

The Conversion of NO_x in a Corona Discharge with an Electrode Material Variation

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Abstract

The spatial and surface chemical products and effectiveness of NO_x removal (abbreviated de NO_x) under the corona discharge action at atmospheric pressure were investigated. The influence of high-voltage electrode material on a discharge character and the heterogeneous influence of the electrode surface are also reported in the article. The qualitative analysis was performed using infrared absorption spectrometry. Special attention was paid to NO and NO_2 calibration measurements.

1 Introduction

In the last decade, our life-sustaining environment has changed more rapidly than it did during any comparable period of history. Acid rain, global warming, the ozone layer depletion are the most important problems today. The environment is polluted by chemicals emitted directly from identifiable sources or by chemicals formed indirectly through photochemical reactions in the air [1]. All these chemicals have more or less toxic effects, endangering human health, therefore their removal or at least maintenance within a certain level is necessary.

The nitrogen oxides are considered as very aggressive chemicals. In their effects on human, vegetation, animals and buildings, they are more toxic and aggressive than SO_x (6-10 times) [2]. They are produced and released in the processes of combustion in the atmosphere, contributing to the photochemical smog production. Moreover, they are responsible for an acid rain, cause many serious diseases (bronchitis, pneumonia, heart diseases) and lower the resistance to influenza.

In principle three methods are used for the reduction of NO_x emissions from stationary sources:

- **Pre-combustion methods**

NO_x emissions are reduced by cleaning fuels (e.g. coal) prior to combustion. In a catalytic process, the nitrogen in coal is transformed mainly to NH_3 . These methods have financial disadvantages.

- **Combustion modification methods**

The emissions are reduced by combination of various combustion modification techniques. Low NO_x burners are designed to achieve two combustion stages, a low flame temperature, a low local oxygen concentration and a short residence time of flue gas in a higher temperature region [3]. However, this reduction is often insufficient to satisfy emission standards.

- Post-combustion flue gas treatment (de NO_x)

Methods treating NO_x after a combustion process. A variety of deNO_x non-plasma techniques (e.g. SCR, NSCR, SNCR, RapreNO_x) and plasma techniques (e.g. electron beam processes and electric discharge processes) are available. At present, the most advanced process for deNO_x is a dry selective catalytic reduction (SCR). Anyway, in the recent years, there is a growing interest for gas cleaning techniques of non-thermal plasma.

Non-thermal plasma is characterised by the fact, that the mean energy of electrons is generally much higher than the energy of other particles (ions, neutrals) in an ambient gas. The energy in the plasma is so directed preferentially to the electron-impact dissociation and ionisation of background gas to produce radicals and in turn, decompose the toxic molecules. For many applications, particularly in the removal of very dilute concentration of pollutants in an ambient gas, the non-thermal plasma conditions would be most appropriate because of their energy selectivity and their capability for simultaneous removal of various pollutants. Non-thermal plasmas can be created by electrical discharges.

Many electrical discharge devices achieve non-thermal conditions by the production of microdischarges called streamers. Streamers are plasma filaments produced by highly localised space-charge waves. The space-charge waves enhance the applied field in front of the wave and propagate because of electrons avalanching in this high field. Streamers yield good power efficiency because, within the short lifetime of the streamer, the ions do not experience significant movement and therefore do not contribute to the power consumption. The short lifetime of the streamer is accomplished with the use of very-short high-voltage pulses (as in pulsed corona discharges) and/or with the use of dielectric coatings on the electrodes (as in dielectric barrier discharges).

However, to obtain "hot electrons" at atmospheric pressure, it is necessary to hinder (or at least to delay) the breakdown. It could be realised either by covering an electrode with dielectric or using a strongly non-homogenous system. The use of the corona discharge is therefore a suitable method for a non-thermal plasma production.

The corona discharge [4, 5, 6] is an electrical discharge phenomena in the vicinity of conductors of small radius of curvature such as sharp points and thin wires. The enhanced electric field in vicinity of the conductors is the cause of strong ionisation processes here (ionisation region). This leads to an electron avalanches development and thus to a production of electrons and ions in this part of the discharge volume. The remaining and much larger part of the discharge space is dominated by electrons and ions drift and conversion processes (drift region).

There are various types of corona discharge. It is possible to classify them according to the electrode configuration / reactor geometry (electrodes in the shape of thin wires, needles or sharp points) and electric power source type (a.c., d.c. or pulsed corona) respectively polarity (positive or negative corona). In a case when a dielectric or ferroelectric material [4] is present between the electrodes, the discharge is referred to a silent (barrier), or ferroelectric bed discharge. The discharge can also propagate along the electrode surface covered with a dielectric material. This phenomenon is known as a surface discharge and often occurs particularly after a surface modification of electrodes caused by a discharge action. The modification of the electrode surface may then be important for the corona stability.

The chemical reactions under the plasma environment are very complicated – hundreds of chemical reactions may be involved. The main aspect in corona discharge induced plasma chemical processes are gas phase radicalic and ionic chemical reactions. Moreover, thermochemical, heterogeneous phase and traditional chemical reactions also play a very important role in the overall removal efficiency. The researchers [4, 7, 8]

performed and discussed the laboratory experiments allowing the possibility of NO_x control by the corona discharge treatment. The results have been improved with the variation of the voltage waveform (amplitude, shape, polarity), the power input, the initial pollutant concentration, the residence time, the gas flow rate, the gas temperature, the moisture, and chemical additives.

A corona discharge has been applied in various industrial processes and products from the beginning of the century. Firstly in applications such as an electrostatic precipitator or ozonizer and later as a source of charged particles. Also the chemical activity of the corona discharge is widely used in the industry. In respect to optimise the activity, various industrial and laboratory scale experiments using corona discharge (mostly pulsed corona [7, 9-14] & d.c. corona [15-18]) have been performed. The removal of various toxic compounds from exhaust gases, such as CO_x, NO_x, hydrocarbons (PAH and VOC), compounds containing heavy metals etc. have been performed. Simultaneously with the laboratory tests and experiments also computer simulations and calculations to elucidate chemical mechanisms and kinetics of pollutants' removal in the discharge are of high interest.

2 The Aim of Experiment

Since 1972 we have performed the research considering corona discharge technologies for an environmental protection. In a great amount of laboratory and small-scale pilot experiments e.g. [16-19] we have observed the corona discharge behaviour, its character, properties and its removal efficiency in different gas mixtures - polycyclic hydrocarbons (1972-74), CO and CO₂ (1974-78), combustion exhaust of natural gas (1981-87), CO with H₂O and H₂ (1983-86), CO and CO₂ in different types of combustion exhaust (1992-93).

The main objective of this work was to ascertain, how effectively a corona discharge is able to decompose the desired gas (NO or NO₂) under atmospheric pressure conditions with electrode material variation. Atypical pressure conditions were designed to state the upper pressure limit for NO_x removal and even to eliminate the influence of additives in the main gas mixture. Experimental results give information about an influence of NO_x on the discharge character and a material corrosion. Even an influence of inner (HV) electrode material on the discharge and surface changes of outer (LV) electrode have been observed and partially analysed. Analyses of volume and surface products were made to ascertain the main reaction products respectively structural groups. The paper also deals with calibration measurements of NO and NO₂ in the middle and far infrared region (4000-200 cm⁻¹).

3 Experimental Setup and Method

This selection describes an experimental apparatus and methods of analyses.

- Gas filling system

The experimental system is presented schematically in Fig.1. The vacuum chamber consisted of the glass cylinder with a diameter of 44 mm and a length of 400 mm. The pressure tanks were connected to the vacuum chamber via the system of flowmeters. The desired gas mixture was transported from the vacuum chamber to the IR gas cell (discharge chamber) through the system of silicon tubes. The pressure inside the chamber was adjusted with 2.7 kPa (20 Torr) precision.

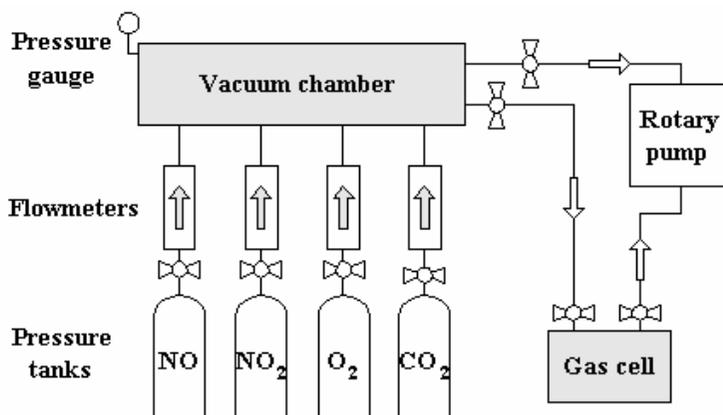


Fig. 1. Experimental set-up (Gas filling system).

- IR gas cell (Discharge chamber)

The gas cell was the glass cylinder (inner diameter 38mm, length 100mm) closed by two KBr (respectively CaF_2) windows at both ends. By fixing the HV electrode in holes drilled in both windows and placing the LV plate electrode underneath, the cell could be easily re-built to a discharge reactor (Fig. 2). The HV electrode consisted of a wire wound on a glass tube with a diameter of 6mm. The used wires (dia 0.2 mm) were made of copper, molybdenum, brass and stainless steel. The LV electrode material (rectangle 35×100 mm) was brass. The electrodes were fastened parallel to the optical axis of the gas cell, in the mutual distance of 10.5mm. The given distance was set up with regard to the necessary scanning area (10×10 mm) of the IR beam. Such a geometry of the discharge chamber allowed us to scan and analyse the gaseous products, almost "in situ", in the discharge chamber. This method forestalls a data deformation, often connected with the gas transport via the system of tubes from a vacuum system to a gas cell.

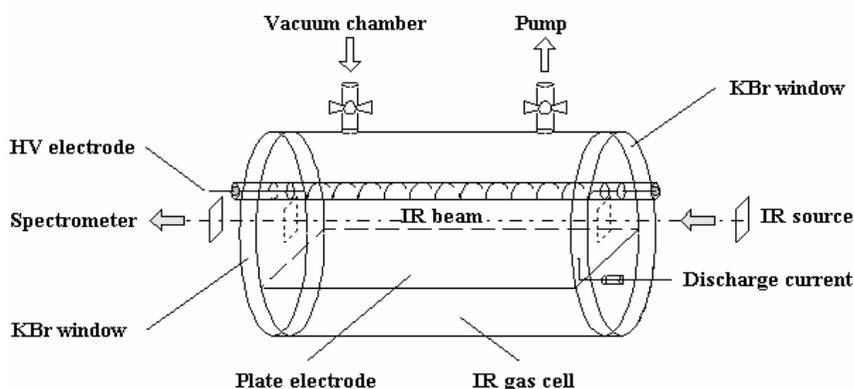


Fig. 2. Experimental set-up (Gas cell - discharge chamber).

- Electrical circuit

The electrical scheme is illustrated in Fig. 3. The HV power supply gave a rectified harmonic voltage, equalised successively by the RC-element. The voltage across the discharge gap was measured as a current through the $200\text{M}\Omega$ resistor coupled to the ground. The discharge current was measured directly on the plate electrode by a microammeter. The circuit was protected either by the lightning ward or two back-to-back Zener diodes.

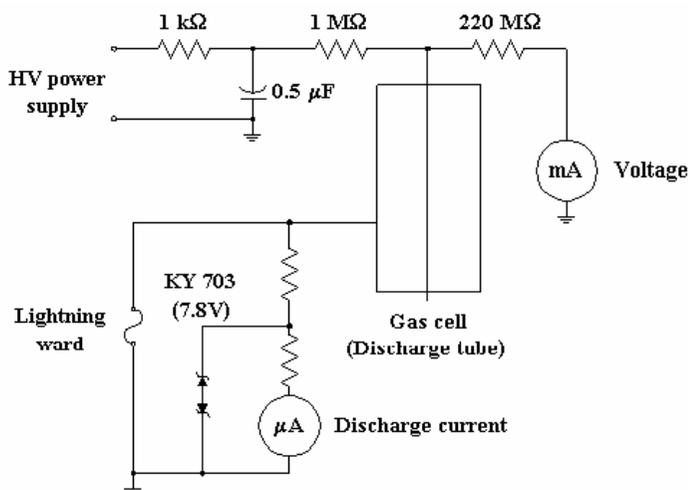


Fig. 3. Experimental set-up (Electrical circuit).

- Infra-red spectrometry

The infra-red absorption spectrometry is a very powerful analytic method. It provides a means of studying pure rotational, pure vibrational and rotation-vibrational energy changes in the ground state of simple and even complex molecules. The method is very suitable for the identification of various materials in gas, liquid and solid state, especially in cases when many reactions take place and the reaction product is almost unknown. Because of the very intensive infra-red absorption bands of the nitrogen oxides (NO, NO₂, N₂O₂, N₂O₄, N₂O) in the infra-red region, we preferred and used this method for analyses of the reaction products.

For analyses of gaseous mixture in the gas cell, we used the IR absorption spectrometer Specord M80 (Carl Zeiss Jena). The reflection spectra of the LV electrode was measured by use of a reflection equipment with a 70° reflecting angle (Fig. 4).

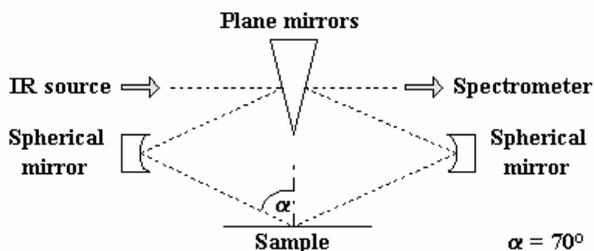


Fig. 4. Experimental set-up (Reflection equipment with a 70° reflecting angle).

4 Calibration Measurements

The calibration measurements were made to determine the extinction coefficients for NO and NO_x [20]. The values of the coefficients helped us further in the specification of the partial pressure changes of nitrogen oxides in gas mixtures exposed to the discharge action. For both gases, we realised series of measurements scanning the IR spectra of the gas inside the gas cell, at different pressures. Thus within the pressure range of 2.4-99 kPa (18-745 Torr), we recorded the spectra for 14 to 18 different gas pressures. In each single IR spectra, 36 to 53 absorption bands were analysed and described.

The purity of the used gases NO and NO₂ was 3.5. However, both gases were very photosensitive, so the changes in the gas composition due to a light influence occurred. Thus, for instance in the case of NO, the mixture contained also N₂O₂, NO₃, NO₂, N₂O₄.

Table 1

The list of the bands suitable and non-suitable for the determination of the nitrogen oxides' partial pressure changes.

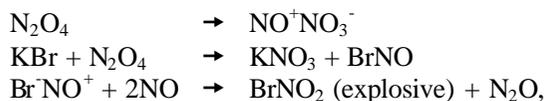
	Suitable bands for determination of partial pressure changes [cm ⁻¹]	Non-suitable bands for determination of partial pressure changes [cm ⁻¹]
NO	1950-1890	3800-3470 (overlaps with N ₂ O) 1890-1800 (o. with N ₂ O ₂)
NO ₂	3000-2900 (weak absorption) 1700-1630 (strong absorption) 1320 (medium absorption) 3450, 3115, 2500 (overtones)	3000-2900 (o. with HC, water, CH ₄) 1815-1700, 1630-1550 (o. with N ₂ O ₄) 1320-1250 (o. with N ₂ O ₄ , N ₂ O, NO ₃ ⁻)
N ₂ O	2250-2100	3760-3470, 2580-2250 (with NO)
NO ₃ ⁻	870-800, 1050-1010 1360 (in KNO ₃)	-

Note: As a material of the windows, we firstly used KBr. However, because of the strong reaction of KBr with the NO_x (associated KNO₃ layer on the windows), we were forced to choose another material. The used CaF₂ windows turned out to be fully inert against NO_x activity.

The results of the calibration measurements showed that for the determination of the pressure changes of the nitric oxide NO (Fig. 5), the bands between 1950-1890 cm⁻¹ (see Tab. 1) were the most suitable ones. Within this range no overlapping of ν_{as}NO bands with other bands appeared. On the contrary the bands between 3800-3470 cm⁻¹ and 1890-1800cm⁻¹ were not applicable because of the overlapping with a N₂O respectively N₂O₂ dimer. The NO band was also very good identifiable in NO₂ spectra (band 1945 cm⁻¹), where it was represented by an NO⁺ ion of the dimer N₂O₄ (NO⁺NO₃⁻).

As a result of the calibration measurements of the nitrogen dioxide NO₂, the bands between 3000-2900 cm⁻¹, 1700-1630 cm⁻¹ and 1320 cm⁻¹ seemed to be convenient for the determination of the partial pressure changes of NO₂ (Fig. 6). According to the further discharge measurements and the partial pressures of the components, it seemed to be the best to use bands in the region where the bands intensity is medium (see Tab. 1). Moreover, in a case when the concentration of the combustion gases is relatively high, the region of 3000-2900 cm⁻¹ is non-suitable, because the band is overlapped with hydrocarbons, water and methane bands. For the same reason also the regions of 1815-1700 cm⁻¹, 1630-1550 cm⁻¹ (overlapping with dimer N₂O₄) and the region of 1320-1250 cm⁻¹ (overlapping with N₂ and NO₃⁻) were not applicable. As well, in the NO₂ spectra it is possible to observe well appreciable bands of NO₂ overtones (bands of 3450, 3115 and 2600-2400 cm⁻¹).

From the standpoint of N₂O, the band of 2250-2100cm⁻¹ is the most convenient one (in combustion gas mixtures are situated between CO and CO₂ bands). Other bands (2580-2250 cm⁻¹, 3760-3470 cm⁻¹) were unusable, because of the overlapping (here with NO). The presence of N₂O in NO_x mixtures has usually several reasons. It could originate as a product in the reaction of N₂O₄ with KBr windows ...



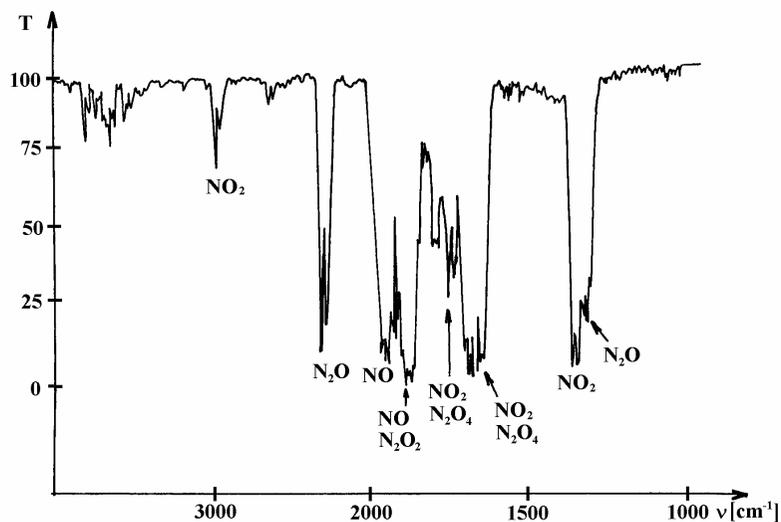


Fig. 5. IR spectra of NO ($p=99.3$ kPa (745 Torr)).

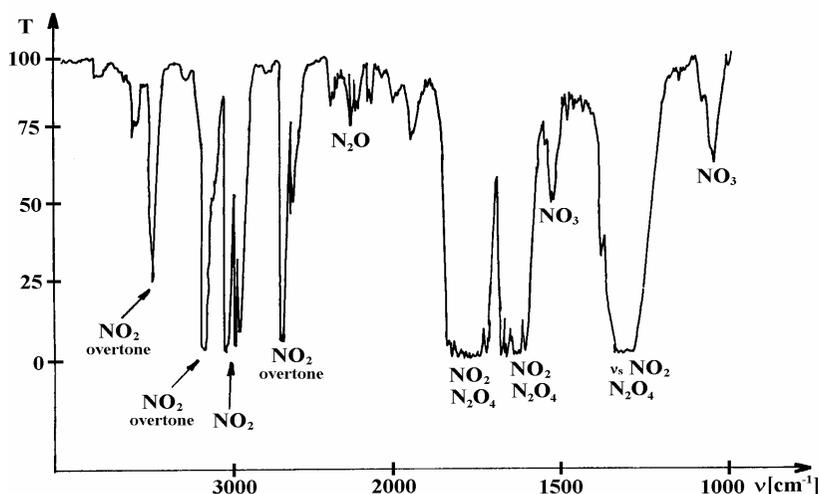


Fig. 6. IR spectra of NO₂ ($p=82.3$ kPa (617 Torr)).

or even by other volume reactions. Another source of N₂O are oxidative and reductive reactions in the mixtures containing nitrogen oxides. Finally, N₂O could be present as an admixture in the pressure tanks (max. 0.05% in NO₂ pressure tank). All aforementioned ways of N₂O origin are spectrometrically indistinguishable.

Generally, the extinction coefficients are consistently valid only if the partial pressure of a gas is small. In the case when a partial pressure is higher than a certain limit, so called association bonds - a typical high pressure phenomenon - originate in gas mixtures. Thus e.g. in the spectra of NO not only a monomer, but also a dimer etc. are presented.

5 Discharge Measurements

The corona discharge measurements in the nitrogen oxides were performed in the gas cell at relatively high pressures. Experimentally, we observed and analysed the discharge

onset; discharge character based on the I-U characteristics; IR spectra of gas mixtures and surface layers of plane electrodes, after each discharge. Apart from a polarity and a gas filling, we also varied the HV electrode (wire) material, while LV electrode material was kept the same. Totally, we observed the discharge in 16 different configurations.

	material of the HV electrode (wire on a glass tube)	material of the LV electrode (plane)
1.	molybdenum	brass
2.	copper	brass
3.	brass	brass
4.	stainless steel	brass

+ polarity (positive or negative) and gas filling (NO or NO₂) variation

From the experimental results follows:

The onset discharge voltage of the negative corona was comparably lower than the positive one (approx. 3 kV in average). Likewise lower was the onset for the NO gas filling than for NO₂ (approx. 5 kV in average). However, in both cases, the onset value strongly varied with the used material of the HV electrode. For a certain polarity and a gas mixture, but different material, the spread of the values increased to 6-10 kV.

With regard to the discharge stability, the negative corona discharge is unambiguously more stable. It means a steady negative glow appeared here throughout an incomparably wider range of U and I, than it was in discharges with the positive polarity. The negative glow regime remained steady within the range of 150-740 μ A (7-15 kV), meanwhile the positive one only on the interval 15-35 μ A (2.5-4 kV).

Note: Though the negative corona is more stable, its deNO_x effect is very unpredictable compare with the positive polarity.

Based on the results of the discharge measurements and the IR analyses, there were two different, but simultaneous plasmochemical processes happening in the discharge chamber.

- The spatial processes had mainly oxidative character. The reactions were very fast and quite complicated here and to know exactly a type and amount of a reaction product was sometimes almost impossible [10, 17-19]. With the help of the IR absorption spectroscopy we investigated the partial pressure drop of NO and NO₂ in the mixture per minute of the corona discharge action (Fig. 7).

In the case, when the NO concentration, before the discharge, was several times (3-6) higher than NO₂ in the gas mixture, the positive corona was the most effective one for the deNO and deNO₂ simultaneous process (Fig. 7a). On the contrary, the discharge of the negative polarity was more stable, but its deNO₂ treatment efficiency was very unpredictable.

In the case, when the concentrations of NO and NO₂ in the gas mixture were almost the same (1:1-2), the deNO_x efficiency in both polarities was smaller than in the previous case (fig.7b.). However, deNO₂ and even also positive polarity processes were more effective here.

The changes of the N₂O contents in the mixture (fig.7c.) seemed to be interesting, too. The content of NO in the gas mixture was higher before the discharge action, less N₂O was presented in the mixture after the discharge. The positive corona was the most effective one.

- The surface processes (reactions between molecules produced by the discharge and a surface of electrodes) had mainly reductive character, however also some

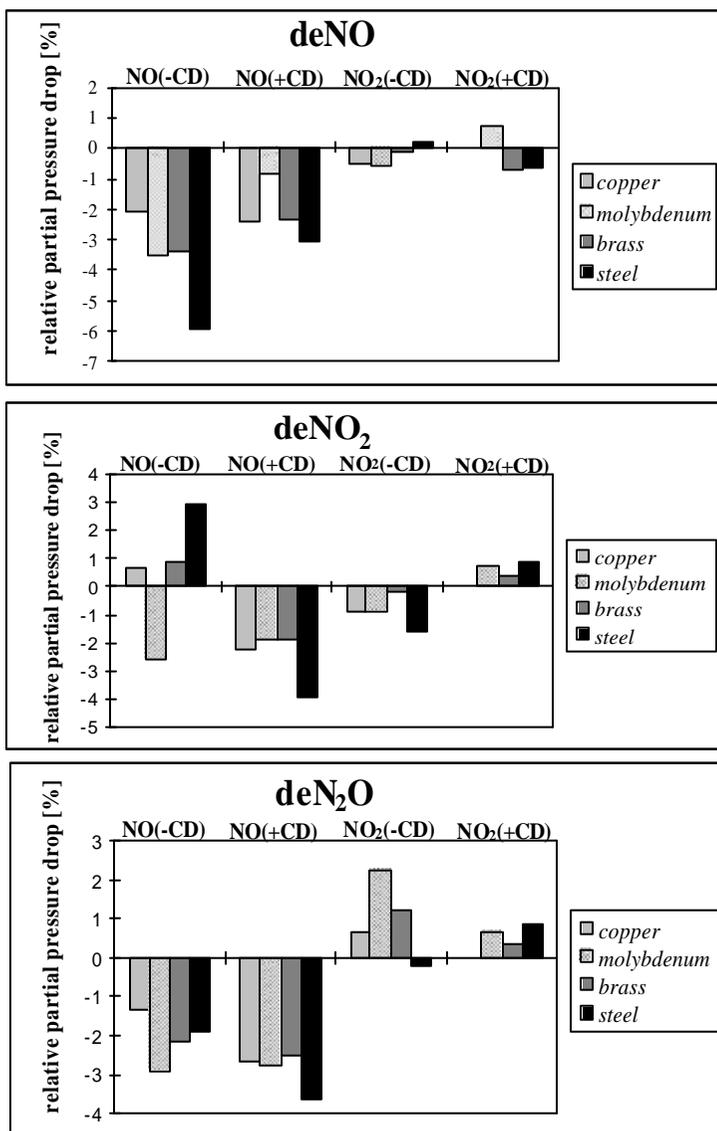


Fig. 7. The partial pressure drop minute of: a) NO b) NO₂ c) N₂O per minute of the corona discharge action (variable parameters: polarity, input gas, HV electrode material).

reactions had oxidative character. The processes lead to arise of solid structures on the LV electrode surface layer. We supposed these structures had an enhanced catalytic activity on oxidative-reduction processes in the volume. The groups –NO₂ and –NO₃ were the result of oxidative processes on the LV electrode surface. Likewise, the groups –NH_x, –N≡N–, –N=N–, –N=N=N– were the evidence of reduction processes.

– The surface analysis of the plane electrode (after the discharge action) showed that the places, where the discharge channel hit the electrode, did not have any sign of corrosion (turquoise-white colour), compared with the rest of the surface. These places were rather dark and shiny. From the CuO₂ (surface oxide on the brass) presence in the IR spectra, we determined the thickness of the corrosion layer.

Based on the experimental results we supposed the groups –NO₂ and –NO₃ passivated the surface and protected it from the corrosion. On the contrary, the

–NH_x groups had an opposite effect and increased the corrosion processes. It is very difficult and sometimes almost impossible to define an exact compound on the basis of these functional groups. However, our analysis of these surface structures are meanwhile only at the beginning, and we are looking for some new explanations, soon.

Generally, both types of the reactions are very closely connected. One could not appraise them separately. The reactions influence each other and moreover they are even influenced by the discharge itself. In the discharge process, many parameters change what makes the process more complicated and hard analysable. However, based on the results we drew the several conclusions.

It is clear that the NO oxidation to NO₂ in a discharge space was caused by ozone. Because the ozone production in a negative polarity is several times higher than in a positive one, the conversion of the NO to NO₂ (and thus the NO decrease) was even more striking in the negative polarity. On the other hand, NO₂ conversion is mainly a surface process and it is much slower than the oxidation in a space. It is much better in the positive polarity. If the NO oxidation in a negative polarity is very rapid and the NO₂ conversion on a surface is slow, the increase of the NO₂ after the discharge action could appear. In a positive polarity, where the NO oxidation is a little slower and NO₂ conversion is more efficient, the processes are almost concurrent. Here, both NO and NO₂ concentrations decrease simultaneously (synergetic process).

4. It is not possible to say unambiguously, what kind of material was the best for the deNO_x processes. More detailed analyses of a material surface layer and more discharge experiments should be done before we answer the question. The influence of a material on a discharge behaviour and reaction rates is also of importance and needs further explanations. Anyway, hitherto experiments showed that mostly deNO₂ processes were dependent on material. Molybdenum for the negative polarity and stainless steel in the positive polarity were the best materials for deNO_x. The catalytic effect of the materials decreased with the NO₂ increase in a mixture.

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