efficiency with lower cost is still a barrier for its industrial application. In order to investigate the impact of the argon additive on electron density, energy and nitric oxide reduction process in plasma, the spectrum of the dielectric barrier discharge at atmospheric pressure in a coaxial reactor was measured using the monochromater with high resolution. The comparative experiments for NO reduction were carried out simultaneously in $N_2/O_2/NO$ plasma stream with and without argon, respectively. The nitrogen molecular spectrum which is attributed to the energy level transition ($C^3\pi_u \rightarrow B^3\pi_g$) was compared in the wavelength range 300–480 nm and the electron density and temperature were determined based on the relative intensities and Stark broadening width of spectral lines. The spectrum results indicated that the argon additive could enhance the intensity of emissive spectrum of plasma, thus the electron concentration as well as the energy was increased, and finally prompted the ionization rate to produce active N, O and O_3. The results of NO reduction showed that NO conversion efficiency increased in the range of 10%–30% with 5% addition of argon in stream comparing with the condition without argon additive. This study will play a positive role in the industrial application of dielectric barrier discharge deNO*x* reactor.

Key words: argon; emissive spectrum; nitric oxide; non-thermal plasma
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Introduction

When gas stream is exposed to an electric discharge, a reactive mixture containing radicals, ions, and excited molecules in the neutral gas is referred to as plasma (Yan *et al*., 1998). Generally, the plasma produced by electrical discharges can be divided into two types. One is the thermal plasma, which is characterized by a high gas temperature and an approximately equal gas and electron temperature. The other is termed as non-thermal plasma and is characterized by low gas temperature and high electron temperature.

Flue gas streams containing pollutants, such as NO*x* and SO*x*, have to be removed or converted to benign species prior to discharge. Non-thermal plasma processing is a promising technology for the conversion of NO*x* and SO*x* pollutants in flue-gas streams (Mizuno *et al*., 1995; Clements *et al*., 1989). Compared to thermal methods, non-thermal plasma techniques are more efficient because a majority of the electrical energy contributed to the production of energetic electrons rather than to gas heating. The use of non-thermal plasma for pollution control has become an active area of research in the past years.

Essentially, there are two methods for producing non-thermal plasmas: a corona discharge and a dielectric-barrier discharge. Corona discharge is due to inhomogenous electrode geometries such as a point electrode and a plane. The discharge takes place near sharp points where the electric field is enhanced. Although corona discharge has numerous applications (Eliasson and Kogelschatz, 1991a), they are limited due to the low active volume available for processing the gas.

The dielectric-barrier discharge, also known as a silent discharge or a partial discharge, is widely used in ozone generation and as a source of UV and VUV radiation (Laroussi, 2002). This is one of the few "cold" discharges that are stable at atmospheric pressures. The discharge is intermittent and the current exhibits a large number of spikes when it is burning. These partial discharges are best characterized by streamers which are a result of space-charge dominated transport at high electric fields.

The kinetic processes occurring in discharge reactor of the atmospheric mixture of $N_2/NOx/O_2/O_3$ gases are presently the subject of many investigations due to their importance in atmospheric and ionospheric physics, and in plasma chemistry (Stefanovic *et al*., 2001; Sathiamoorthy *et al*., 1999). In fact, the knowledge of formation kinetics active of radical such as electron, N and O atoms is important for understanding the working mechanisms of plasma reactors used for air pollution control. However, the existence and effects of these active radicals are difficult to

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be measured.

The important noninterfering plasma diagnostic technique based on optical emission spectroscopy (OES) has been developed to determine the characteristics of plasma (Ishihara *et al*., 1989; Touzeau *et al*., 1991). Plasma-broadened and shifted spectral line profiles have been used for a number of years as a basis of an important noninterfering plasma diagnostic technique. The emissive spectral line shapes of plasma represent important sources of information about the physical conditions in the place of radiation birth. A great deal of theoretical and experimental work has been done for the line shape investigations (Griem, 1794, 1997; NIST, 2002). In the plasmas with electron densities higher than 10^{21} m^{-3}, where the Stark effect plays an important role on plasma spectral lines broadening, the Stark broadening characteristics can be used for plasma diagnostic purposes (Milosavljevica and Djenize, 2003). The Stark FWHM (full-width at half intensity maximum, W) has been well investigated.

Military applied inert gas to gain higher electron density in plasma in stealth aircraft (Alexeff *et al*., 1998). The aim of this study was to investigate the impact of the argon additive on the electron density and therefore the nitric oxide conversion process in plasma. The spectrum of the dielectric barrier discharge at atmospheric pressure in a coaxial reactor was measured using a monochromater with high resolution. The comparative experiments for nitric oxide reduction were carried out simultaneously in N_2/O_2/NO plasma stream with and without argon, respectively. The nitrogen molecular spectrum attributed to the energy level transition ($C^3\pi_u \rightarrow B^3\pi_g$) was compared in the wavelength range 300–480 nm and the electron density and temperature were calculated based on the relative intensities and Stark broadening width of spectral lines.

1 Experimental apparatus and method

A schematic of the experimental apparatus is shown in Fig. 1. The simulated flue gas mixture was regulated with mass flow controllers connected to the entrance of reactor. The gas mixture was composed of NO (2000 ppmv), N_2 (as balance), O_2 (2.5% in volume) and argon (from 0 to 5.0% in volume). The simulated gas was treated in plasma reactor and then collected by a gas sampling cell. The concentration of NO in gas stream was monitored online by a gas analyzer (Testo-360, Testo Instruments, Germany). The conversion of NO in N_2/O_2/argon system is defined as Eq. (1).

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where, C_0 and C are the concentrations of NO at the outlet of the reactor before and after discharge, respectively.

A schematic of non-thermal plasma (NTP) reactor is shown in Fig. 2. This reactor consists of a 4.0-mm diameter copper pole electrode and double coaxial quartz glass tubes as dielectric barrier around which the copper screen is wrapped as the other electrode.

A pulse high-voltage power supply (CTP-2000K, Corona Lab of Suman Company, China) was used to energize the plasma reactor. The maximum discharge power was 500 W, the output voltage obtained could be regulated between 0 and 30 kV and the pulse frequency was changed from 1 to 100 kHz. Although the dielectric-barrier discharge (DBD) type plasma reactor can be driven by a conventional ac power supply, higher energy efficiency can be realized with a pulse high-voltage power supply.

Spectroscopic observation of spectral lines was made end-on along the axis of the discharge tube. The range of measuring spectrum was 200–700 nm. The spectrum line profiles were recorded by a step-by-step technique. Light signals emitted from NTP discharge through the window of quartz glass, convergent lens (f = 170 mm) to MODEL KD-300G grating monochrometer (Anrui Corp., China) (grating constant d = 1200 line/mm, the entrance slit width is 0.05 mm). A photomultiplier was used to detect the light from discharge, and the signal was digitized using an oscilloscope that was finally recorded by a computer.

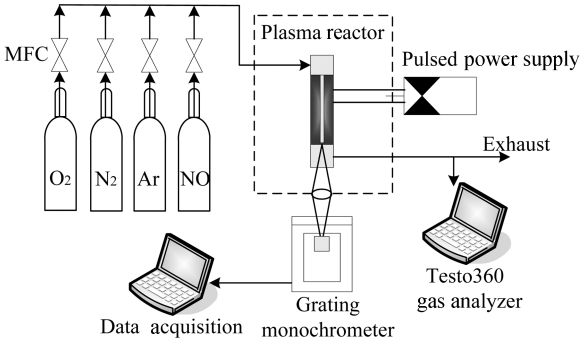

Fig. 1 Schematic of the experimental apparatus.

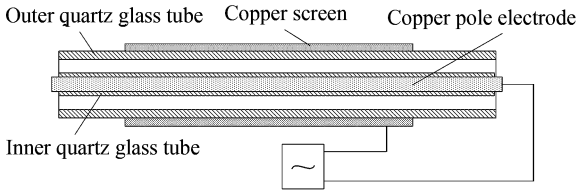

Fig. 2 Schematic of non-thermal plasma (NTP) reactor. Inner tube: 5 mm inner diameter and 8 mm outer diameter; outer tube: 22 mm inner diameter and 25 mm outer diameter.

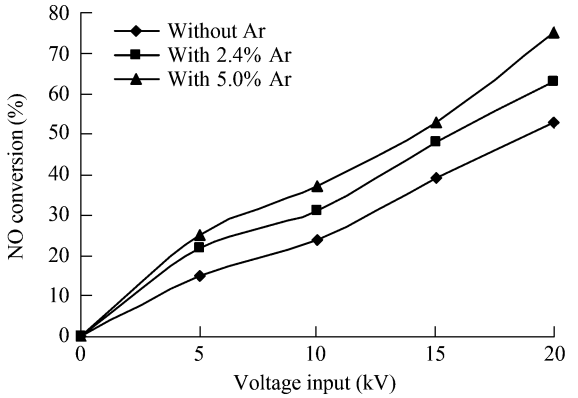

Fig. 3 Effect argon additive on the conversion of NO in N_2/O_2/argon plasma system.

2 Results of NO conversion

The experiment on NO conversion was carried out under various argon contents (0, 2.4% and 5.0%) at flow rate 6.4 L/min, reactor pressure 108.0 kPa, with different voltage inputs (5, 10, 15, 20 kV). The effect of argon used as additive on the conversion of NO in plasma stream is presented in Fig. 3. The addition of argon caused a higher conversion efficiency of NO under the same experimental condition. In $NO/O_2/N_2$/argon system, the NO reduction was produced by N and O atoms, and the reaction mechanism could be described as Reactions (2)–(5) (Penetrante *et al*., 1999):

$$N + NO \longrightarrow N_2 + O \quad (2)$$

$$O(^1D) + NO \longrightarrow O_2 + N \quad (3)$$

$$O + NO + M \longrightarrow NO_2 + M \quad (4)$$

$$O + NO_2 \longrightarrow NO + O_2 \quad (5)$$

The conversion of NO in N_2/O_2/argon plasma system was dependent on the competition between oxidation and reduction. The plasma N and O atoms were produced through electron-impact dissociation of N_2 and O_2 in the simulated gas (Reactions (6)–(8)).

$$e + N_2 \longrightarrow e + N + N \quad (6)$$

$$e + O_2 \longrightarrow e + O + O \quad (7)$$

$$e + O_2 \longrightarrow e + O + O(^1D) \quad (8)$$

In this article, the promotion of NO conversion with an addition of argon was explained by increasing amounts of active electron, O, $O(^1D)$ and N atoms, because argon was ionized in the reaction chamber through the charge-transfer mechanism (Zhao *et al*., 2004) (Reactions (9) and (10)).

$$Ar + e \rightarrow Ar^+ + 2e \quad (9)$$

$$Ar^+ + e \rightarrow Ar \quad (10)$$

Therefore, the dominate radical formed from argon can be an active electron. In the presence of argon the charge-transfer mechanisms play a significant role in NO conversion.

3 Theoretical model of electron density with spectral profile in plasma

The spectral line profile method is one of the most convenient methods for measuring micro-discharge because of its simple equipment and non-intrusive characteristic. Spectral line shapes represent important information about the physical conditions of the radiation from radical sources. Plasma-broadened and shifted spectral line profiles have been used for a number of years as a basis of an important non-interfering plasma diagnostic technique. In order to verify the hypothesis proposed above, the spectrum of the dielectric barrier discharge at atmospheric pressure in reactor was measured using the monochromater in N_2/O_2/NO/argon plasma stream. The results of the spectral investigation are shown in Fig. 4. The typical spectrum peaks of N_2 molecular under discharge at 337.1, 357.5, 380.4 and 404.2 nm are identified in wavelength range 300–480 nm. These spectral lines are attributed to the energy level transition ($C^3\pi_u \rightarrow B^3\pi_g$) under the excitation of electrons. Figure 4b shows the spectrum profile in N_2/O_2/NO/argon plasma system with 5% argon. It is shown that most of the spectrum lines of argon are located in the range of 680–800 nm. The typical spectrum peaks of argon atom under discharge at 696.7, 763.7 and 772.7 nm are identified in the wavelength range 680–800 nm, which can be attributed to the excitation of the neutral argon atom. Compared with the spectral profile without argon additive, since the intensity of emissive spectrum of argon in the wavelength range 300–480 nm was much lower than that of N_2 molecule, the typical spectrum peaks of N_2/O_2/NO/argon plasma system still kept at 337.1 and 357.5 nm. The lower spectrum peaks at 404.2 and 434.4 nm disappeared and the new peaks at 425.4 and 427.2nm were found in N_2/O_2/NO/argon plasma system, which might be attributed to the interference between the N_2 and argon spectra. The emissive intensity and width of spectral line profile of nitrogen molecular was enhanced obviously in the examination with high resolution of 0.01 nm.

Generally, the spectral line emitted from plasma was subject to various broadening mechanisms such as Stark and Doppler broadening. The Stark broadening is determined by electrons and plasma ions impact broadening.

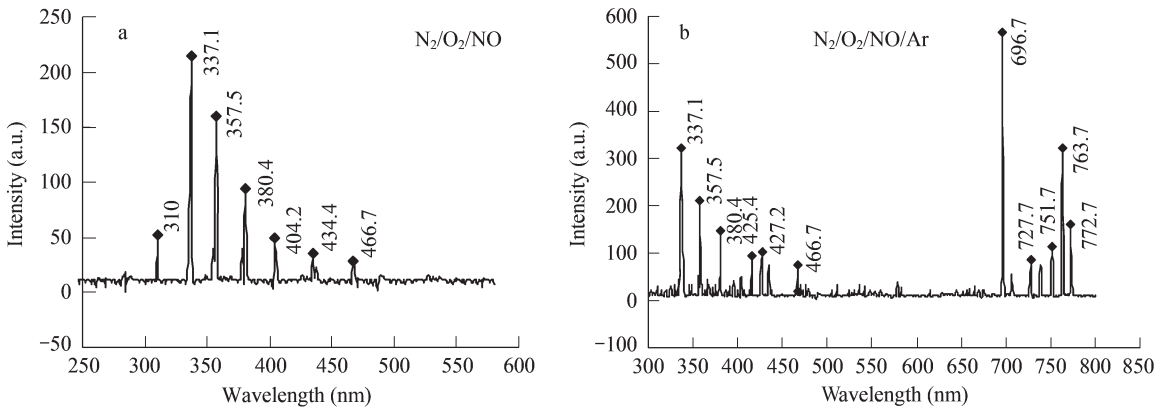

Fig. 4 Effect of argon additive on the emissive spectra for N_2/O_2/NO plasma system (a) and N_2/O_2/NO/argon plasma system (b).

Table 1 Predicted electron density in different experiment conditions

Reaction system	Initial concentration of gas mixture (%)	Electron density (10^{16} cm^{-3})	$W_{1/2}^{Stark}$ (nm)	Voltage input (kV)
$N_2/O_2/NO$	balance/2.5/20×10^{-4}	7.112	0.101	15
$N_2/O_2/NO$/argon	balance/2.5/20×10^{-4}/2.4	8.791	0.125	15
	balance/2.5/20×10^{-4}/5.0	9.613	0.137	15

ω: 0.0066; α: 0.047; electron temperature: 10000 K. $W_{1/2}^{Stark}$: full width at half maximum of stark broadening.

Stark profile is described by the sum of these two broadenings leading to asymmetrical Lorentzian spectral line profile. The isolated spectral lines of neutral atoms are mostly broadened by electron impact. This electron impact broadening gives a symmetrical Lorentzian profile. For non-hydrogenic atoms, the full width at half maximum (FWHM) of Stark broadening is defined as $W_{1/2}^{Stark}$, which is a complex function of electron density N_e (cm^{-3}) and electron temperature T_e (K). The expression for FWHM of Stark broadening can be approximated by Eq. (11) (Penache *et al*., 2002; Pellerin *et al*., 1996).

$$W_{1/2}^{Stark} = 2 \times 10^{-16} \omega N_e (1 + 1.75 \times 10^{-4} N_e^{1/4} \times \alpha(1 - 0.068 N_e^{1/6} / T_e^{1/2})) \quad (11)$$

where, ω is the electron impact parameter and α is the ion impact parameter. The values of ω and α for N_2 spectral line (337.1 nm) were given by Griem (1974), which is 0.0066 and 0.047, respectively. The electron excited temperature is estimated in the range of 5000–10000 K. It is generally believed that the electron temperature in DBD plasma stream is in the range of 7000–13000 K, which is greater than the electron excited temperature (Eliasson and Kogelsahatz, 1991b). Therefore, the average value (10000 K) was chosen to be the electron temperature in this study. Although various N_2 molecular lines were obtained in the wavelength range 300–500 nm, the N_2 spectral line (337.1 nm) was well resolved and separated from other lines.

Based on the theoretical model of Stark broadening presented above, the electron densities under different experiment conditions were calculated according to Stark broadening width of spectral lines and the results are shown Table 1. Compared with the baseline condition in $N_2/O_2/NO$ system, with increasing argon additive ratio from 0 to 5%, the Stark broadening width increased from 0.101 to 0.137 nm, correspondingly, the electron density increased from 7.112×10^{16} to 9.613×10^{16} cm^{-3} at the input voltage of 15 kV. The result proved that the positive effect of argon additive on NO conversion in $N_2/O_2/NO$ system was related with increasing electron density. More active electrons will promote the collision and excitation of N_2 and O_2, and thus more active radical N and O will be generated.

4 Conclusions

In $N_2/O_2/NO$ plasma stream, NO conversion could be increased with the addition of argon which related with increasing electron density. Argon additive prompted the generation of electrons and the ionization rate, giving more active N, O and O_3 radicals. The result from spectrum diagnosis and the theoretical model of Stark broadening indicated that argon additive enhanced and broadened the emissive spectral line profile of plasma, and with the increase of argon additive ratio from 0 to 5%, the electron density increased from 7.112×10^{16} to 9.613×10^{16} cm^{-3}.

Acknowledgments

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References

Alexeff I, Kang W L, Rader M, Douglass C, Kintner D, Ogot R, 1998. Plasma stealth antenna for the U.S. Navy. In: Proceedings of the 1998 IEEE International Conference on Plasma Science. June, Raleigh, NC, USA. 277–285.

Clements J S, Mizuno A, Finney W C, Davis R H, 1989. Combined removal of SO_2, NO*x*, and fly ash from simulated flue gas using pulsed streamer corona. *IEEE Transactions on Industry Applications*, 25(1): 62–69.

Eliasson B, Kogelsahatz U, 1991a. Non-equilibrium volume plasma chemical processing. *IEEE Transactions on Plasma Science*, 19(6): 1063–1077.

Eliasson B, Kogelschatz U, 1991b. Modeling and applications of silent discharge plasmas. *Transactions on Plasma Science*, 19(2): 309–323.

Griem H R, 1974. Spectral Line Broadening by Plasma. New York: Academic Press. 546–654.

Griem H R, 1997. Principles of Plasma Spectroscoy. Cambridge: Cambridge University Press. 546–654.

Ishihara S, Otsuka A, Nagata S, 1989. *In situ* monitoring of silicon nitride surface temperature from rotational temperature of a nitrogen molecule during glow discharge processing. *Applied Physics Letters*, 55(23): 2396–2398.

Laroussi M, 2002. Nonthermal decontamination of biological media by atmospheric-pressure plasmas: Review, analysis, and prospects. *IEEE Transactions on Plasma Science*, 30(41): 1409–1415.

Milosavljevica V, Djenize S, 2003. The He I 706.52 nm line shape characteristics in the plasma diagnostics. *The European Physical Journal D*, 23: 385–390.

Mizuno A, Shimizu K, Chakrabarti A, Dascalescu L, Furuta S, 1995. NO*x* removal process using pulsed discharge plasma. *IEEE Transactions on Industry Applications*, 31(5): 957–964.

NIST (National Institute of Standards and Technology), 2002. Atomic Spectra Data Base Lines. http://physics.nist.gov.

Penache C, Miclea M, Bräuning-Demian A, Hohn O, Schössler S, 2002. Characterization of a high-pressure microdischarge

using diode laser atomic absorption spectroscopy. *Plasma Sources Science and Technology*, 11(4): 476–483.

Pellerin S, Musiol K, Pokrzywka B, Chapelle J, 1996. Stark width of 4p prime [1/2]-4s[3/2]^0 Ar I transition. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 29(17): 3911–3924.

Penetrante B M, Brusasco R M, Merritt B T, 1999. Environmental applications of low-temperature plasmas. *Pure and Applied Chemistry*, 71(10): 1829–1835.

Sathiamoorthy G, Kalyana S, Finney W C, Clark R J, Locke B R, 1999. Chemical reaction kinetics and reactor modeling of NO*x* removals in a pulsed streamer corona discharge reactor. *Industrial and Engineering Chemistry Research*, 5(38): 1844–1855.

Stefanovic I, Bibinov N K, Deryugin A A, Vinogradov I P, 2001. Kinetics of ozone and nitric oxides in dielectric barrier discharges in O_2/NO*x* and N_2/O_2/NO*x* mixtures. *Plasma Sources Science and Technology*, 10(3): 406–416.

Touzeau M, Vialle M, Zellagui A, Gousset G, Lefebvre M, Pealat M, 1991. Spectroscopic temperature measurements in oxygen discharges. *Journal of Physics D: Applied Physics*, 24(3): 41–47.

Yan K P, Hui H X, Cui M, Miao J S, Wu X L, Bao C G, Li R N, 1998. Corona induced nonthermal plasmas: fundamental study and industrial applications. *Journal of Electrostatics*, 44(1-2): 17–39.

Zhao G B, Hu X D, Ovid A P, Maciej R, 2004. Energy consumption and optimal reactor configuration for nonthermal plasma conversion of N_2O in nitrogen and N_2O in argon. *Energy & Fuels*, 18(5): 1522–1530.